ANALYZING & TESTING

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INFLUENCE OF THE TEMPERATURE AND SIZE ON THE SAFETY CONDITIONS FOR REACTIONS IN BIG VOLUMES

Elena Moukhina

September, 17th, 2024 NATAS Conference, Knoxville

1 Problem definition and Solution Method

What kind of conditions must we use for thermal simulations? Partial cases

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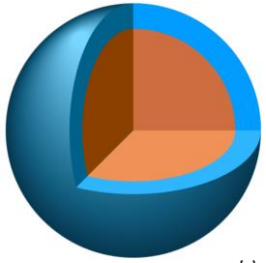
Low thermal effect

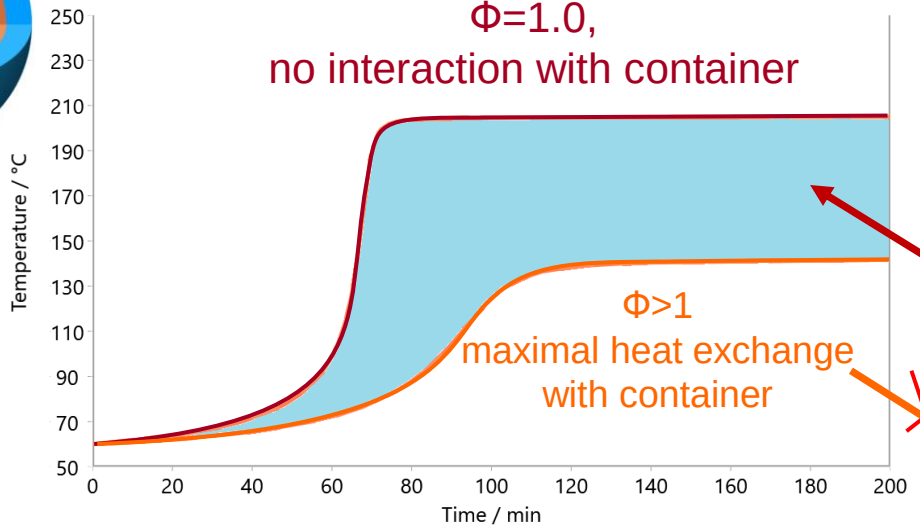
• Long time predictions	known uniform temperature
• Industry	simulation of temperature in volume simulation of reaction rate for known temperature

High thermal effect

• Industry	simultaneous simulation of temperature and reaction in volume
• Thermal Stability	simultaneous simulation of temperature and reaction in volume
• Thermal Explosion	simultaneous simulation of temperature and reaction in volume

Materials with high energetic effect in adiabatic container





$$Cp\frac{1}{\Phi}\frac{dT}{dt} = A \cdot f(\alpha) \cdot \exp\left[\frac{-E_A}{RT}\right] \cdot \Delta H$$

$$\Phi = \frac{m_c Cp_c + m_s Cp_s}{m_s Cp_s}$$

Reality:

- ~~Infinite~~ thermal conductivity of material,
- Stirring **is off**
- ~~Infinite~~ thermal conductivity of container wall

Is this reality safe or dangerous?
How it depends on the material mass?

Complete Solution for Customer‘s Problem: from Measurement to Simulation

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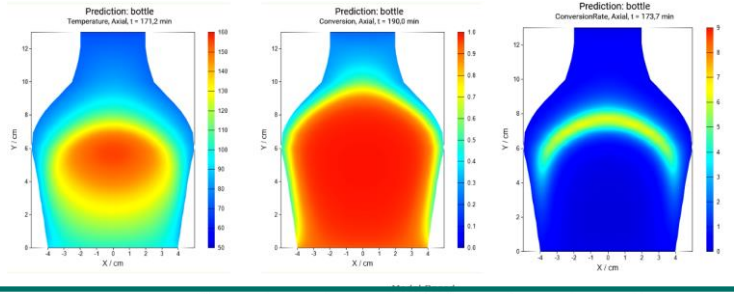
3. Simulation

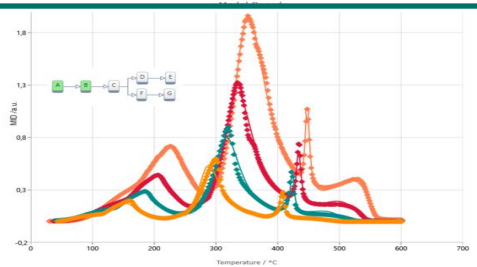
g, kg, tons, temperature gradients,



TERMICA NEO

2. Chemical Kinetics

mg, uniform known temperature, measurement impossible



KINETICS NEO

1. Laboratory measurements

mg, known temperature

DSC
TGA
ARC, …

Step 1: measured data

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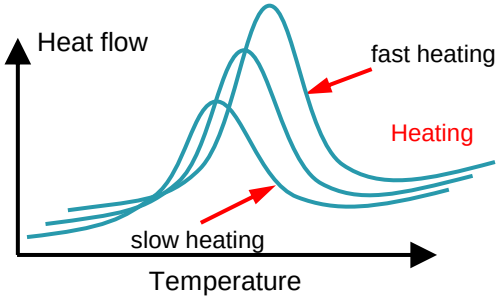
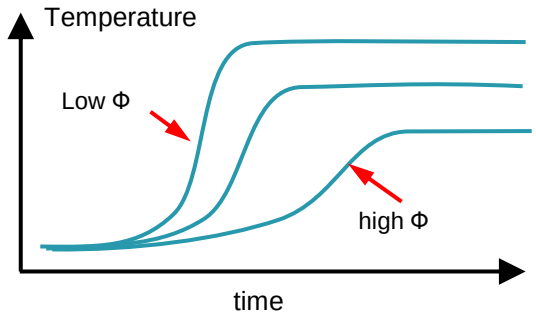
Thermosets, Composites
Curing, Cross-linking

DSC



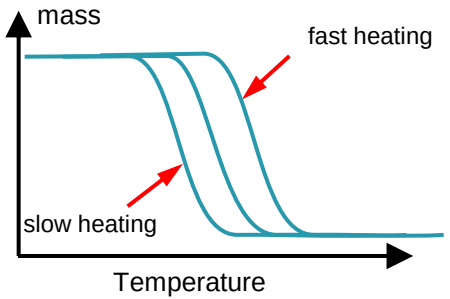
Energetic materials
Chemical industry

ARC



Degradation
Decomposition

TGA



Additional instruments: Other calorimetric or non-calorimetric instruments (HFC, Rheology, DIL, HFC, C80, TAM and others)

Kinetics Analysis Must Fulfil ICTAC Kinetics Recommendations

International Confederation for Thermal Analysis and Calorimetry

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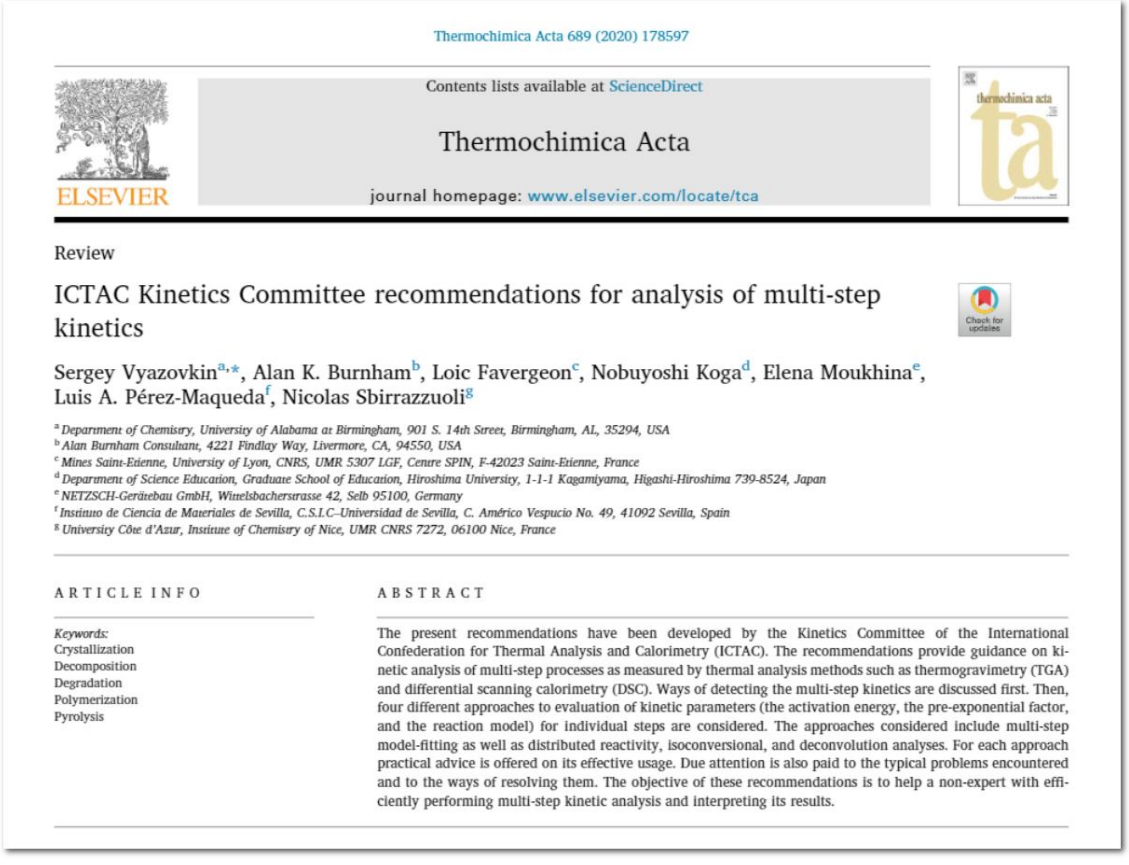

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Review

ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics

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ARTICLE INFO

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Polymerization
Pyrolysis

ABSTRACT

The present recommendations have been developed by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC). The recommendations provide guidance on kinetic analysis of multi-step processes as measured by thermal analysis methods such as thermogravimetry (TGA) and differential scanning calorimetry (DSC). Ways of detecting the multi-step kinetics are discussed first. Then, four different approaches to evaluation of kinetic parameters (the activation energy, the pre-exponential factor, and the reaction model) for individual steps are considered. The approaches considered include multi-step model-fitting as well as distributed reactivity, isoconversional, and deconvolution analyses. For each approach practical advice is offered on its effective usage. Due attention is also paid to the typical problems encountered and to the ways of resolving them. The objective of these recommendations is to help a non-expert with efficiently performing multi-step kinetic analysis and interpreting its results.

KINETICS NEO

- Model free analysis
- Multi-step model-fitting (model based)
- Diffusion control for curing
- Crystallization kinetics
- Kamal model for curing
- Deconvolution analysis (sum of peaks)

kinetics.netzsch.com

Step 2: measured dataKinetic Analysis Methods in Kinetics Neo

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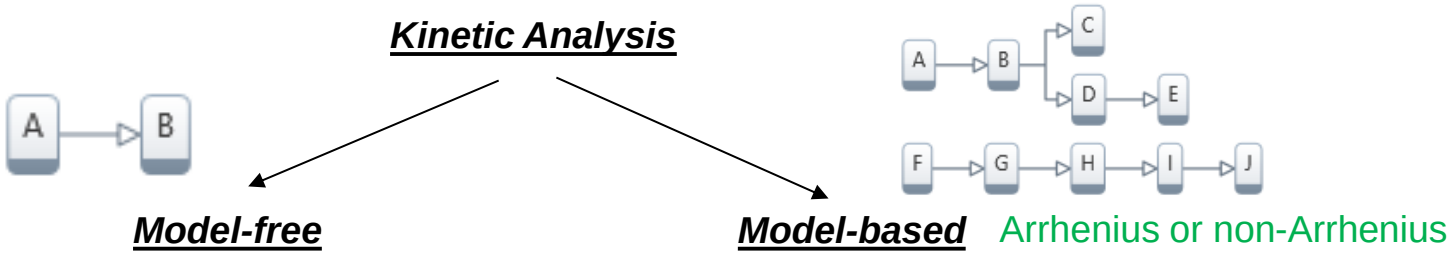
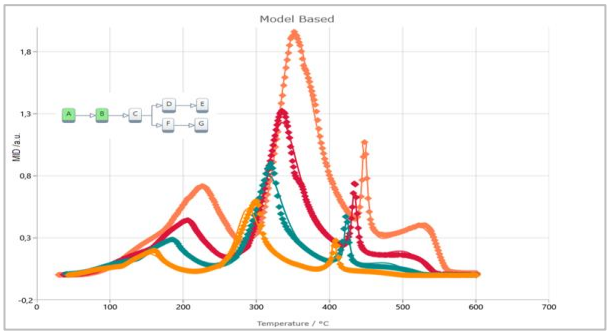
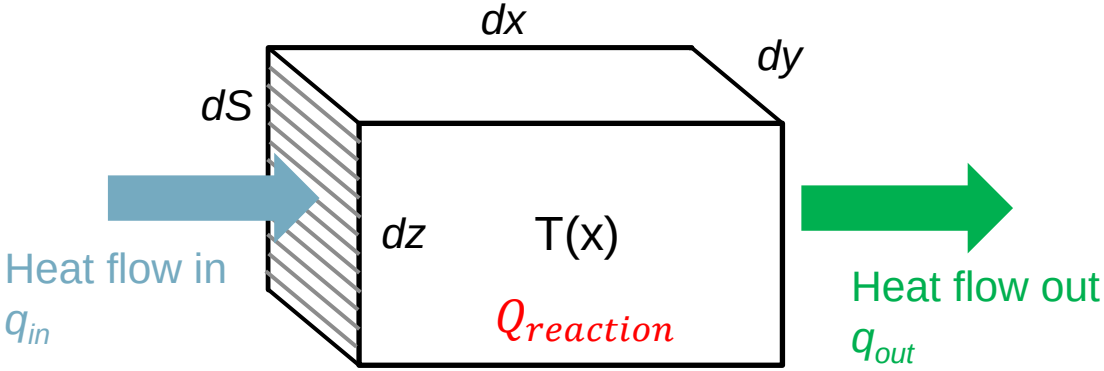
KINETICS NEO





1. Simple geometry, but complex processes
2. Automatic loading of kinetic parameters and equations from NETZSCH Kinetics Neo
3. No limitation for complexity of the chemical system

Heat balance for small element with reaction heat as the heat source



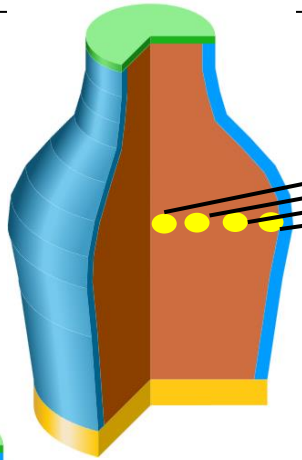
$$Cp \cdot dm \cdot \frac{dT}{dt} = q_{in} - q_{out} + Q_{reaction}$$

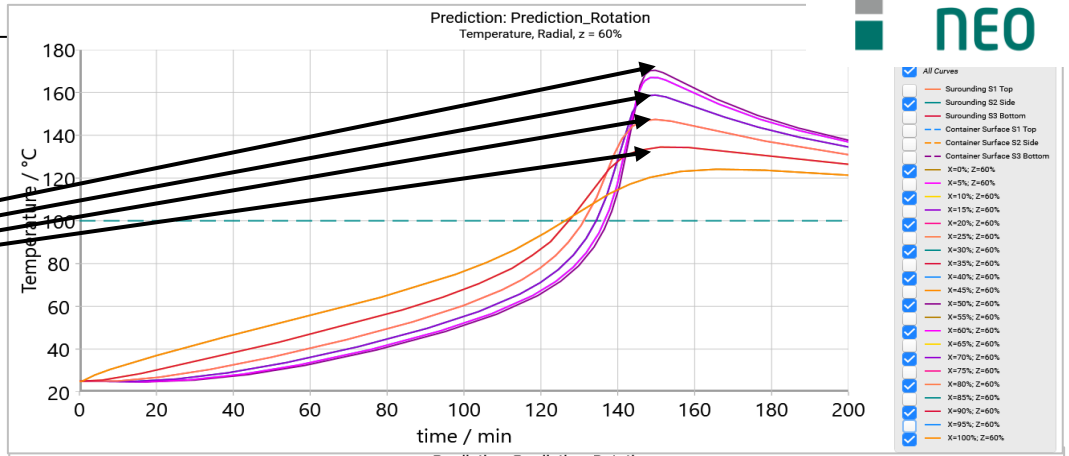
$$\frac{\partial T}{\partial t} = a\frac{\partial^2 T}{\partial^2 x} + \Delta T_{ad}\frac{d\alpha}{dt}$$

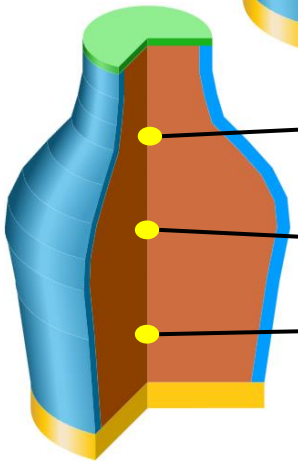
$$\frac{\partial T}{\partial t} = a\left[\frac{\partial^2 T}{\partial^2 x} + \frac{\partial^2 T}{\partial^2 y} + \frac{\partial^2 T}{\partial^2 z}\right] + \Delta T_{ad}\frac{d\alpha}{dt}$$

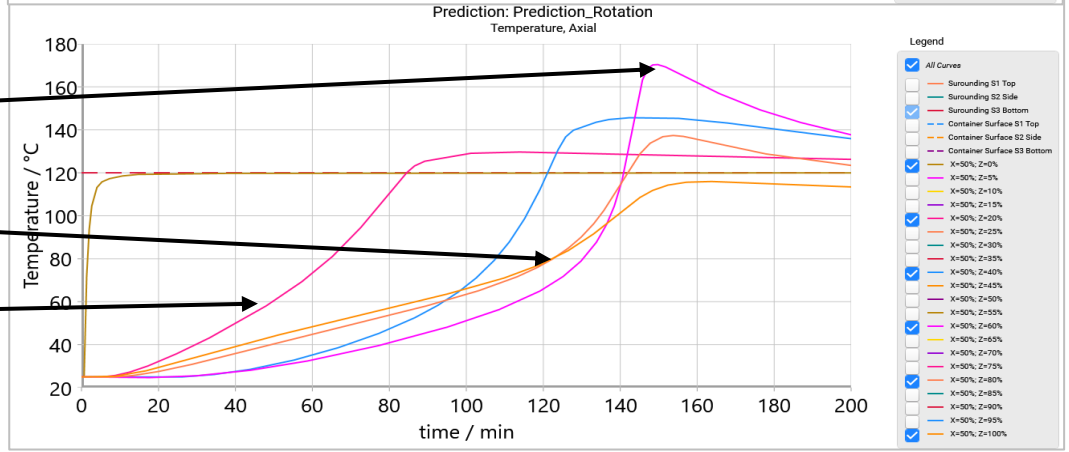
$dS = dy\,dz$	Area
$dV = dx\,dy\,dz$	Volume
$dm = \rho\,dV$	Mass
$q_{in} = dS\,\lambda \left.\frac{\partial T}{\partial x}\right\|_{x-\frac{dx}{2}}$	Heat flow *in* at point x-dx/2
$q_{out} = dS\,\lambda \left.\frac{\partial T}{\partial x}\right\|_{x+\frac{dx}{2}}$	Heat flow *out* at point x+dx/2
$Q_{reaction} = \Delta H \cdot dm \cdot \frac{d\alpha}{dt}$	Reaction Heat
$Cp \cdot dm \cdot \frac{dT}{dt}$	Self-heating
$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot \exp\left[\frac{-E}{RT}\right]$	Reaction rate
$q_{in} - q_{out} = dS\,\lambda \frac{\partial^2 T}{\partial^2 x}$	Heat flow difference
$a = \lambda\,/(Cp \cdot \rho)$	Thermal diffusivity
$\Delta T_{ad} = \Delta H/Cp$	Adiabatic Temperature increase

Results: Temperature vs time at any point of the reacting volume: Vertical or horizontal



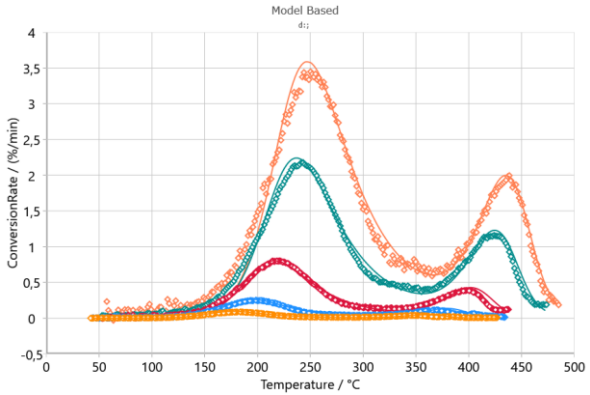


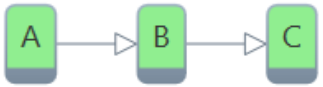


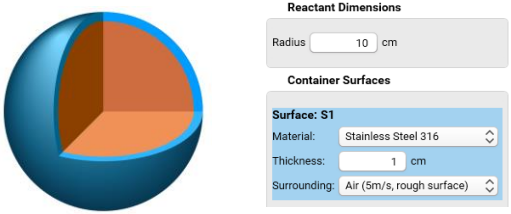


Possible to show: Temperature, conversion, conversion rate, concentrations vs time

2. Concentrations for multi-step processes

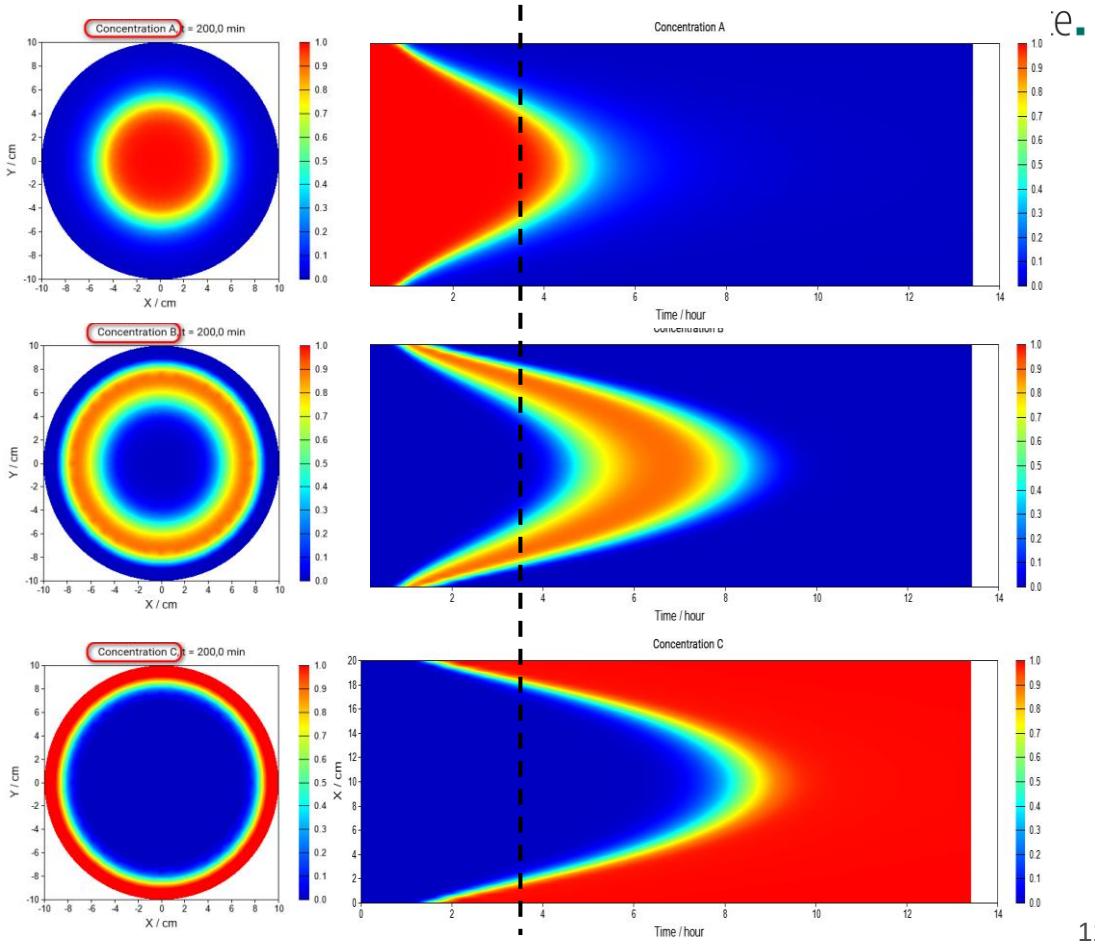






Initial temperature 50°C
Surrounding Isotherm 600°C

t=200min



SADT for Azo-bis-Isobutyronitrile (AIBN), 50kg package in Air

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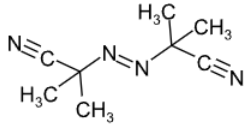
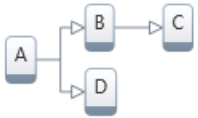
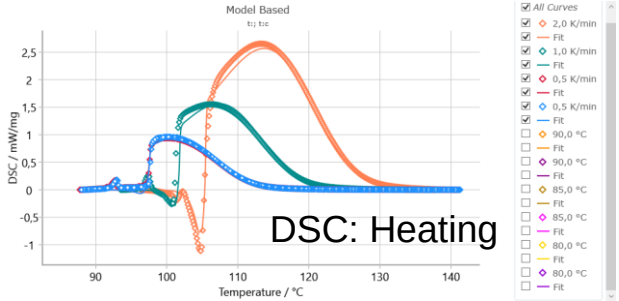
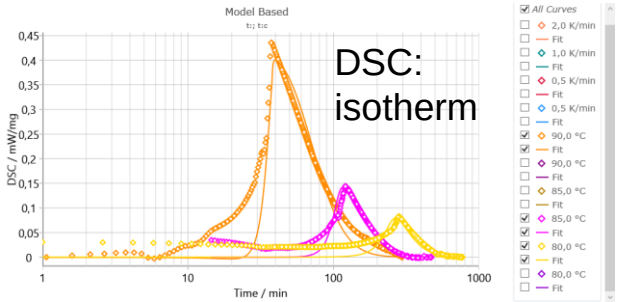








Experiment

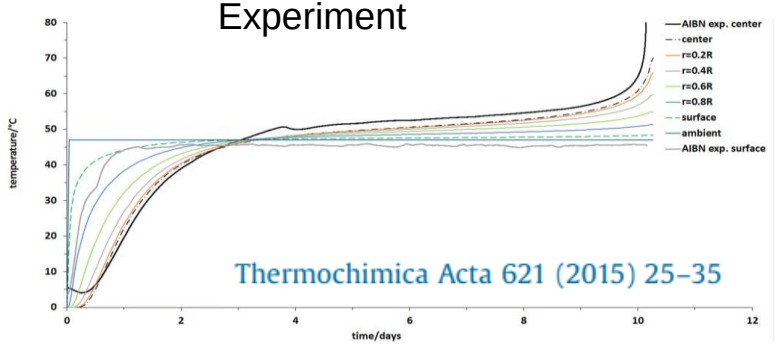
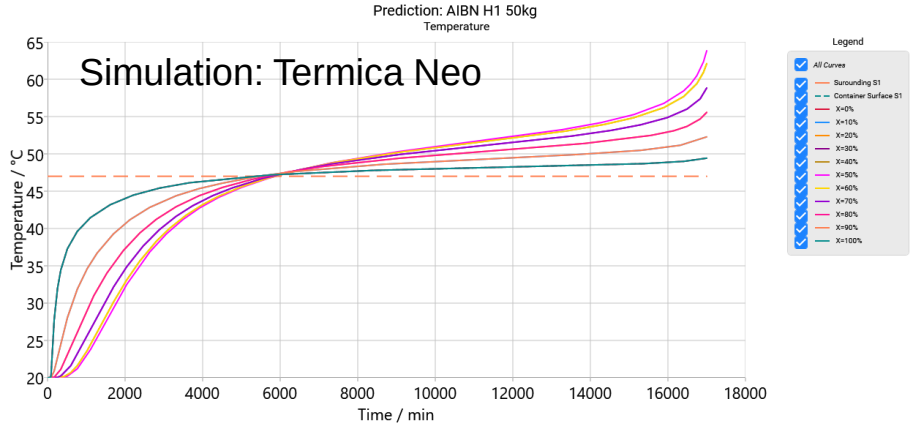


Fig. 7. Experimental temperatures in the center (thick solid line) and simulated temperatures in sample at the different distances from center for 50 kg package 47 °C.



Rotation geometry of arbitrary profile

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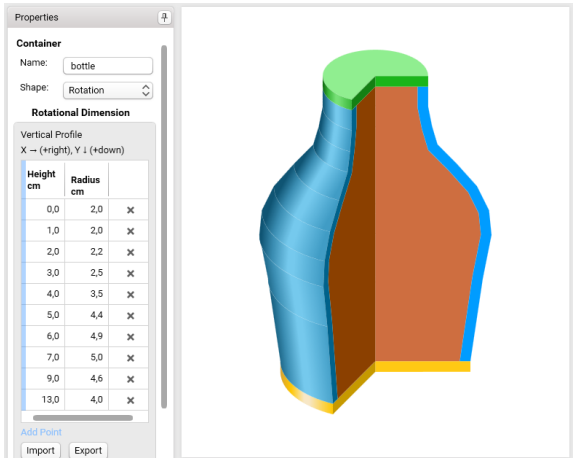
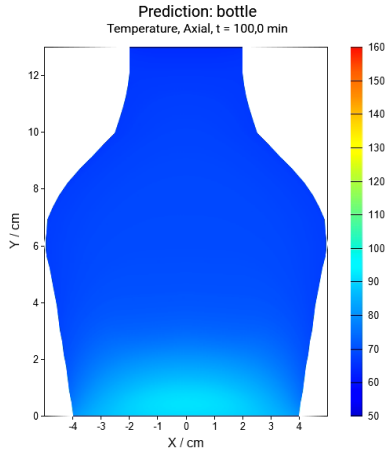
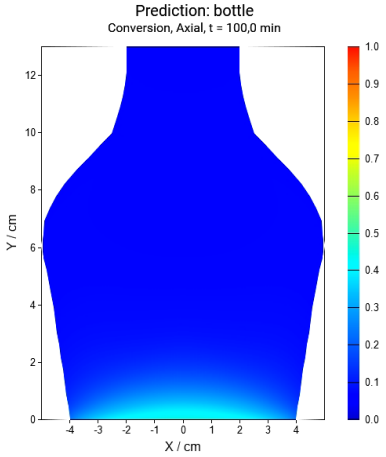
Temperature

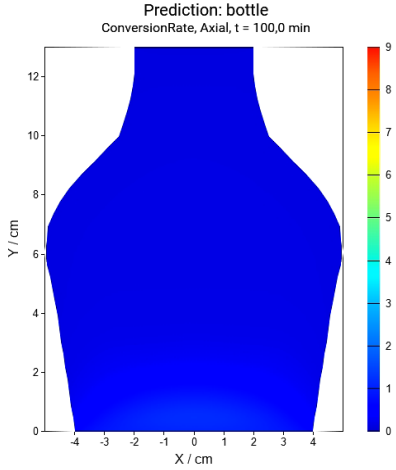
Conversion

Conversion rate









Surface: S1 Top

Isothermal

Temperature	60,00	°C
Time	250,00	min

Surface: S2 Side

Isothermal

Temperature	60,00	°C
Time	250,00	min

Surface: S3 Bottom

Isothermal

Temperature	100,00	°C
Time	250,00	min

Rotation geometry of arbitrary profile

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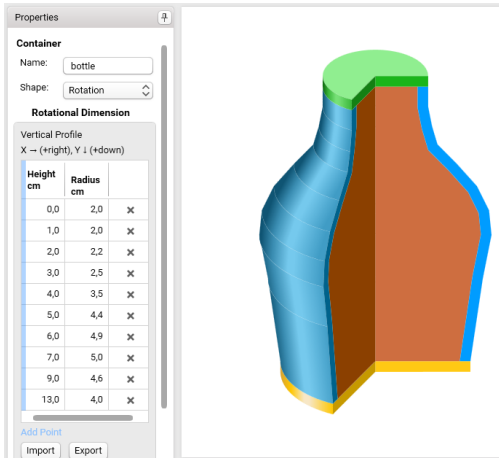

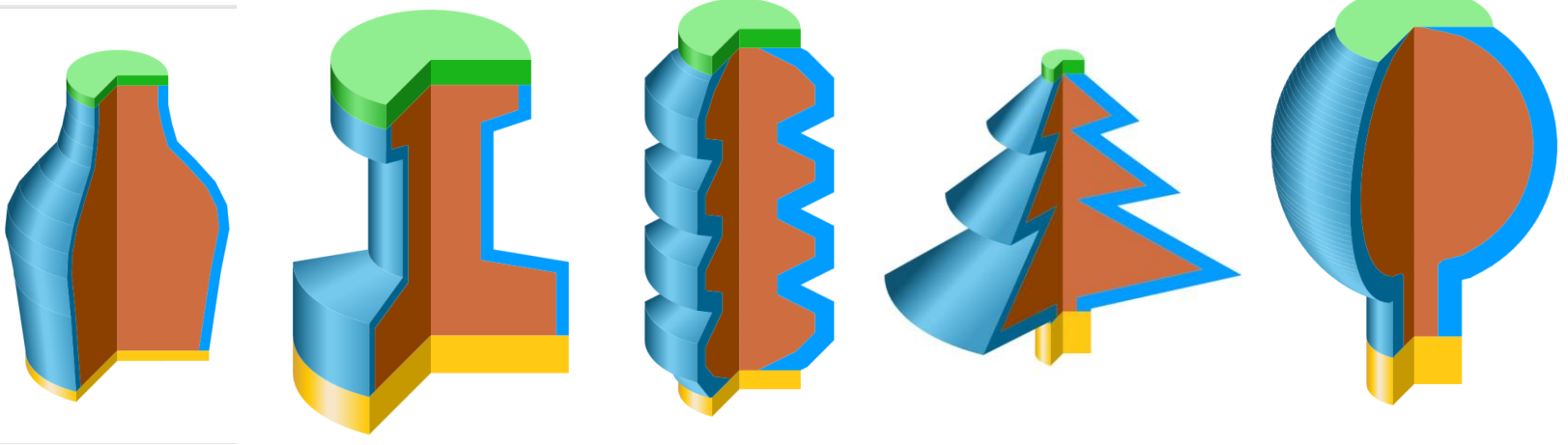

Will be released in July 2024

2 Single step reaction Simulation examples

2. Decomposition of 20% DTBP in Toluene

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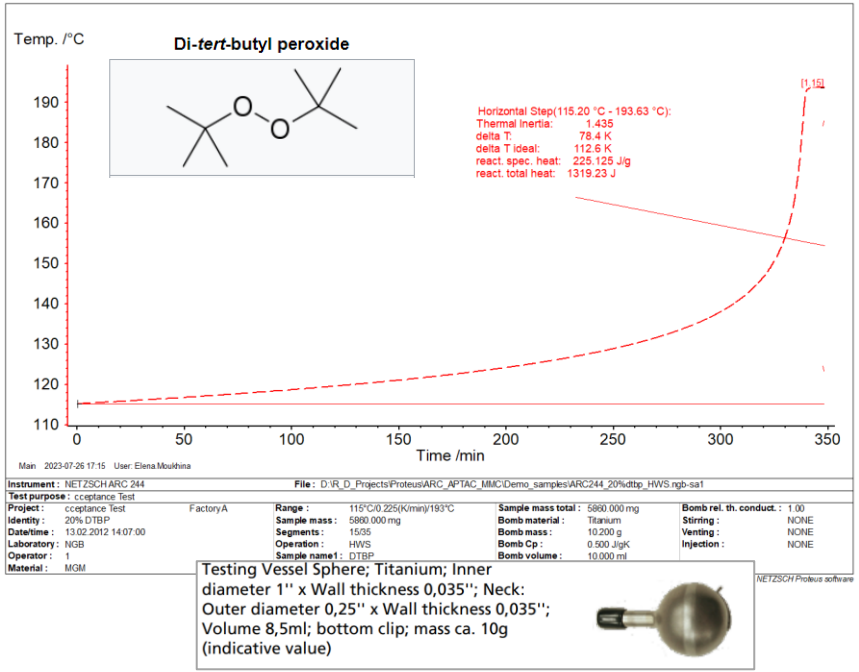
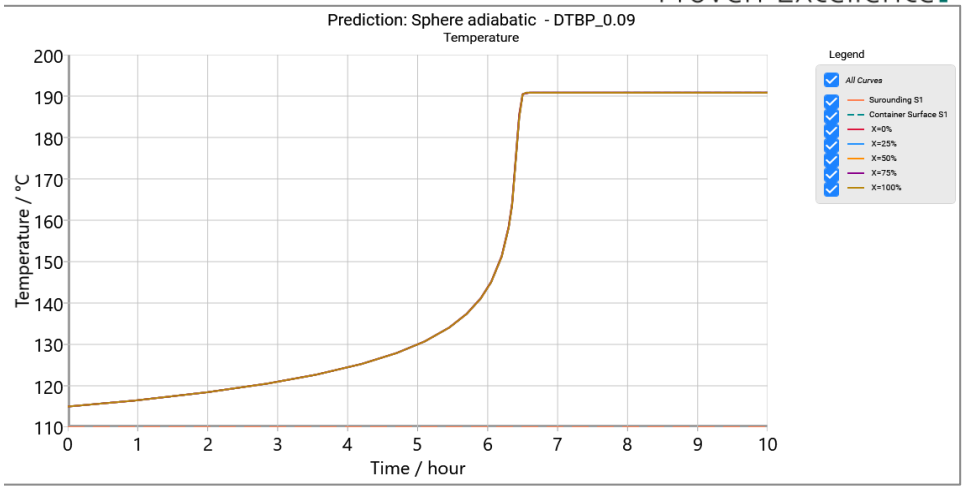
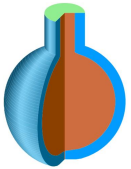






T_{start} = 115°C ΔH = 225J/g

T_{end} = 191°C Container sphere Titanium R=1.3cm

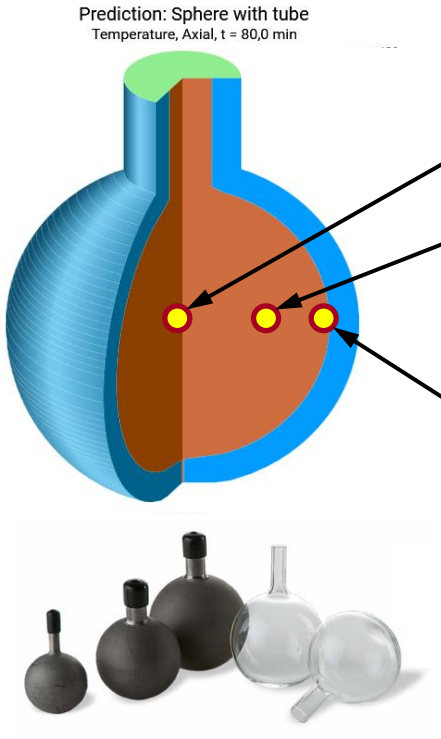
Experiment, ARC 244

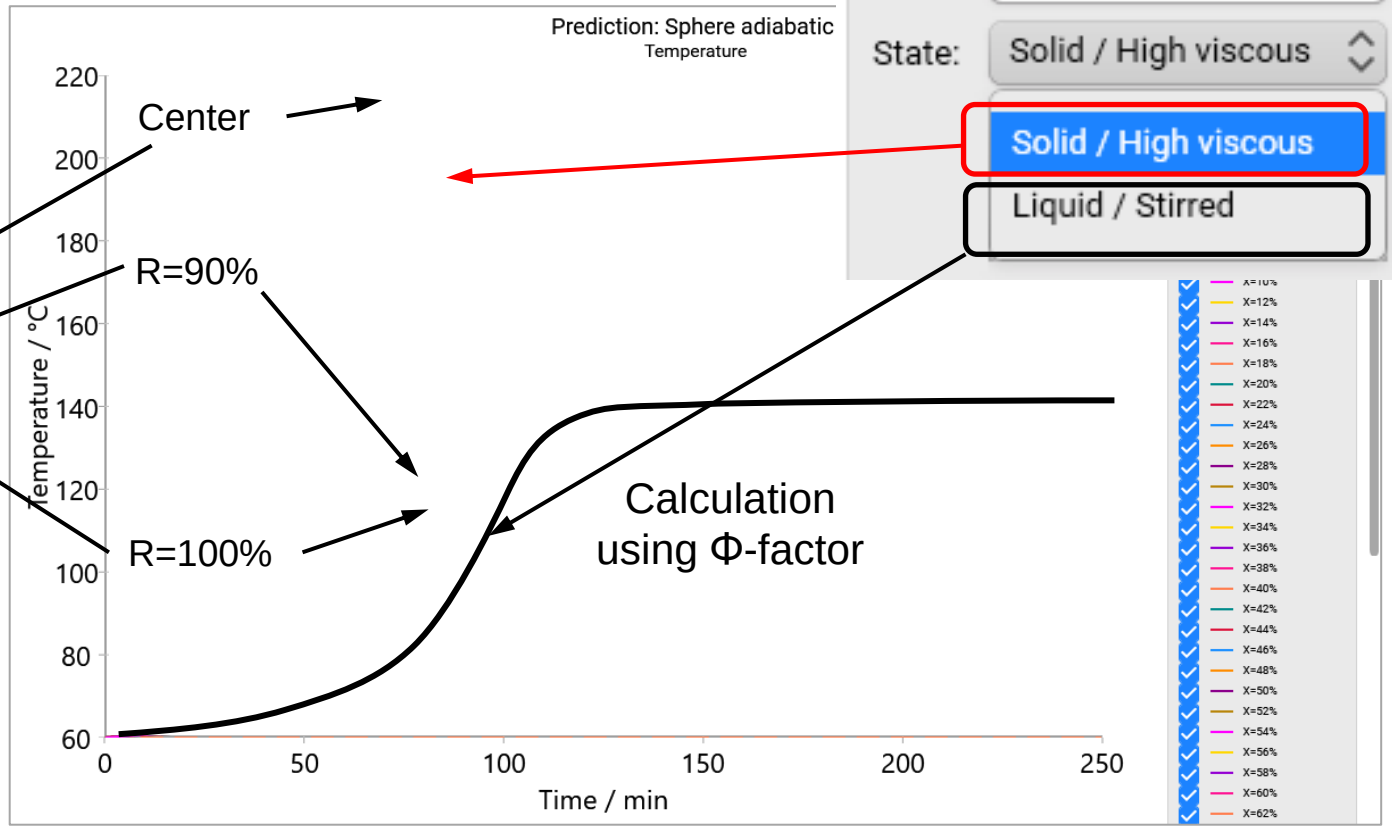
Simulation, Termica Neo

Simulation corresponds to real measurement

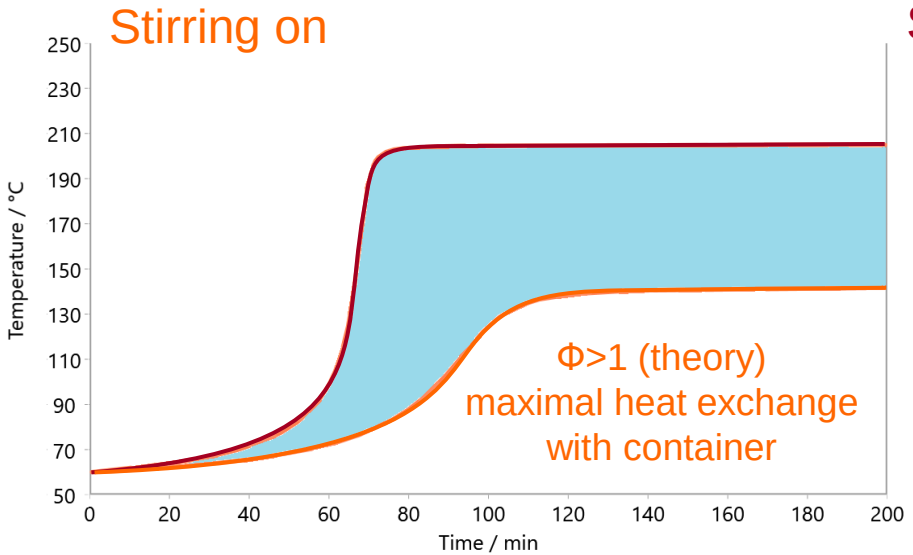
Single step: Adiabatic simulation for solids

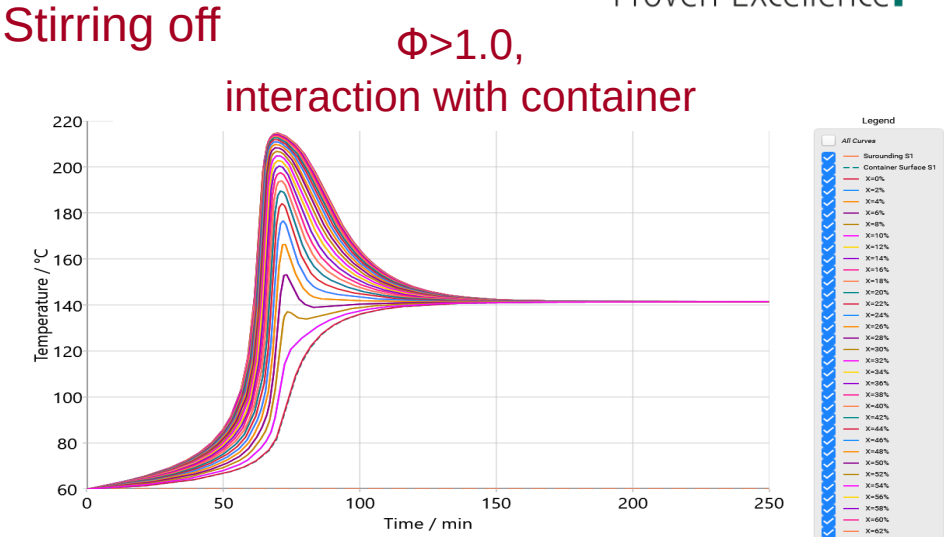
R=3.2cm, h=0.9cm,
stainless steel 316





Single step adiabatic simulation: theory vs reality





Comparison with calculation for Φ>1 (theory):

- Temperature rate is faster
- Maximal temperature is higher
- Final temperature is the same because of heat balance

Single step for solids: Adiabatic Simualtion with Φ=1.4 and different sizes

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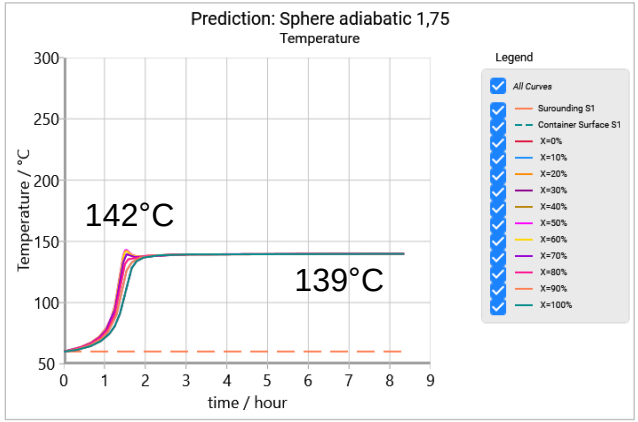
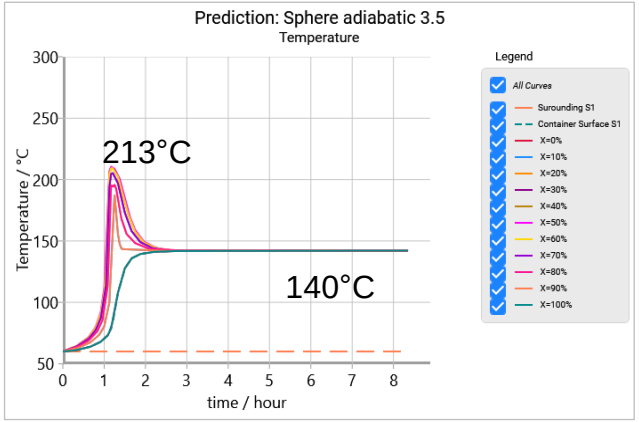
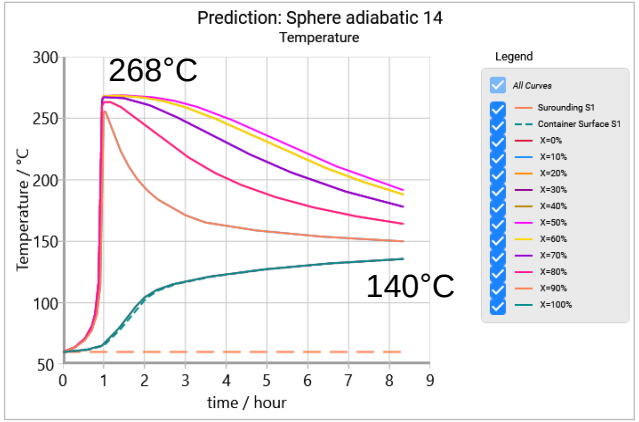
The higher radius the higher temperature in the center.
Maximal Temperature corresponds to Phi=1



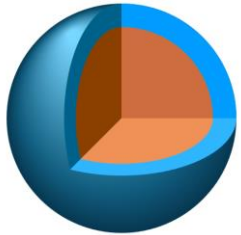




R=1.75cm

R=3.5cm

R= 14 cm



Reaction enthalpy 395 J/g,
Φ=1.4 for all simulations

Single step reactions: dependence on reactor size

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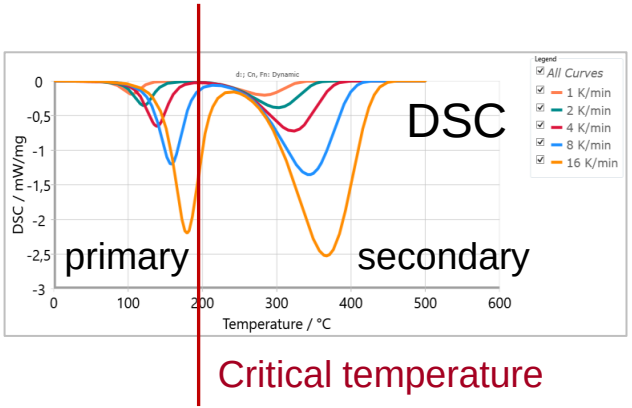
For higher material mass under adiabatic conditions:

- Temperature rate is faster
- Maximal temperature is higher
- Final temperature is the same because of heat balance

2 Double step reaction Simulation examples

Industrial processes: primary and secondary reaction

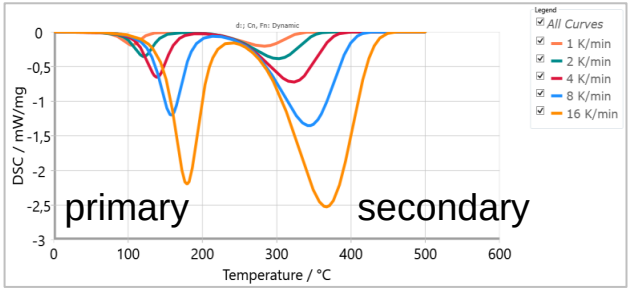


	Primary reaction (main process)	Secondary reaction (non desired decomposition)	total reaction heat
Cyclohexane	80J/g	140J/g	220J/g
Diazotization 2.5mol/kg	65kJ/mol(162J/g)	150kJ/mol(375J/g)	537J/g
Amination	175kJ/mol(457J/g)	840J/g	1297J/g
Condensation reaction in aceton	230J/g	150J/g	380J/g
Sulfonation	150J/g	350J/g	500J/g
Example reaction 2mol/kg	150kJ/mol(300J/g)	575kJ/mol(1150J/g)	1450J/g

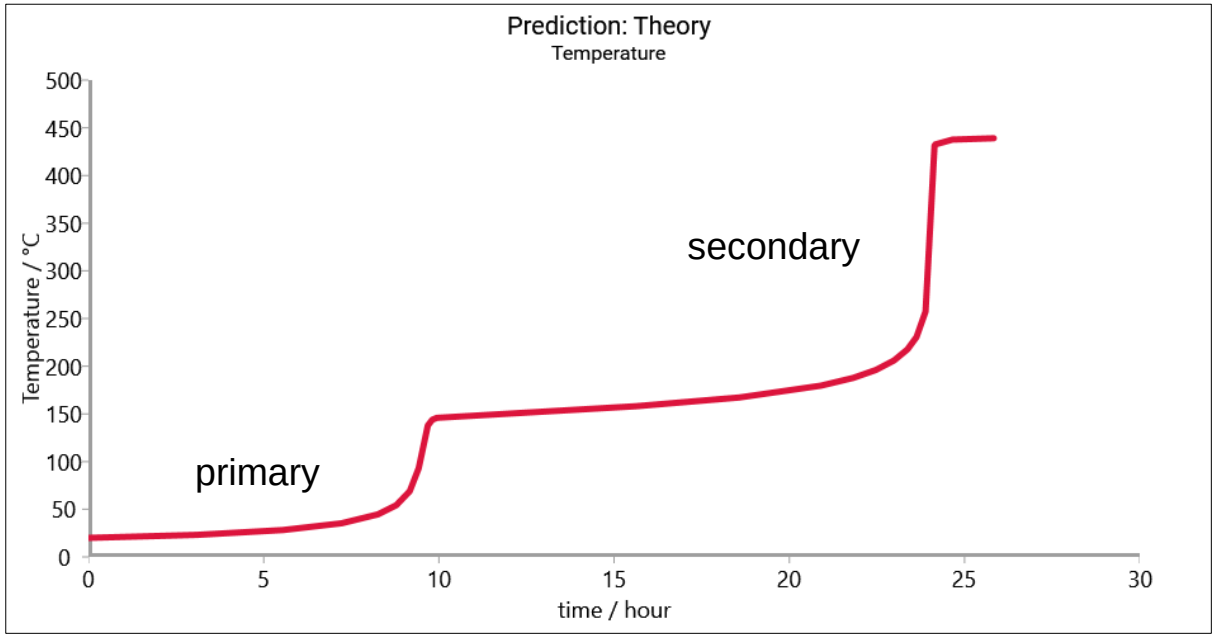
Severity: catastrophic for ΔH>800J/g
critical for ΔH>400J/g
medium for ΔH>100J/g
negligible for ΔH<100J/g

Source: Fransis Stoessel, Thermal Safety of Chemical Processes, 2008, ISBN: 978-3-527-31712-7

Industrial processes: Theory of adiabatic self-heating



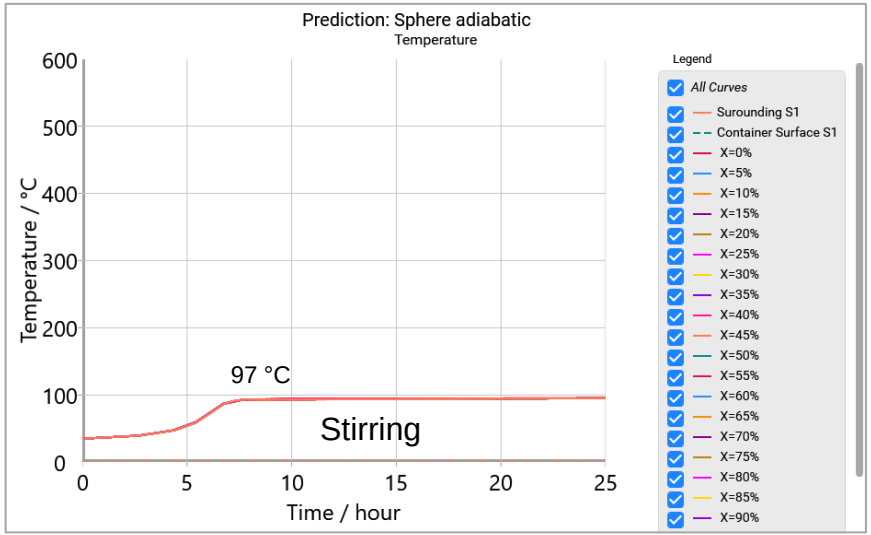
Primary reaction enthalpy 300 J/g,
Secondary reaction enthalpy 700 J/g,

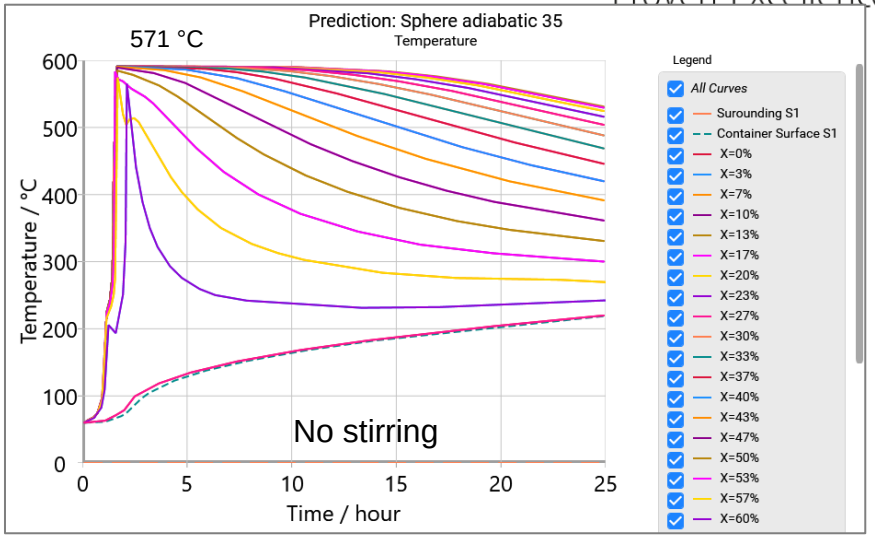


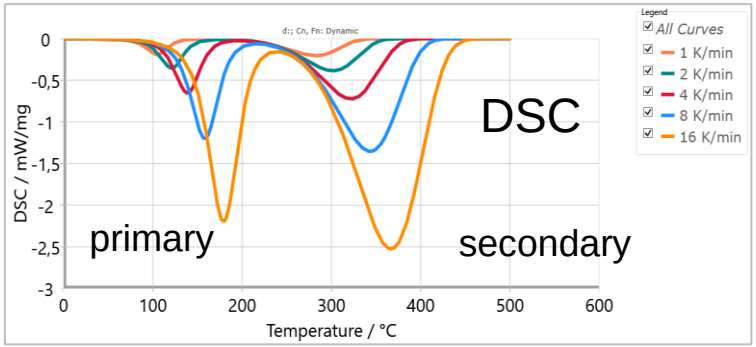
How to avoid secondary reaction:

1. Stirring
2. Cooling
3. Careful selection of size

Adiabatic simulation for 24h: stirring failure







Φ=1.4 for all simulations

Primary reaction enthalpy 300 J/g,

Secondary reaction enthalpy 700 J/g,

Adiabatic simulation for 24h: when the secondary reaction started?

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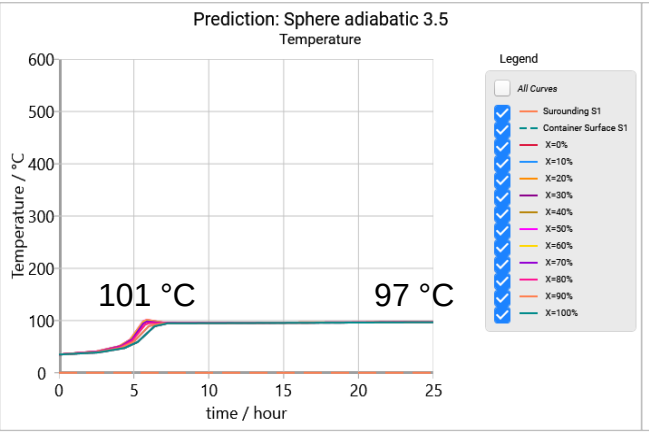
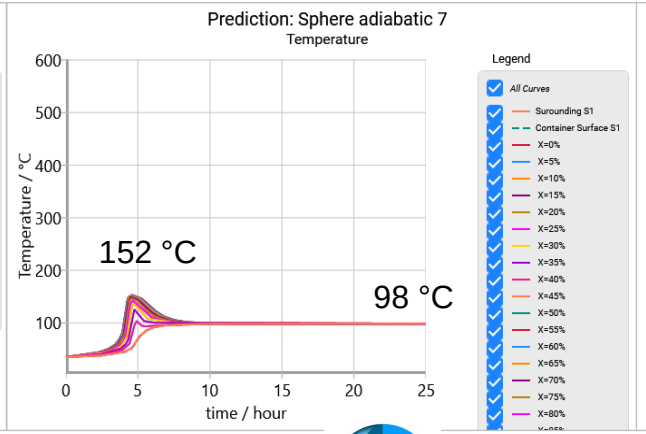
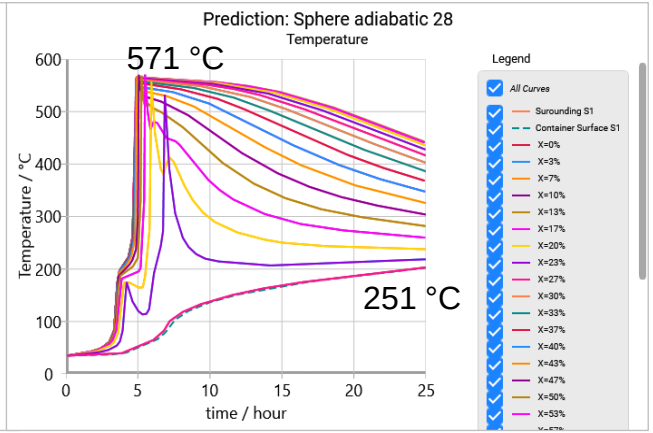


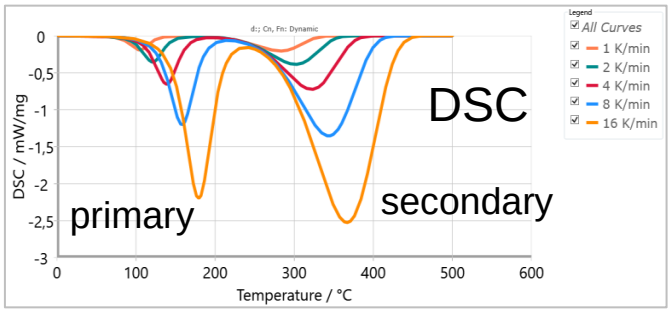
R = **4** R0



R = **8** R0



R = **32** R0



Simulations Φ=1.4
Different size

Primary reaction enthalpy 300 J/g,
Secondary reaction enthalpy 700 J/g,

Primary and secondary reactions: dependence on reactor size

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For higher material mass under adiabatic conditions:

Secondary reaction is not triggered:

- Temperature rate is faster
- Maximal temperature is higher
- Final temperature increase is the same and corresponds to the effect of primary reaction

Secondary reaction is triggered:

- Temperature rate is faster
- Maximal temperature is higher
- Final temperature increase corresponds to the sum of thermal effects for primary and secondary reaction

General functionality of Termica Neo

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1. Simulation of the chemical reactions in big volumes
2. Calculation of the following properties at each point of volume as the function of time
    1. Temperature
    2. Degree of conversion
    3. Conversion rate
    4. Concentrations
    5. Glass transition temperature for curing processes
3. Self-accelerating decomposition temperature (SADT)
4. Simulation of reactions for reactor with container, also under adiabatic condition
5. The kinetic modes are taken directly from Kinetics Neo project
   (results of any method including model based and model free)
   Kinetics is based on ICTAC Methods for multi-step reactions

You can rely on NETZSCH.

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