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THERMAL BEHAVIOR AND PYROLYSIS KINETICS

29th January 2024, Dr. Mohammed Bouzbib, Chemist, NETZSCH Analyzing & Testing

Agenda

1. Pyrolysis
2. Kinetics in Solids
3. Kinetics Neo Software
4. Review Example Study: Thermal behavior and pyrolysis kinetics of olive stone residue

Pyrolysis

- Pyrolysis is the thermal **Decomposition reaction** of organic compounds in an inert atmosphere.
- During pyrolysis, solid, liquid or gaseous products can be generated. If gases are released from the sample during pyrolysis, the changes in mass can be detected by TGA (thermogravimetry).

Materials for pyrolysis

- Biomass
- Plastics
- Rubber

→

Thermogravimetric Analysis (TGA)

Stages of Decomposition (Pyrolysis)

Kinetics Analysis

→

Products from Pyrolysis

- Gases
- Liquids
- Solid Residue (Charcoal)

- The poor choices of the kinetic methods and experimental conditions
- kinetic complexities of multi-step pyrolysis processes

Chemical Kinetics Definition

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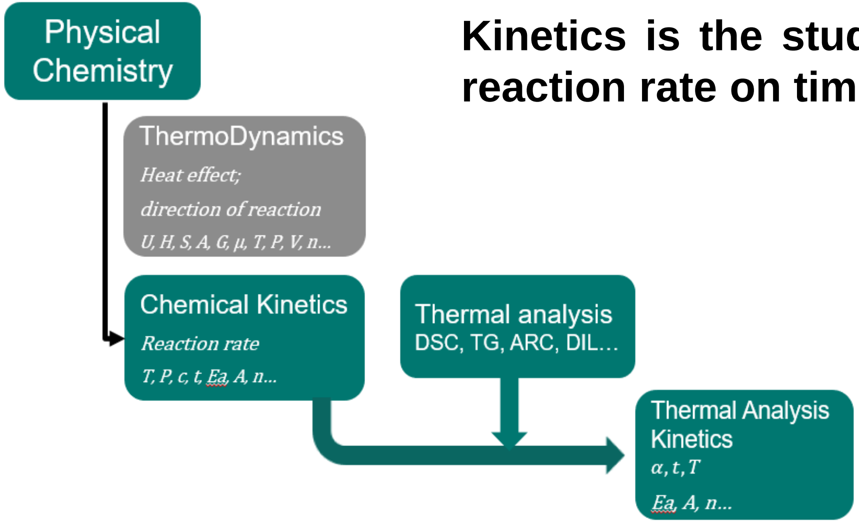

Kinetics is the study of the dependents of a chemical reaction rate on time and temperature.

Dependence of reaction rate on temperature: Arrhenius equation

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General equation

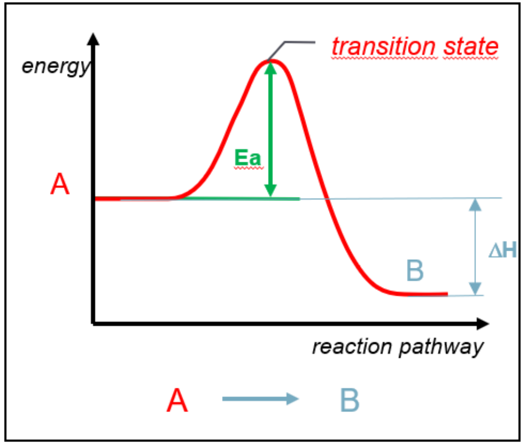
$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha)$$

Arrhenius dependence

$$k(T) = A \cdot exp\left(\frac{-Ea}{RT}\right)$$

Arrhenius equation

$$\frac{d\alpha}{dt} = A \cdot exp\left(\frac{-Ea}{RT}\right) \cdot f(\alpha)$$



A: pre-exponential factor [1/s].
Ea: activation energy [kJ/mol]
R: gas constant 8.31 [J/(gK)]
T: absolute temperature [K]   T[K]=T[°C]+273.15

Measurements for kinetic analysis: Thermogravimetry

- **Mass sample 5-10 mg**
- At least 3 measurements at **different heating rates with R^2 value greater than 0.995**
- Example: 0.25, 0.5, 1, 2, 5, 10, 20 K/min
- **Reproducibility**

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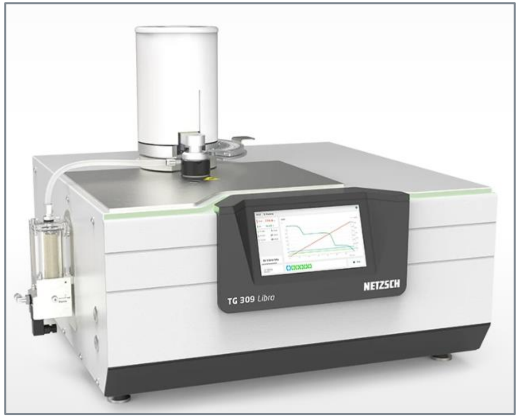
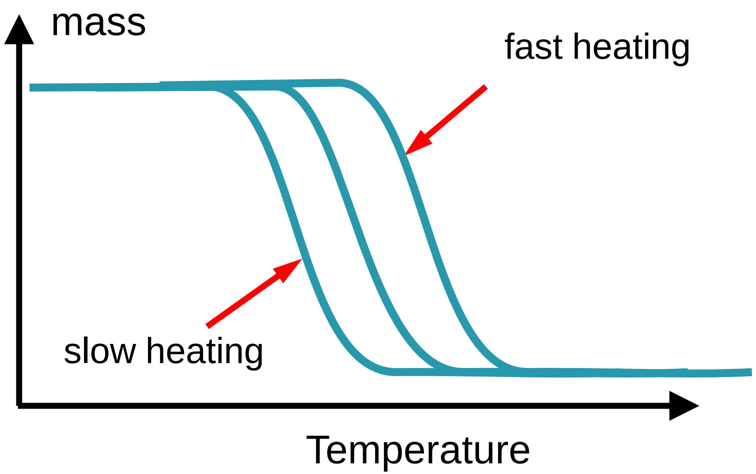
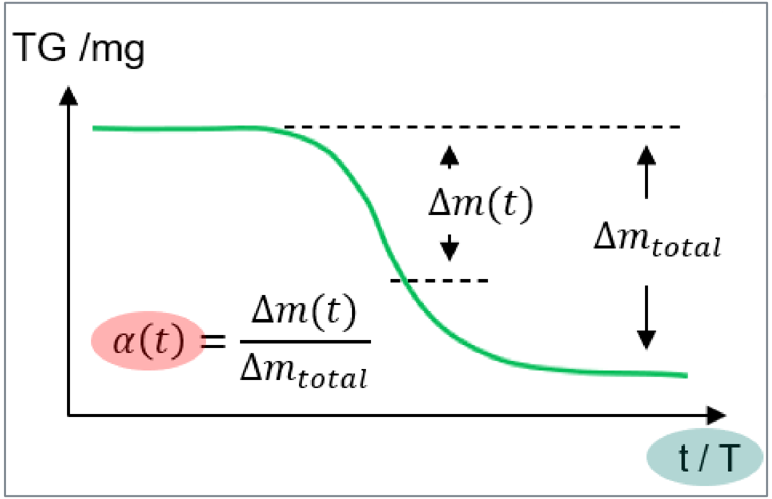
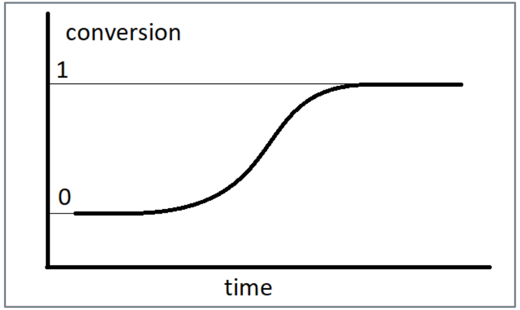




Thermogravimetry: mass change is measured during heating

Conversion α(t) for TGA data





$$\alpha(t) = \frac{\Delta m(t)}{\Delta m_{total}}$$

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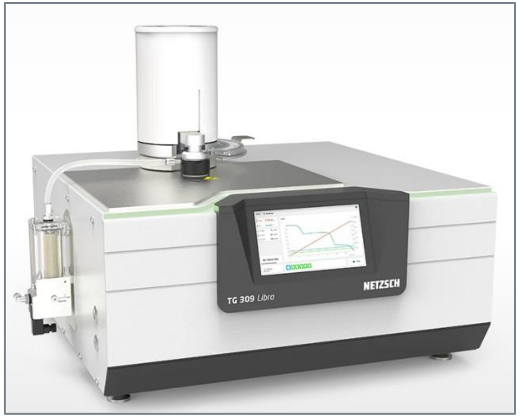


$$\mathbf{A} \xrightarrow[\alpha:\,0..1]{t,\ T} \mathbf{B}$$

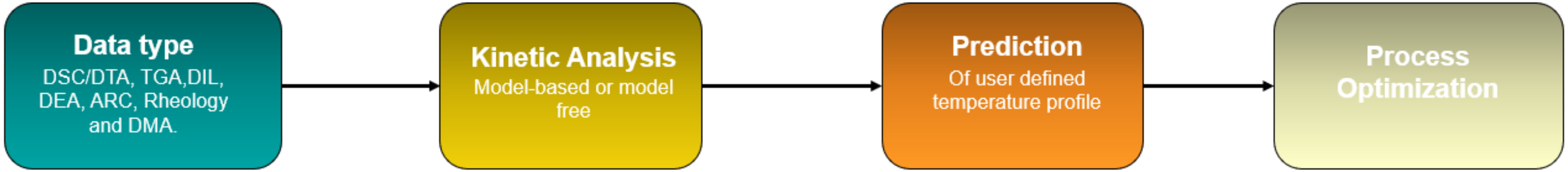
$$\begin{array}{ccc} c_A & \rightarrow & 1-\alpha \\ c_B & \rightarrow & \alpha \end{array}$$

- α(t) : Conversion is the ratio of the partial mass loss at given time point to the total mass loss at the final time point

2 Kinetics Neo Software

Kinetics Neo Software

- Kinetics Neo is a software tool for the kinetic analysis and simulation of thermoanalytical data.
- **Fitting Experimental Data by using Mathematical models:** Mathematical models enable the fitting of experimental data to theoretical equations, which helps in determining kinetic parameters like **Activation energy**, **Pre-exponential factor**, **f(α)** and **Coefficient of determination R^2**.



Approaches: model free and model based

Model free

$A \rightarrow B$

α – degree of conversion

$$\frac{d\alpha}{dt} = A(\alpha) \cdot f(\alpha) \cdot exp\left(\frac{-E_A(\alpha)}{RT}\right)$$

Unknown: Ea(α) and A(α)
A(α) can be found only with assumption of f(α)

Assumptions:

1. Only **one** kinetic equation
2. Ea and A **depend on α**
3. Reaction rate at the same conversion is only a function of temperature
4. Total effect (total mass loss or total peak area) must be the **same for all curves**
5. **Changes** of mechanism should be at the **same conversion** value

Model based

$A \rightarrow B \rightarrow C \rightarrow \ldots$

a – concentration of A
b – concentration of B
c – concentration of C

$$\frac{d(a \rightarrow b)}{dt} = A_1 \cdot f_1(a.b) \cdot exp\left(\frac{-E_{A1}}{RT}\right)$$

$$\frac{d(b \rightarrow c)}{dt} = A_2 \cdot f_2(b.c) \cdot exp\left(\frac{-E_{A2}}{RT}\right)$$

The number of unknown kinetic triplets equals the number of the steps

Assumptions:

1. Reaction consists of **several individual reaction steps** with own equations.
2. All kinetic parameters which are the **constant values**
3. The **total signal** is the **sum** of the signals of the single reaction steps having **own weight**

Kinetic Analysis Methods in Kinetics Neo Software

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$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$$

Kinetic Analysis

Arrhenius only

Model-free

Multi-point

Ozawa-Flynn-Wall
Friedman
Kissinger Akahira Sunose
Vyazovkin for heating
Numerical

Model-based Arrhenius or non-Arrhenius

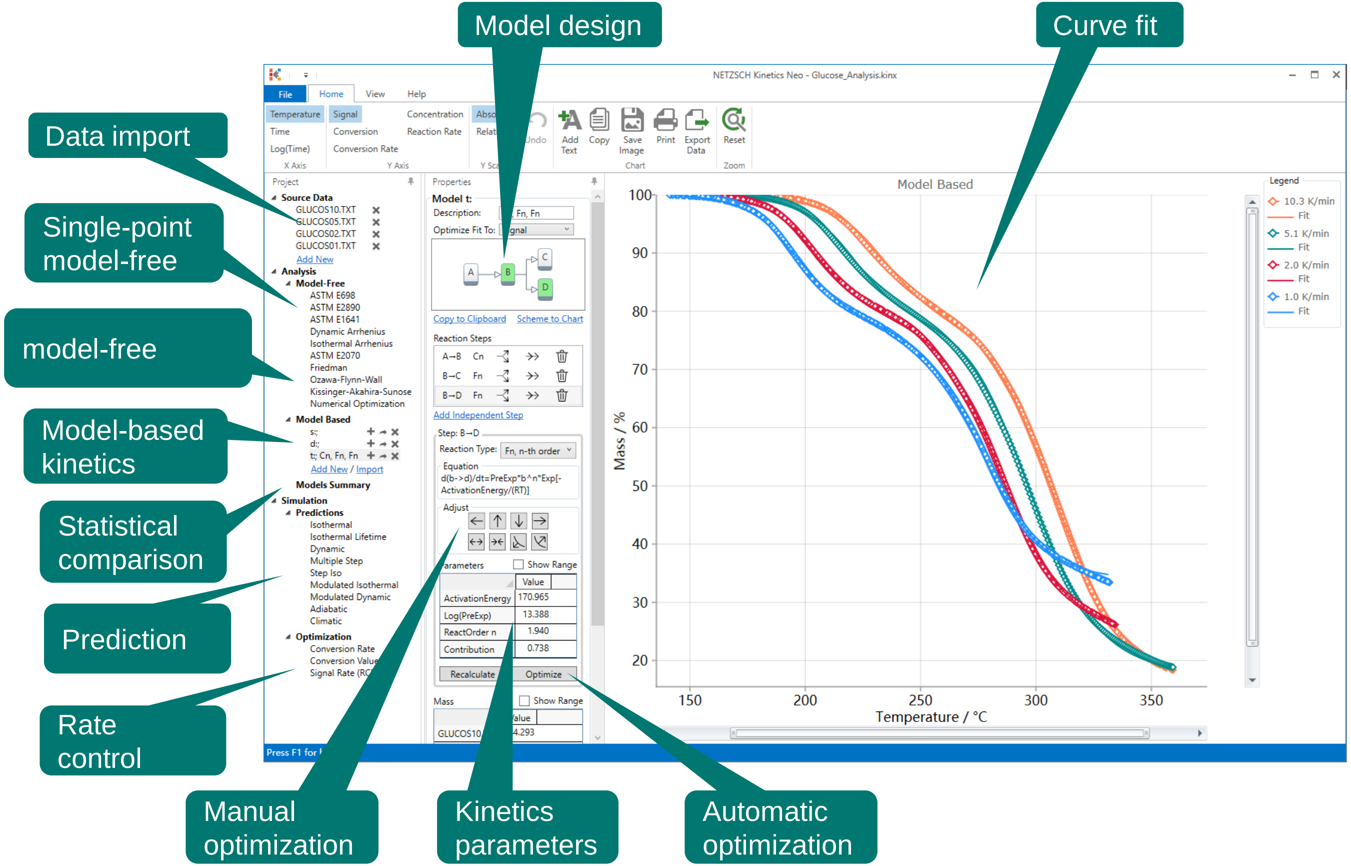
Multi-step model (connection of steps)

independent
consecutive
competing

Reaction type for each step (f(α))

n-th order
autocatalysis
nucleation
Diffusion control

Kinetics Neo Software



Prediction and Rate Control
– Technical application of kinetics model

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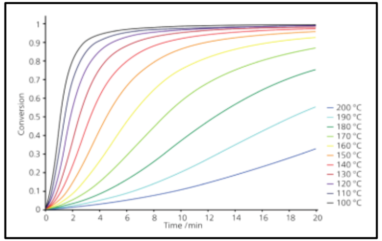
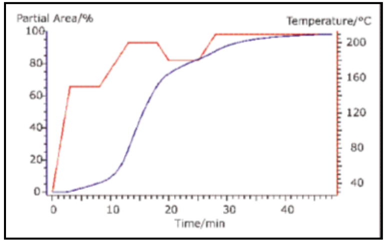
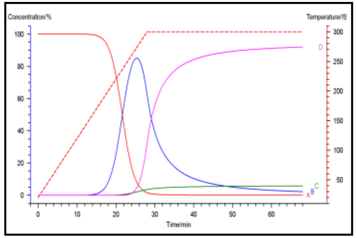


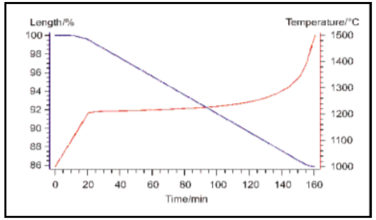
Isothermal process prediction



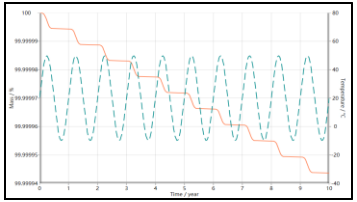
Complex process prediction



Concentration change prediction



Reaction rate control



Storage stability prediction under waving temperature

3 Step-by-Step Guide to Kinetics Analysis

Kinetic Analysis Using Non-Isothermal Thermogravimetry Measurements

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Kinetics Neo Software is **compatible** with measurements (tests) data made by both **NETZSCH** and **NON-NETZSCH** instruments

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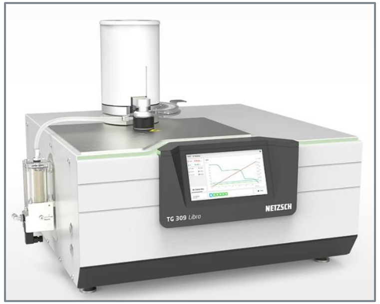

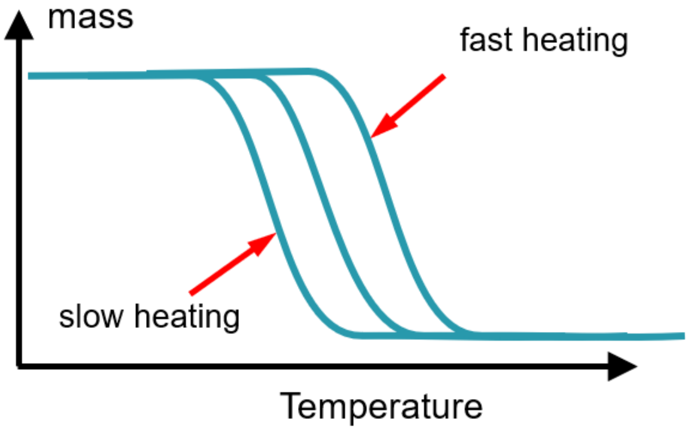

Thermogravimetry: mass change is measured during heating

How to Determine Thermal Stability of an Olive Stone With TGA?

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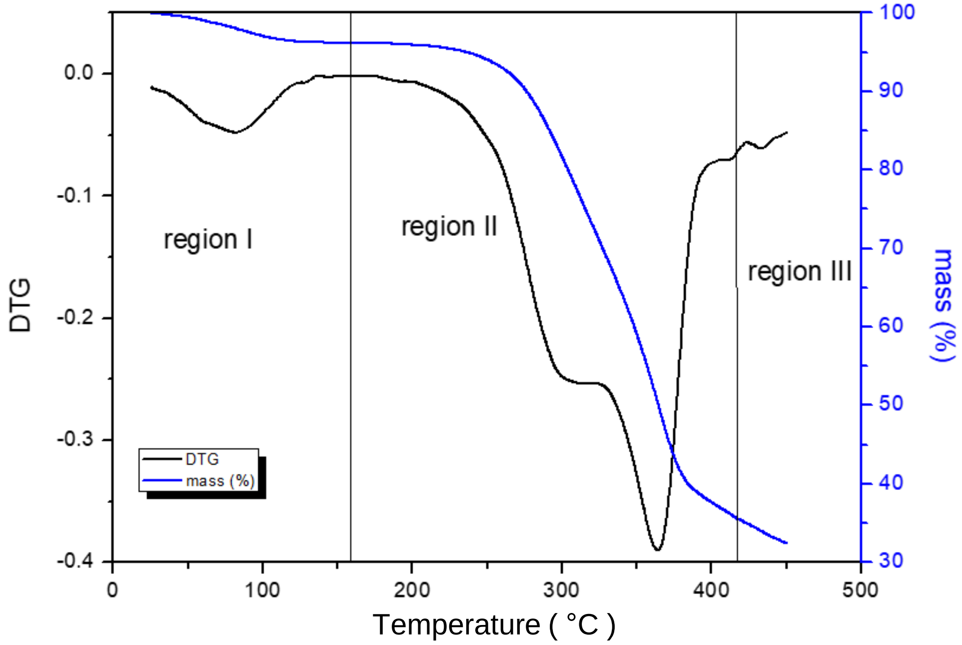
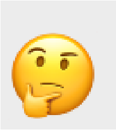


Mass loss versus temperature (TG) and derivative thermogravimetric (DTG) curve of **olive stone sample** for heating rate 10 °C min−1 in N2

More Than Thermal Stability?

TGA measurement

→ decomposition temperature



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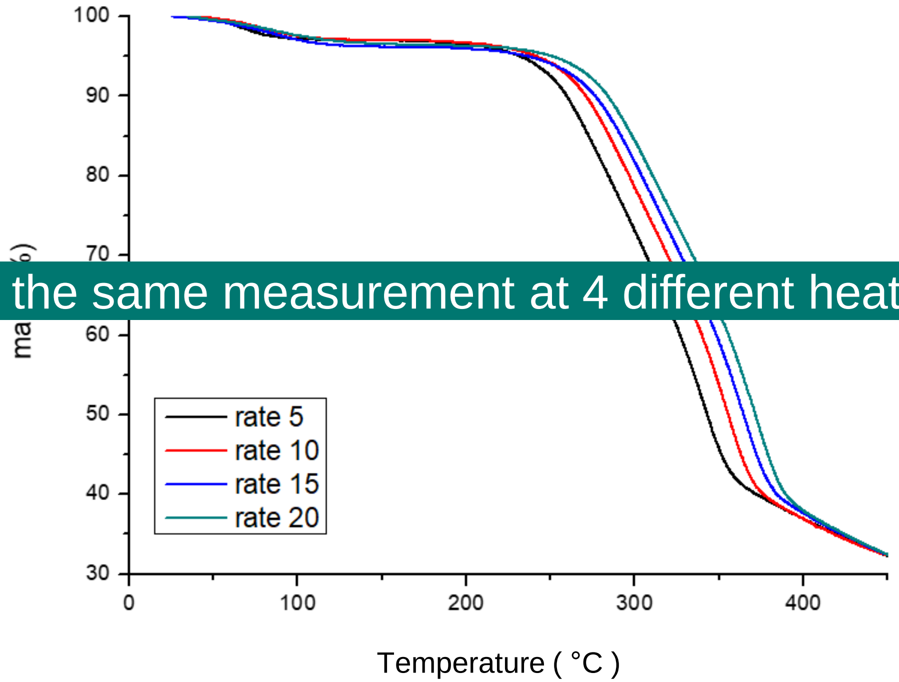
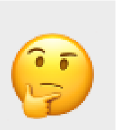
Measurements at 4 Different Heating Rates

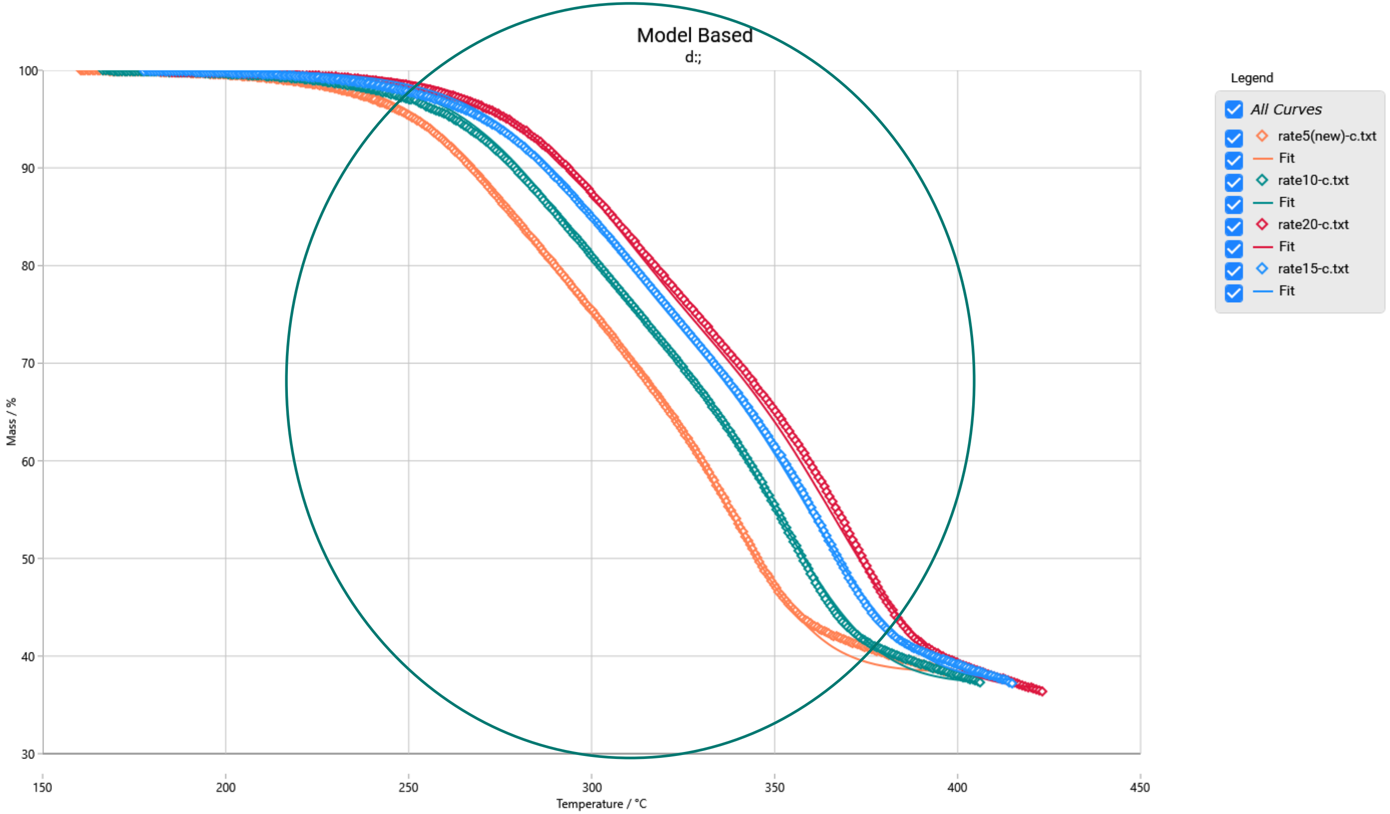


1. Carry out the same measurement at 4 different heating rates

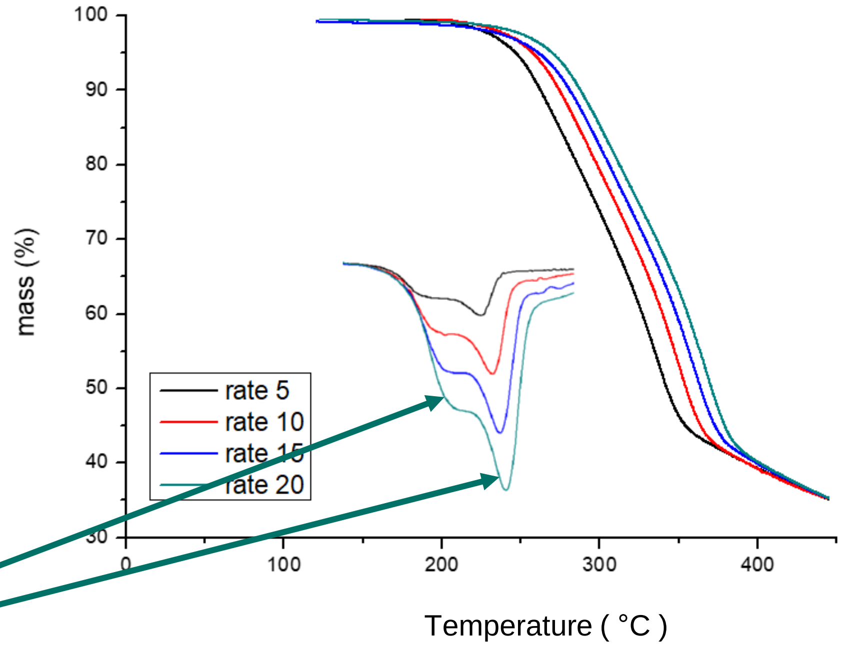
How to Determine the number of steps?



Decomposition Steps…



… Or More????



DTG curve of measurement

Kinetic evaluation of the decomposition of olive stone

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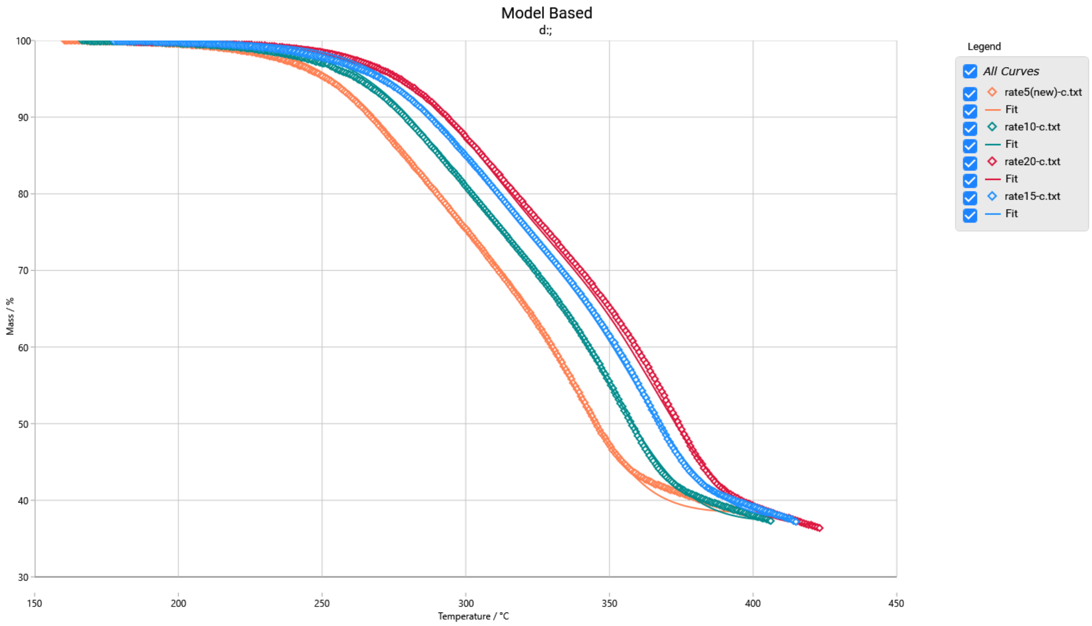
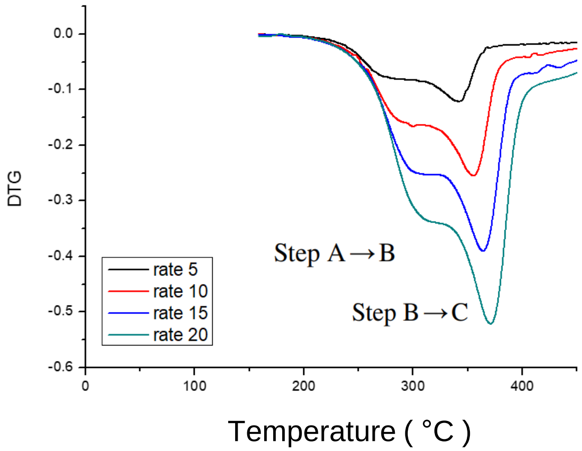


	Reaction model	Activation energy E_a (kJ/mol)	Pre-exponential factor logA, A(1/s)	Reaction order (n)	Contribution	R^2
Step A→B	Fn	130	10.04	1.29	0.36	0.99974
Step B→C	Fn	150.4	10.53	1.26	0.63	



5 Termica Neo Software

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

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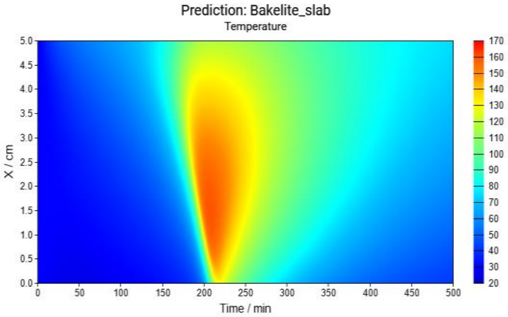
3. Simulation (kg, ton)



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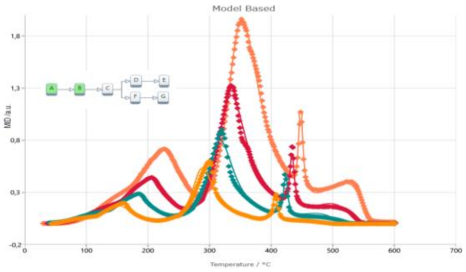
2. Chemical Kinetics (mg)



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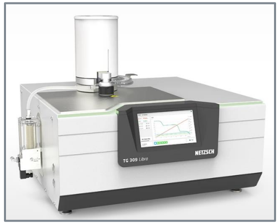
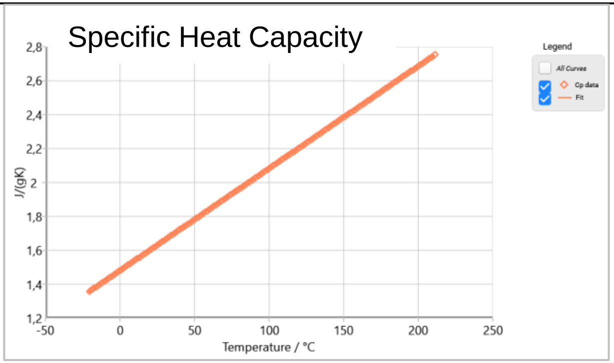
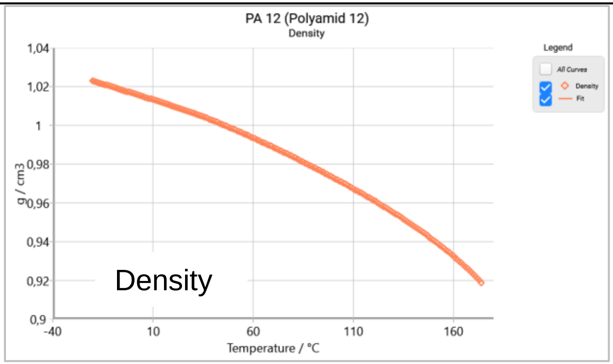
1. Laboratory measurements (mg)

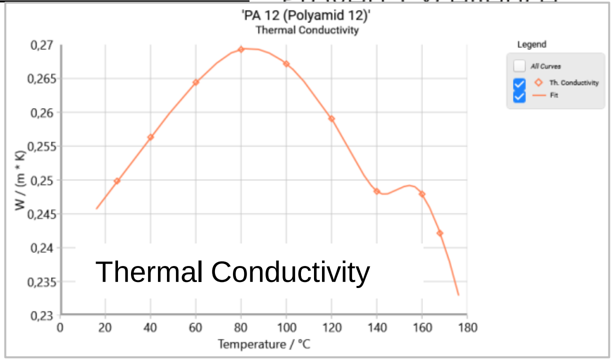


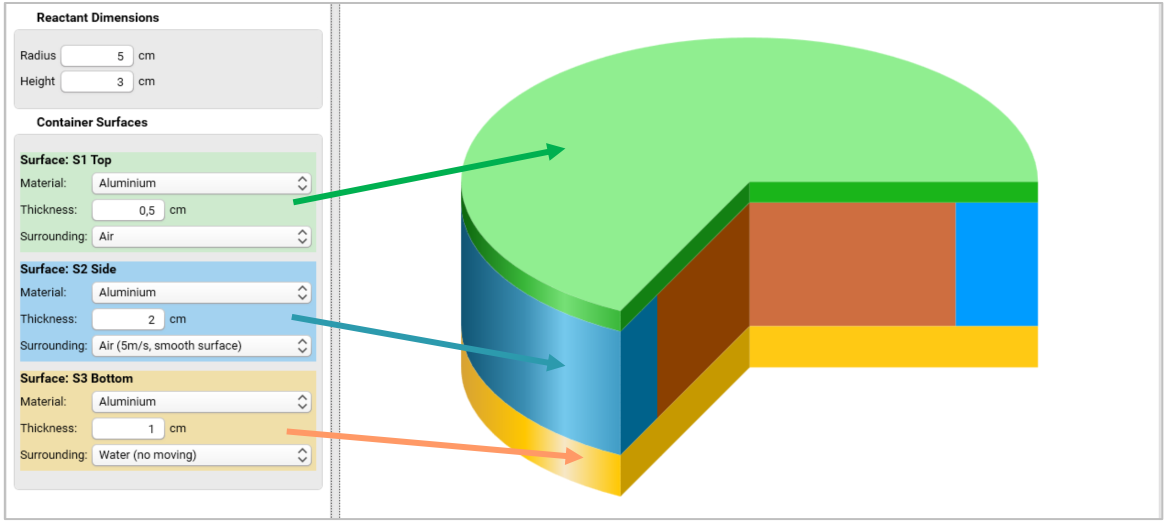
Laboratory Instrument: DSC / TGA / ARC / HFC, …

Physical data for simulation: reacting media and containers









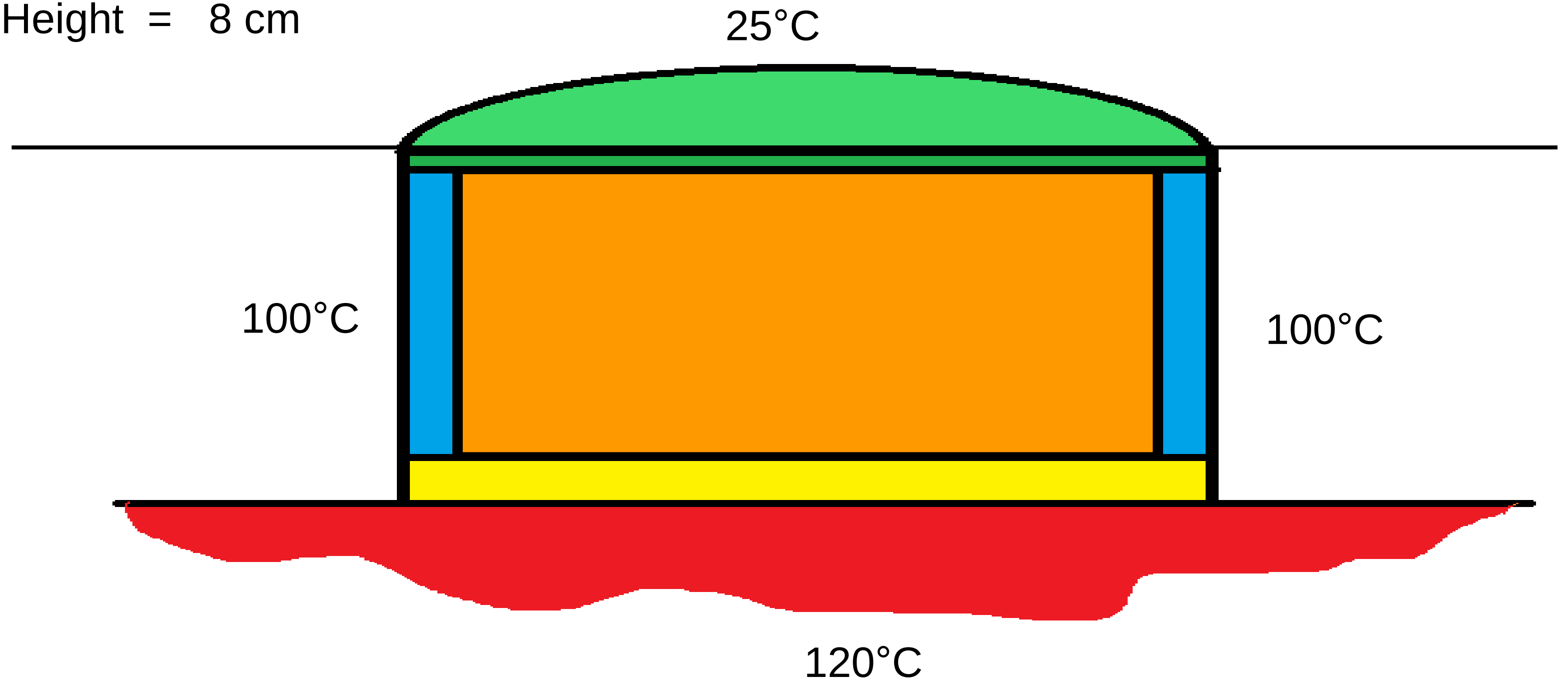
<u>Surface properties:</u>
Heat transfer coefficient and emissivity

All physical properties are temperature-dependent

<u>Material library</u>
contains mostly used materials like polymers, metals, alloys

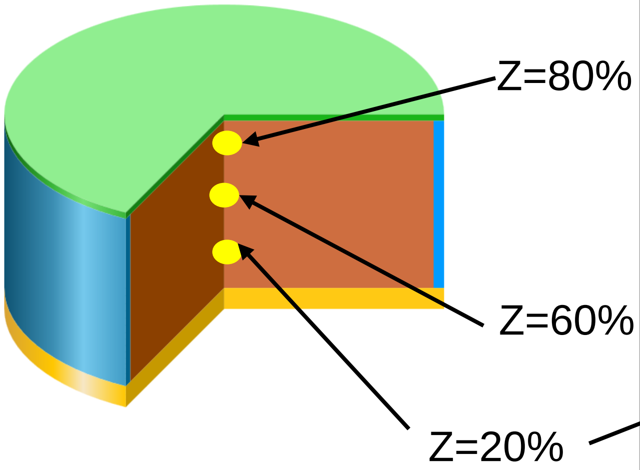
Simulation example Pyrolysis

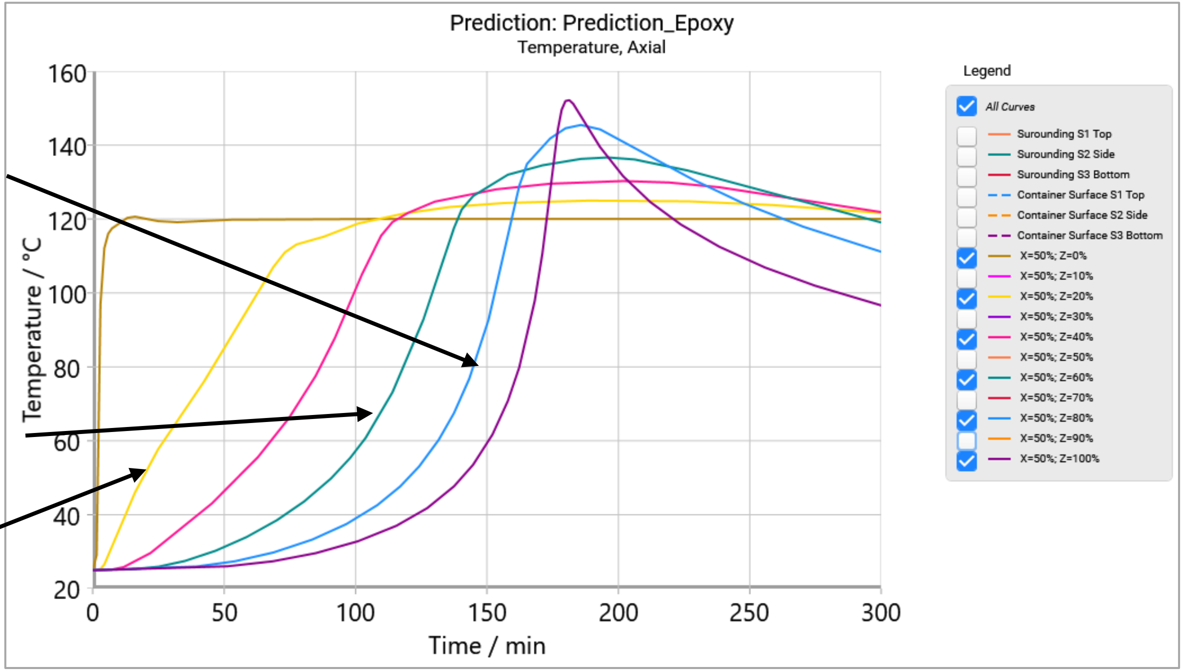
Radius = 10 cm
Height = 8 cm



Temperature vs time at any point of the reacting volume

Horizontal position: R=0

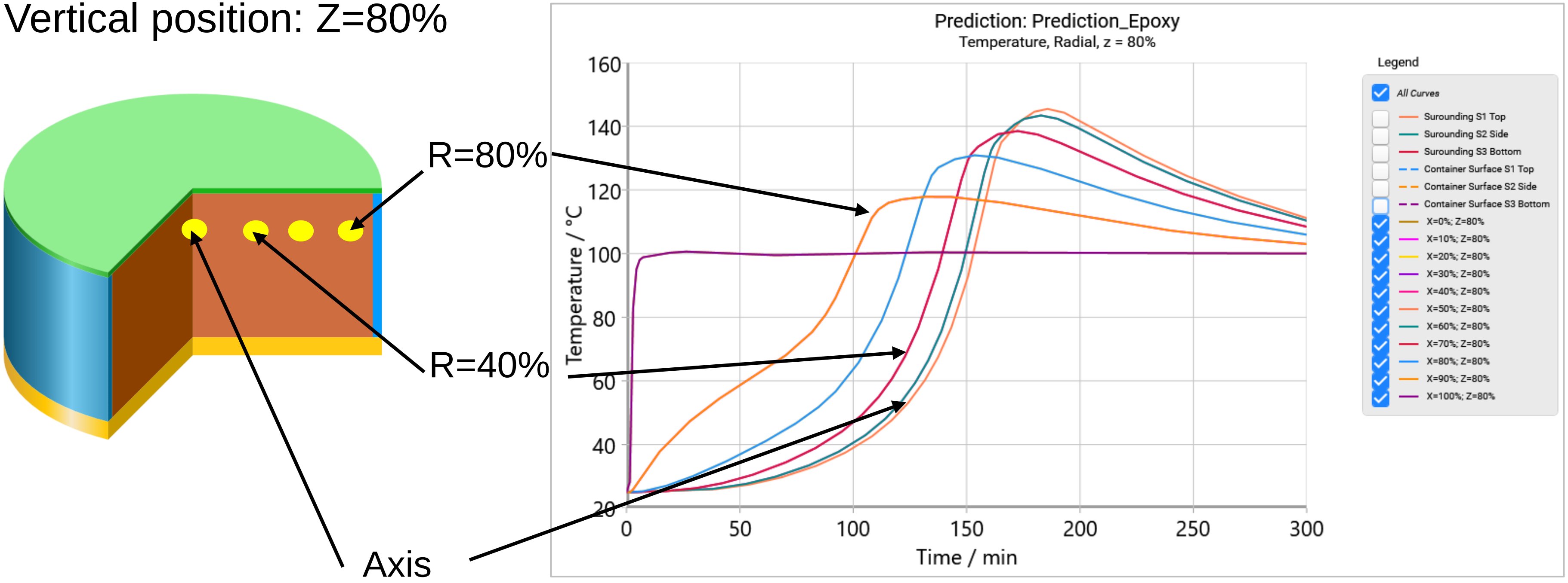




Possible to show: Temperature, conversion, conversion rate vs time

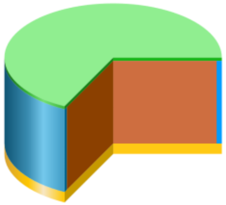
Temperature vs time at any point of the reacting volume

Vertical position: Z=80%

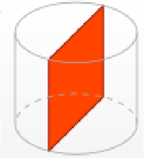


Possible to show: Temperature, conversion, conversion rate vs time

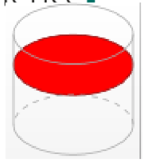
Simulation Results for cylinder

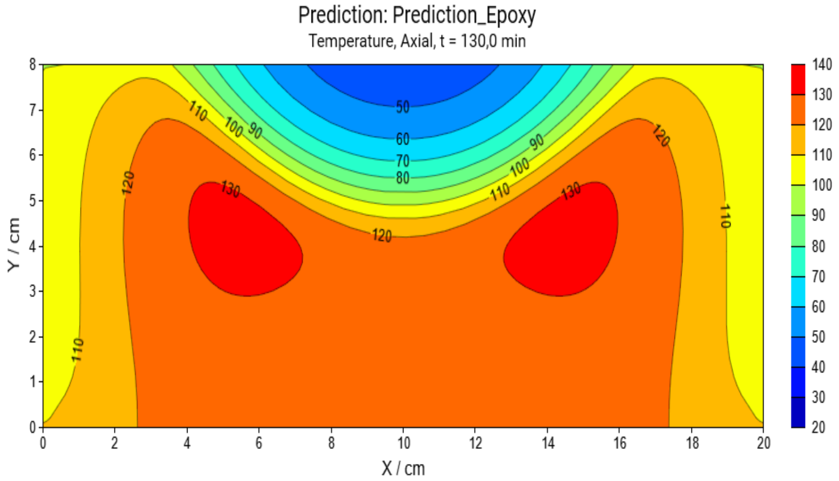


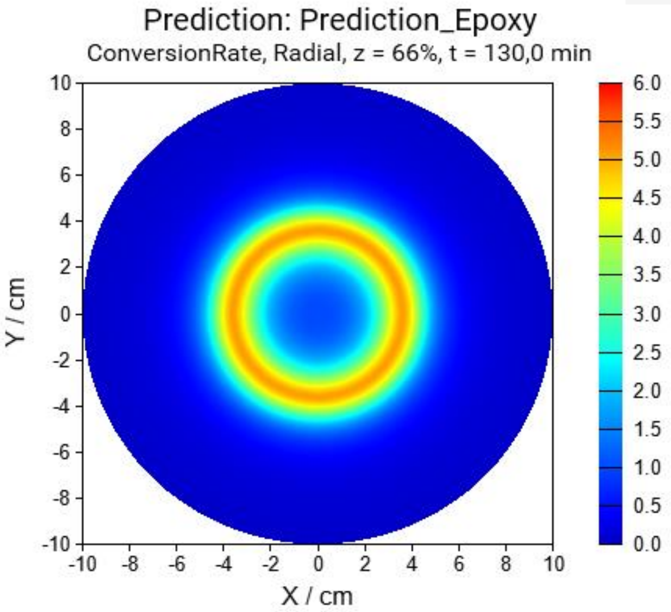
Vertical Section



Horizontal Section







Output from Termica Neo

Step-by-Step Recap

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Starting material

Measured data TGA,….

At least **3** measurements at different heating rates.

Kinetics Analysis

- Import data
- Create the most suitable model
  - ❑ Reaction type for each step
    - nth order
    - Autocatalysis

Kinetics Triplet, Prediction and Process Optimization

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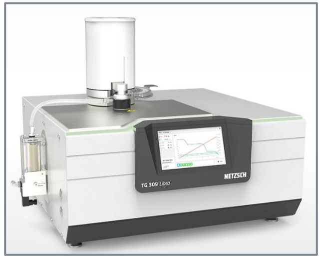

KINETICS NEO

What Makes Kinetics Neo and Termica Neo So Valuable

- Fast and easy to handle with improved user interface
- Includes all model-free and model-based methods; statistical comparison of the results obtained from different methods
- The most accurate kinetic triplet can be obtained
- Predictions and optimizations possible with model-free and model-based methods

Unique: Kinetics Analysis must fulfil ICTAC kinetics recommendations

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***ICTAC:** International Confederation for Thermal Analysis and Calorimetry*

KINETICS NEO

- Model free analysis
- Multi-step model-fitting (model based)

ELSEVIER

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Review

ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics

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NETZSCH Kinetics Neo Web Site: How to get a trail version

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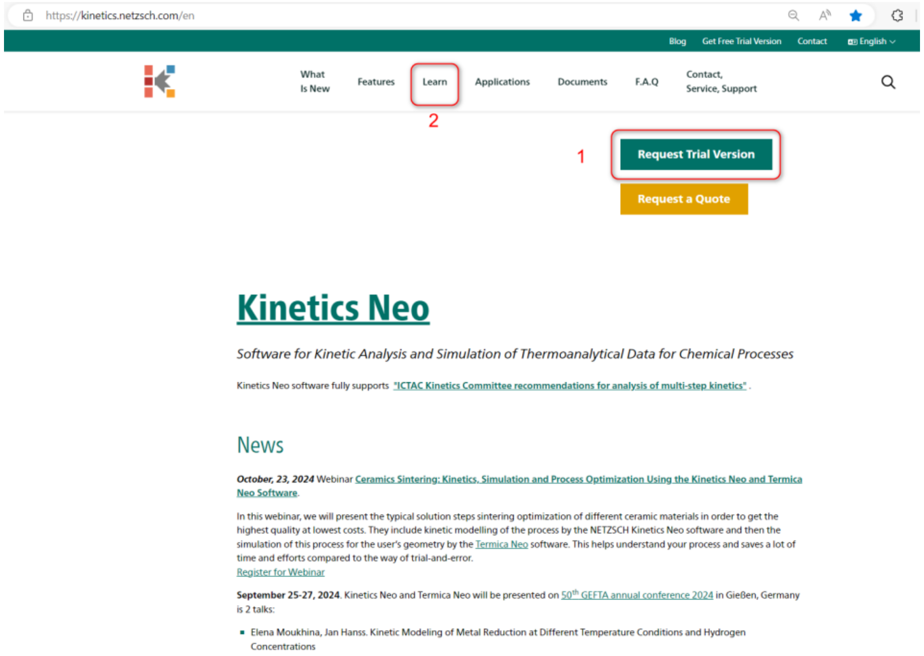
- Go to: https://kinetics.netzsch.com

- *Trial Version 30 days*



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Thank you for your attention!

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