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UNLOCKING PYROLYSIS KINETICS

Practical Analysis with Kinetics Neo Software

The NETZSCH Group

and its three globally operating divisions

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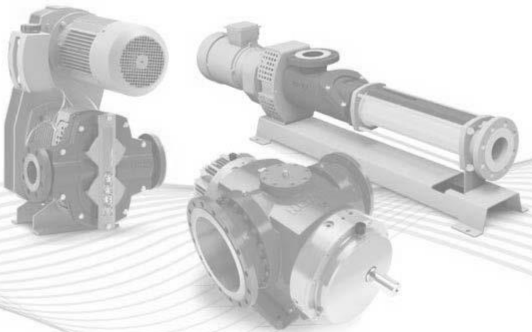
Erich NETZSCH GmbH & Co. Holding KG



Analyzing & Testing

Devices for thermal analysis, determining thermophysical properties and rheology as well as fire testing systems

Grinding & Dispersing

Extensive range of machines for wet and dry grinding, mixing, dispersing, homogenizing and separating

Pumps & Systems

Always the right positive displacement pump for your application

Business areas Analyzing & Testing

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Products and services for applications in the low and high temperature range from -260°C to 2800°C

Thermal Analysis

Determination of dimensional and mass changes, phase transitions and enthalpies as a function of temperature

Thermophysical Properties

Determination of thermal diffusivity and thermal conductivity, specific heat capacity and thermal expansion coefficients

Adiabatic Calorimetry

Analysis of decomposition processes and reaction processes with regard to temperatures, released heat quantities and pressure curves

Rheology

Measurement of rheological properties of non-Newtonian fluids and soft solids - from formulation to product use

Fire Testing Devices

Determination of the fire behavior of products in the automotive, construction, electronics and polymer sectors; classification into "European fire classes"

The Business Unit Analyzing & Testing

NETZSCH
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>150M €
Sales

>700
Employees worldwide

>10
Laboratories worldwide

6
International production sites

> 50
Sales and service locations worldwide

NETZSCH Analyzing & Testing - worldwide presence

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Europe

Germany
HQ Selb - Ahlden - Weimar

France
Lyon

Great Britain
Wolverhampton

Italy
Verona

Austria
Graz

Poland
Krakow

Spain
Barcelona

Sweden
Stockholm

Czech Republic
Prague

Production site   Branch office

Agenda

1. **Pyrolysis and current challenges**
2. **Kinetics in Solids and Kinetics Neo software**
3. **Review Example Study of the Olive Stone Biomass Pyrolysis**
4. **Software Demonstration**

Pyrolysis and current challenges

Pyrolysis

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- 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)**

→

Products from Pyrolysis

- Gases
- Liquids
- Solid Residue (Charcoal)

Kinetics Analysis

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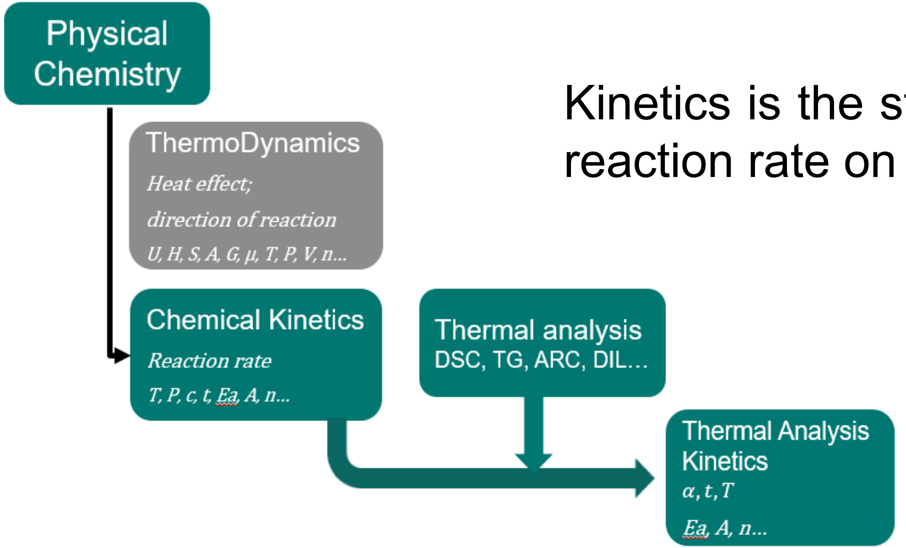
- The poor choices of the kinetic methods and experimental conditions
- kinetic complexities of multi-step pyrolysis processes

Kinetics in Solids

Kinetics in Solids



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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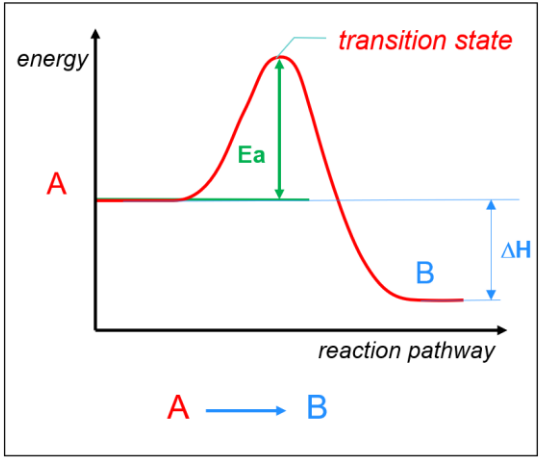
General equation

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

Arrhenius dependence

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

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

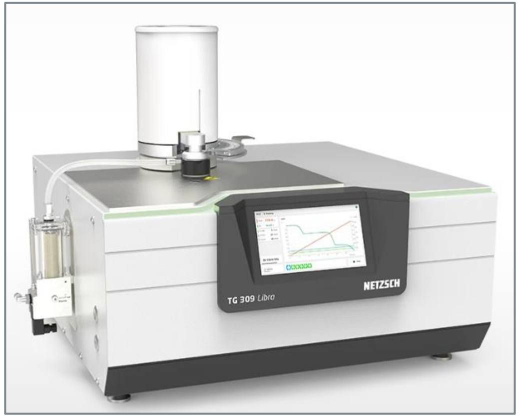


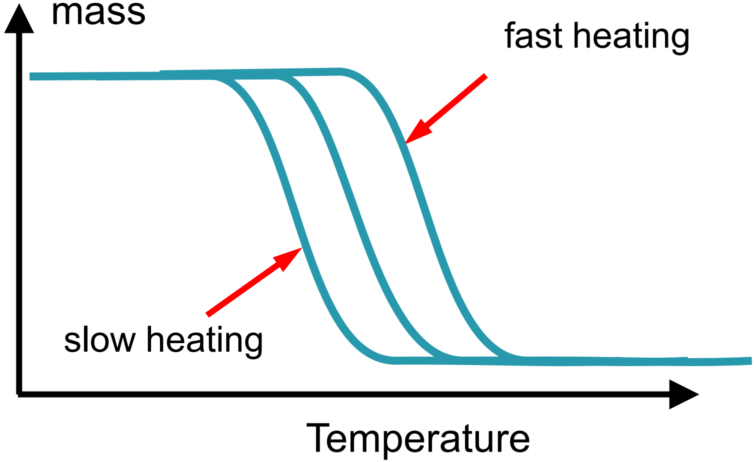
α : conversion
A: pre-exponential factor [1/s]
Ea: activation energy [kJ/mol]
R: gas constant 8.31 [J/(mol.K)]
T: absolute temperature [K]   T[K]=T[°C]+273.15

Measurements for kinetic analysis: Thermogravimetry

- **Mass sample 10 mg**
- At least 3 measurements at **different heating rates with R^2 value greater than 0.995**
- Heating rates of **1, 2, 5, 10, and 20 K/min** are the most commonly reported in the literature for pyrolysis.
- **Reproducibility**

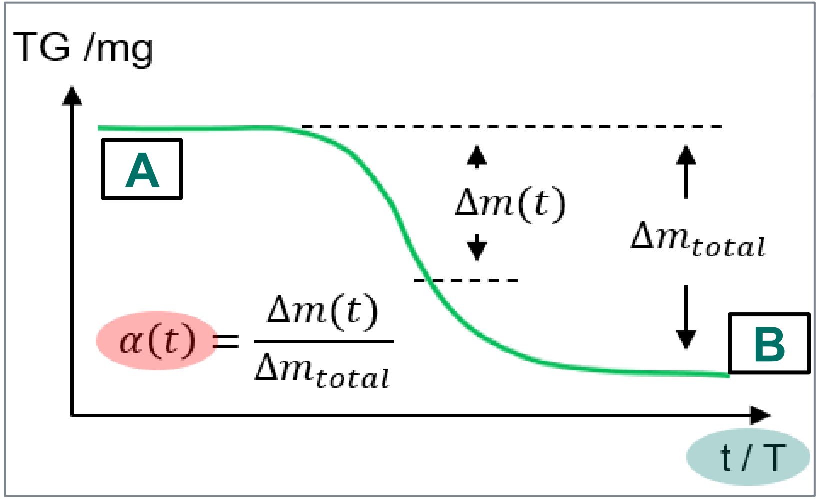
TG 309 Libra Classic

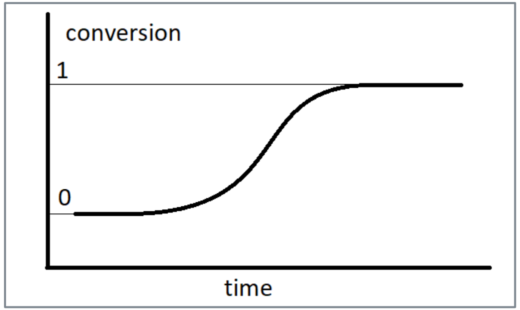




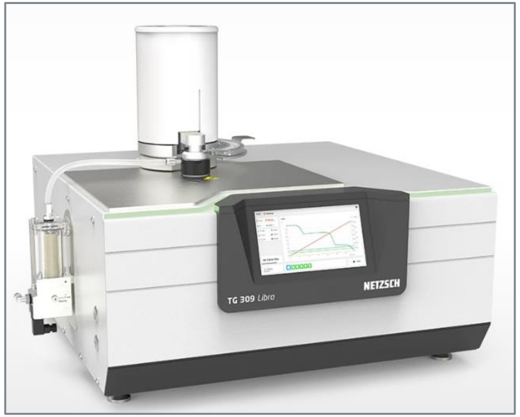
Thermogravimetry: mass change is measured during heating

Conversion α(t) for TGA data





TG 309 Libra Classic



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

$$c_A \rightarrow 1-\alpha$$
$$c_B \rightarrow \alpha$$

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty}$$

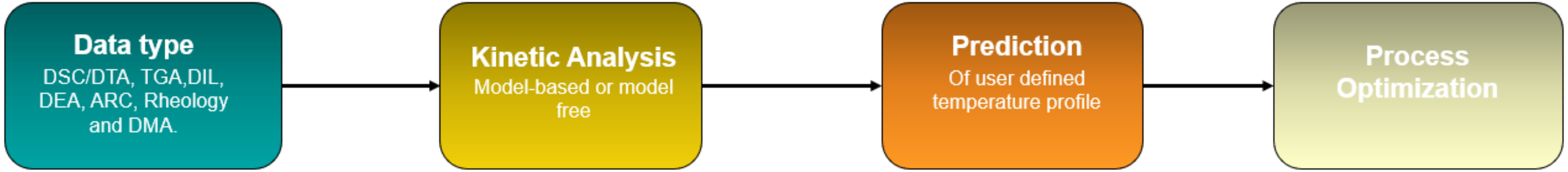
m_0: initial mass
m_t: mass at time t
m_∞: final mass

- 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

Kinetics Neo Software

Kinetics Neo Software

- **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**.
- **Kinetics Neo software** can simulate and **predict** the behavior of chemical processes under various temperature conditions, such as isothermal, dynamic, and adiabatic profiles.
- **Kinetics Neo Software** allows users to **optimize** temperature programs.



Supported Measurement Types

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ARC / MMC

Rheology

DMA

DIL

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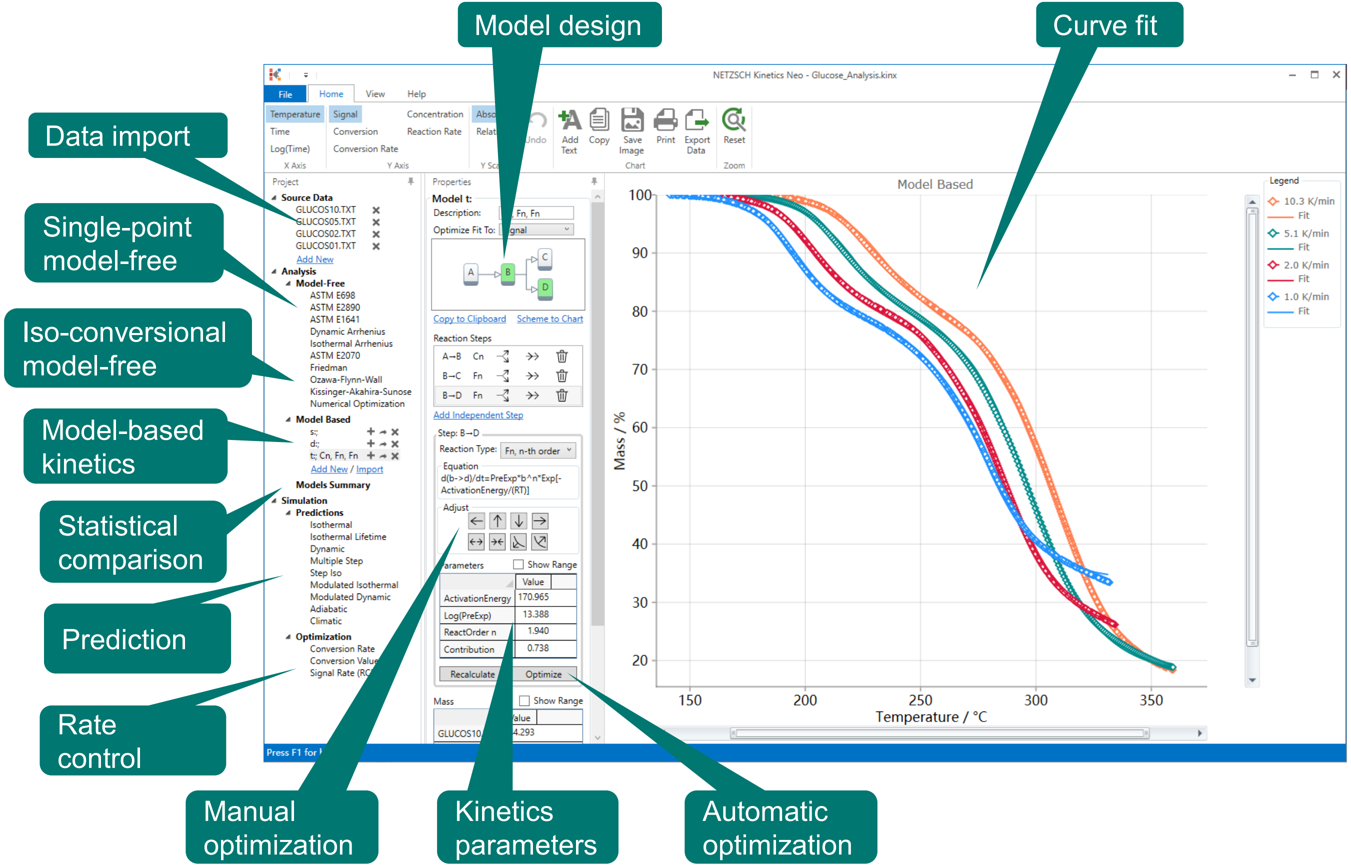
DSC

- NETZSCH and non-NETZSCH data
- ASCII text files like TXT or CSV
- Data Columns (Temperature, Time and Signal)

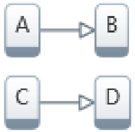
DEA

TGA

Kinetics Neo Software

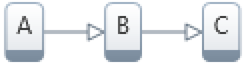


Multi-step Model-fitting: Connection Between Steps



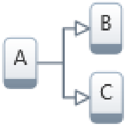
Independent

Mixture of non-interacting components



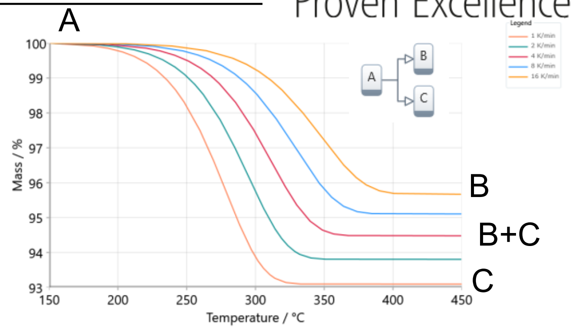
Consecutive

Reaction in the single component

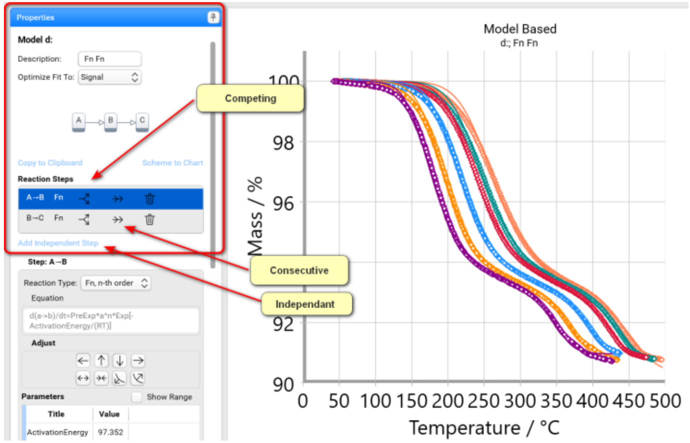


Competing

Product depends on heating rate



Competing



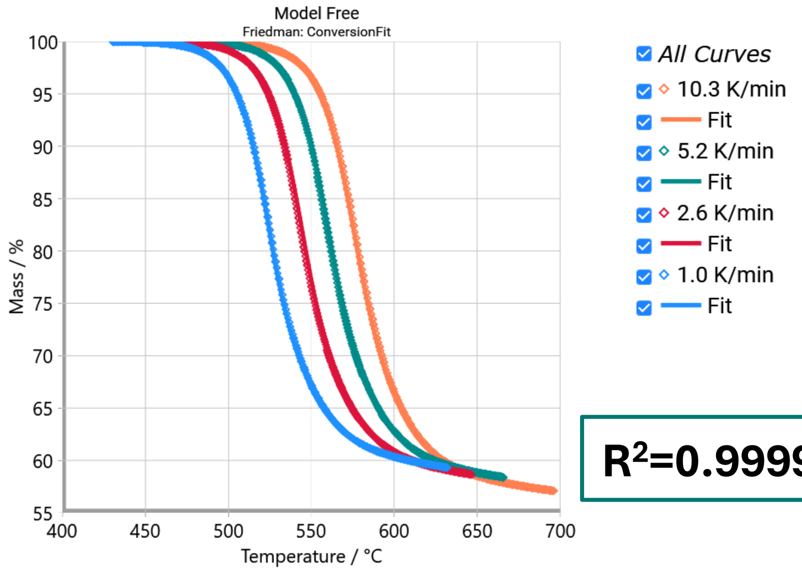
Independent: reactant and product are not involved in other steps

Consecutive: product of one step is a reactant of another step

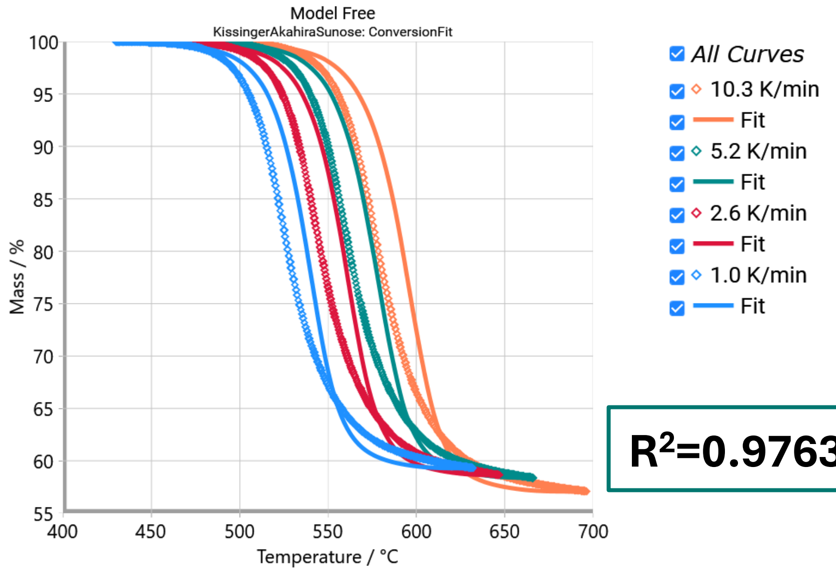
Competing: involve the same reactant

Coefficient of determination R^2

Coefficient of determination R^2 or R-squared : The value R^2 expresses the deviations between the calculated model curves and the experimental data compared to the deviations of the experimental data from their average value.



R^2=0.99994

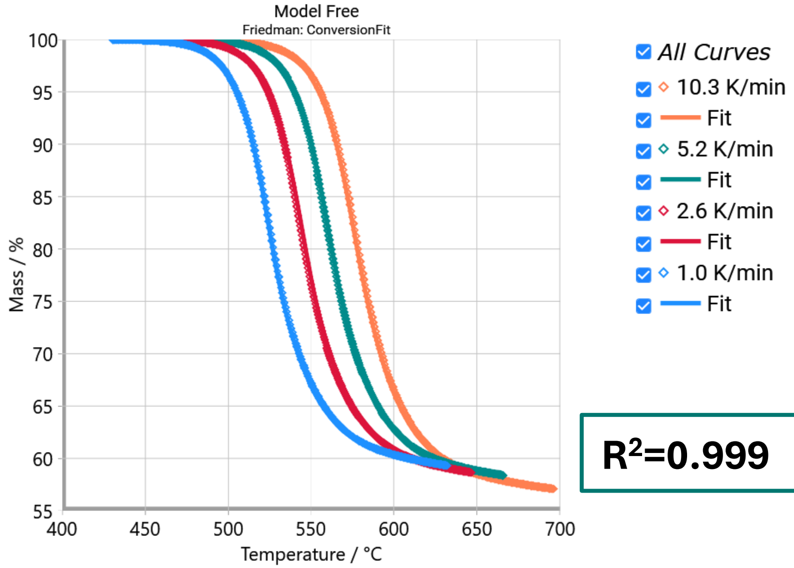


R^2=0.97634

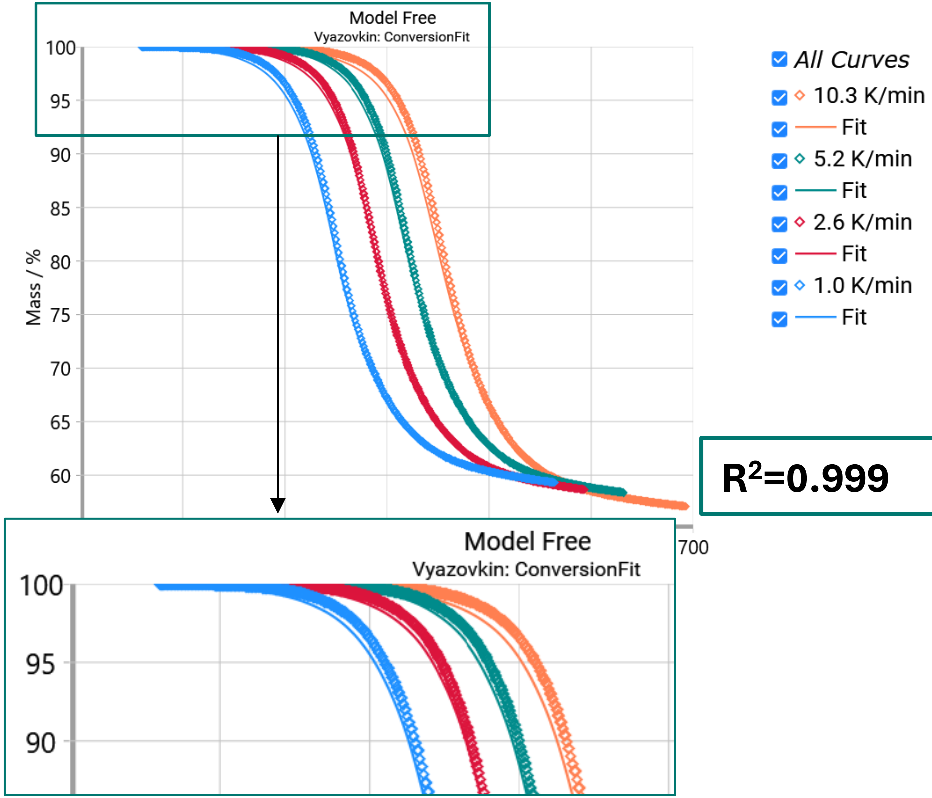
Without R^2, kinetic analysis lacks quantitative validation and is more prone to error.
R^2 confirms model accuracy and ensures reliable kinetic predictions.

Curve fitting visualization

Curve fitting visualization: Visualization helps validate how well a model fits the data and reveals errors like outliers or poor model choices



R^2=0.999



R^2=0.999

R² is a helpful but it doesn't tell the whole story. Without curve fitting plots, you're "fitting blind"

Step-by-Step Guide to Kinetic Analysis

Unlocking the Pyrolysis of Olive Stone Biomass: TGA Analysis and the Appropriate Kinetic Approach

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

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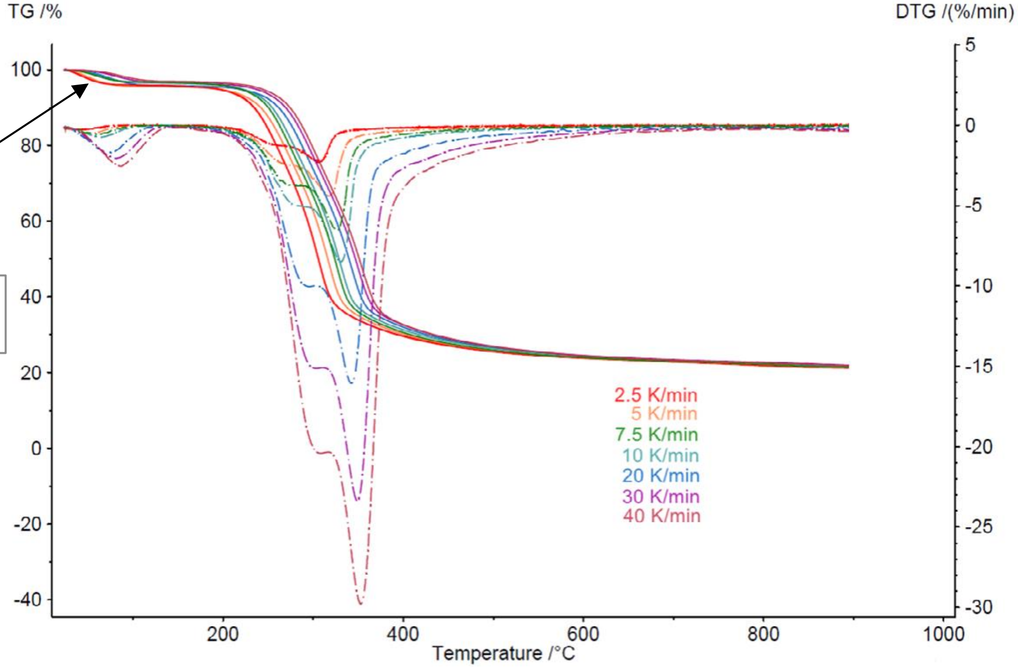
3.3% mass loss moisture evaporation



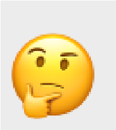
Instrument	NETZSCH TG 309 *Classic*
Crucible	Al_2O_3, open
Sample mass	9.65 mg to 9.85 mg
Temperature range	25°C to 1000°C
Atmosphere	Nitrogen (40 ml/min), switch to synthetic air (40 ml/min) at 900°C
Heating rates	2.5 K/min, 5 K/min, 7.5 K/min, 10 K/min, 15 K/min, 20 K/min,

TGA measurement on olive stone at different heating rates; solid lines: TGA, dashed lines: DTG

More Than Thermal Stability?

TGA measurement

→ decomposition temperature



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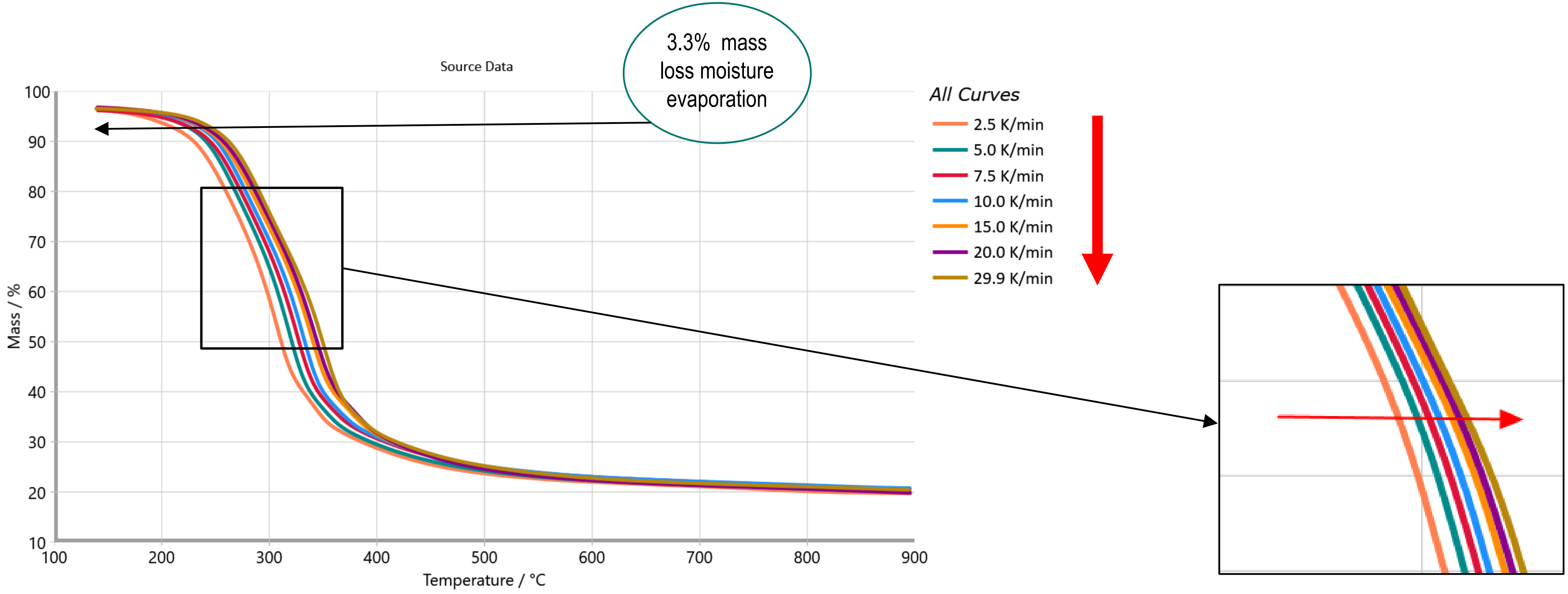
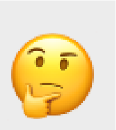
Measurements at Different Heating Rates

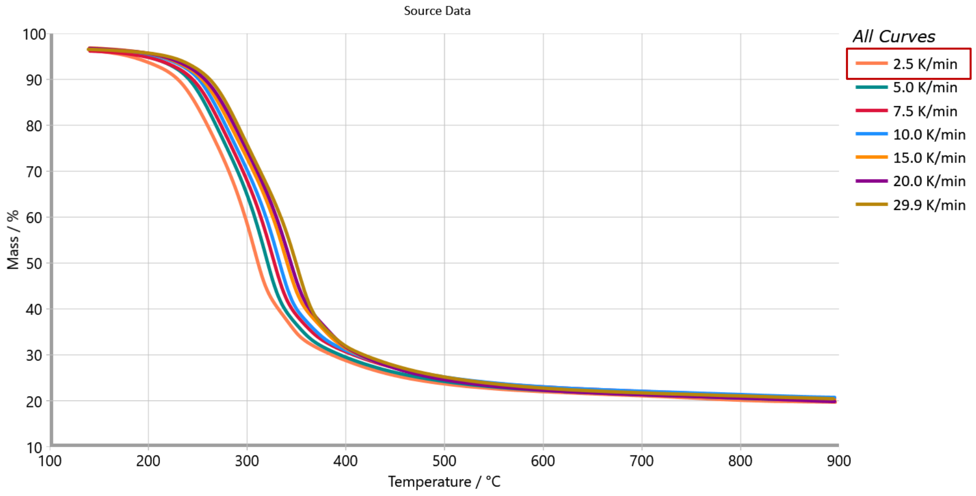


Decomposition of olive stone to 900°C at different heating rates, measured TGA data

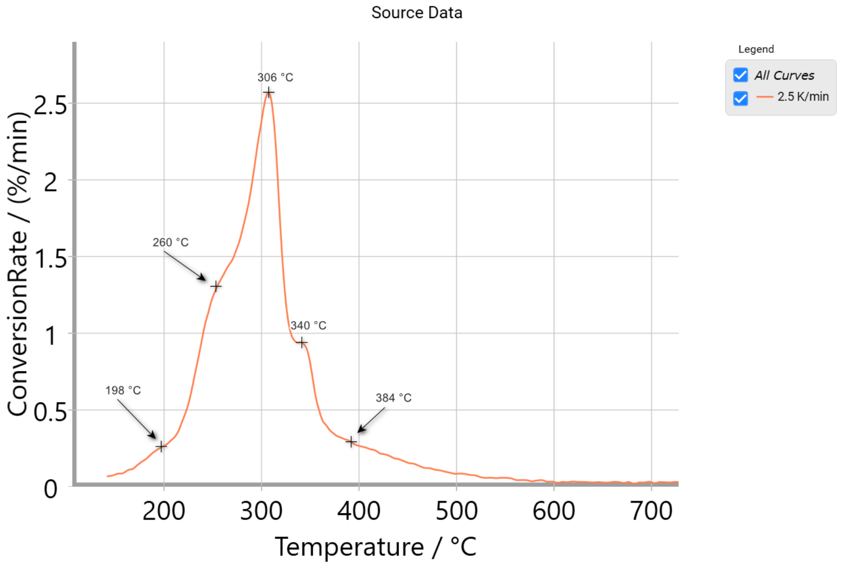
How to Determine the number of steps?



Decomposition Steps…



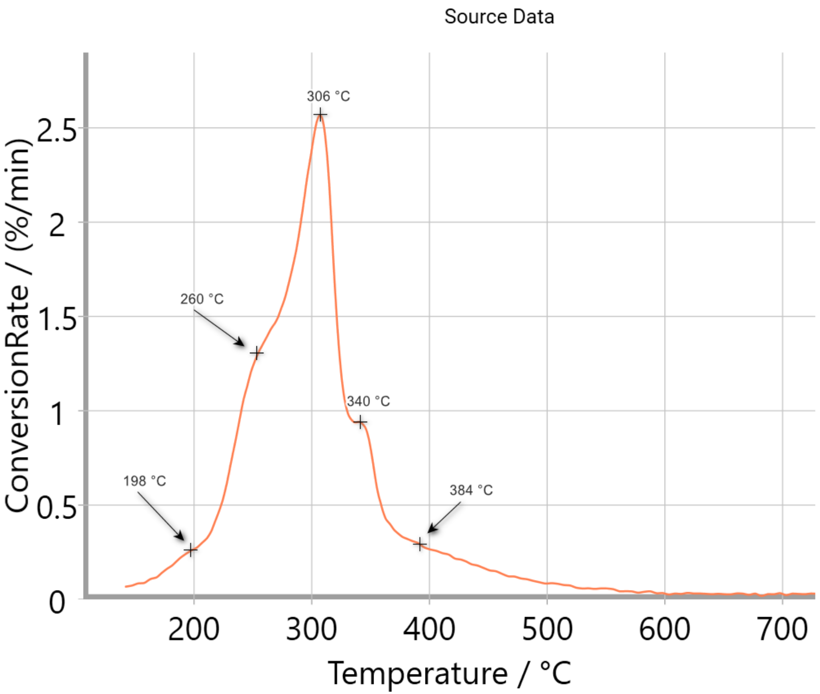
Decomposition of olive stone to 900°C at different heating rates, measured TGA data

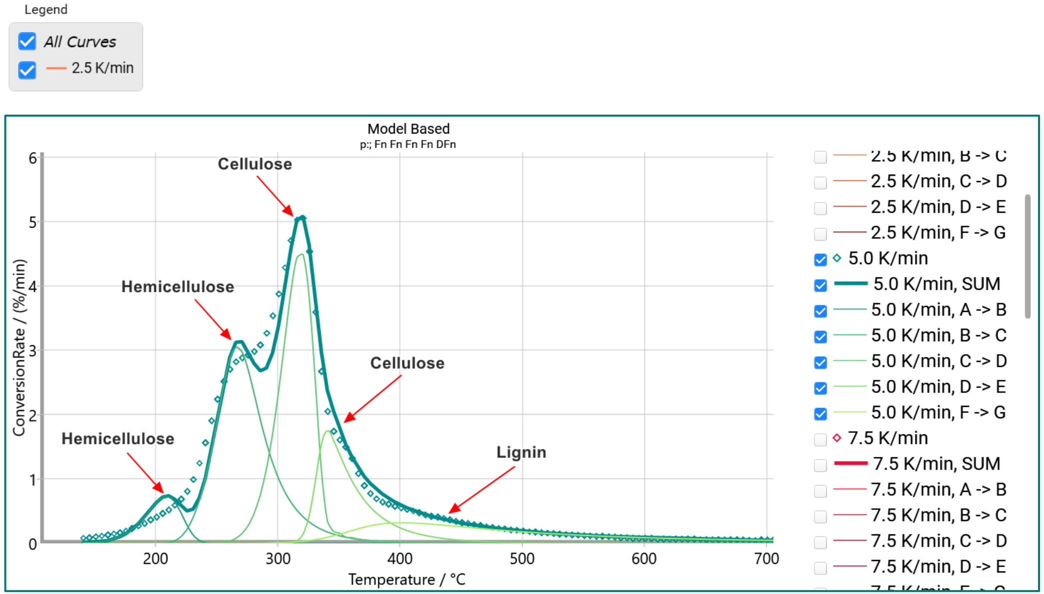


Conversion rate of the measurement at 2.5 K/min to 700°C. One peak and 4 shoulders indicate a 5-step decomposition process

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

Sum of peaks





- **Bouzbib, M., Moukhina, E., & Schmölzer.** ***Unlocking the Pyrolysis of Olive Stone Biomass: TGA Analysis and the Appropriate Kinetic Approach*****. www.netzsch.com**

Kinetic evaluation of the decomposition of olive stone

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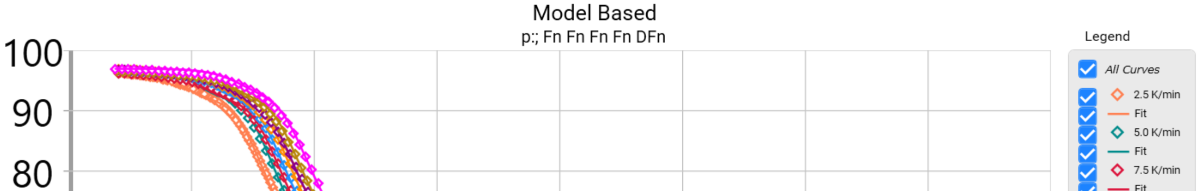
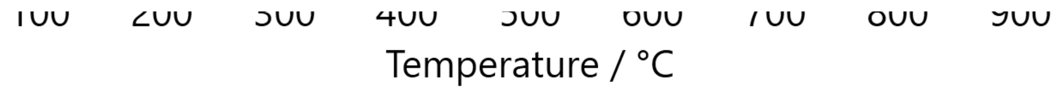


Kinetic parameters of the thermal degradation of olive stone

Reaction step	A → B Fn[1]	B → C Fn[1]	C → D Fn[1]	D → E Fn[1]	F → G DFn[2]
Activation energy [kJ/mol]	151.824	165.479	194.592	206.720	179.468
Log (Pre-Exp) Log (1/s)	14.083	13.792	15.116	15.286	12.093
Reaction order	1.832	2.732	1.039	1.466	6.304
Contribution	0.061	0.336	0.313	0.073	0.217
Coefficient of determination			0.999		

[1]Fn: Reaction of n^{th} order
[2]DFn: One-dimensional diffusion of n^{th} order



Kinetic evaluation of the decomposition of olive stone. Rhombus lines: measured curves; solid lines: calculated curves based on a five-step reaction

Conversion rate controle

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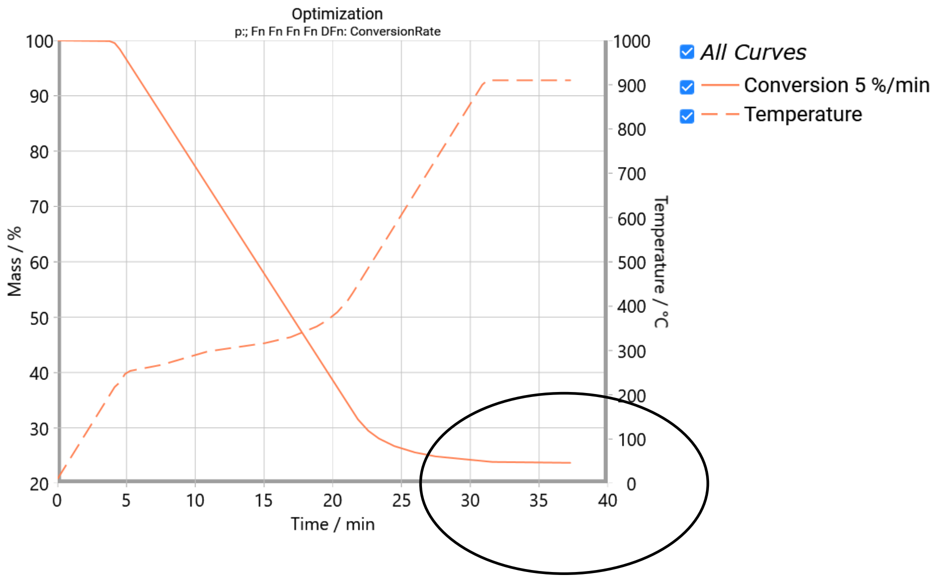
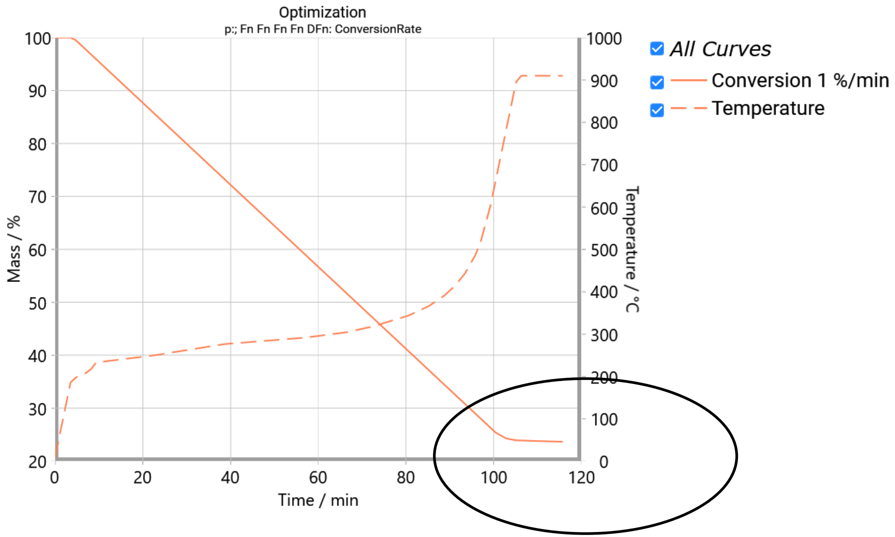
Conversion 5 %/min



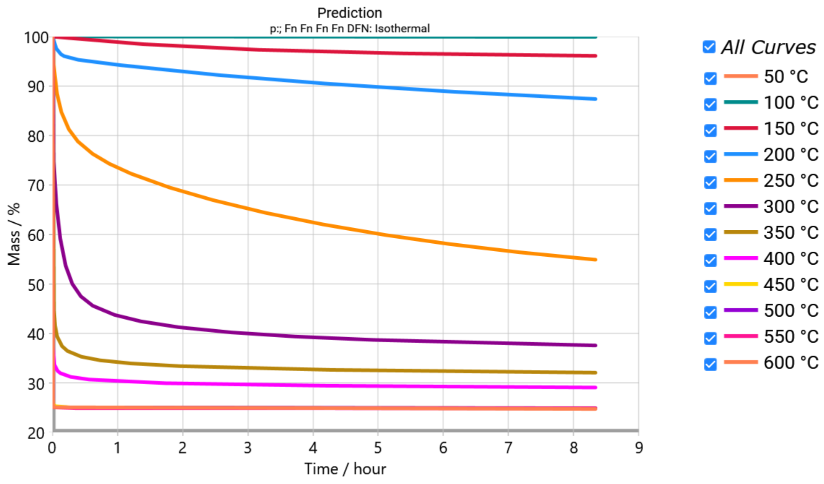
Mass-loss control for process optimization at the same temperature program: solid line (mass loss %) and dashed line (temperature)

Conversion 1 %/min

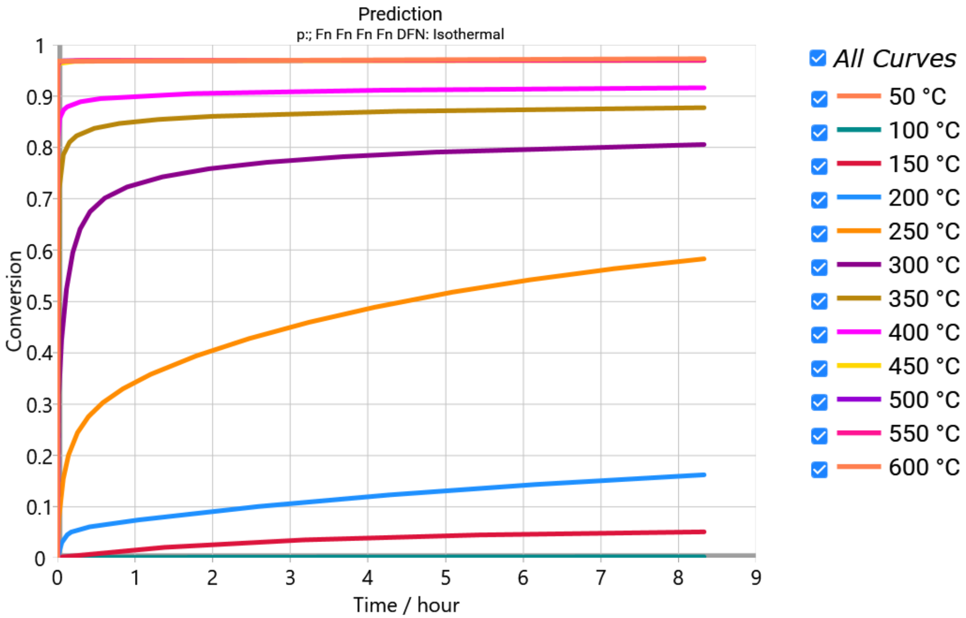


Mass-loss control for process optimization at the same temperature program: solid line (mass loss %) and dashed line (temperature)

Isothermal Prediction



Prediction of mass change over time under different isothermal conditions



Prediction of conversion over time under different isothermal conditions

MultipleStep Prediction

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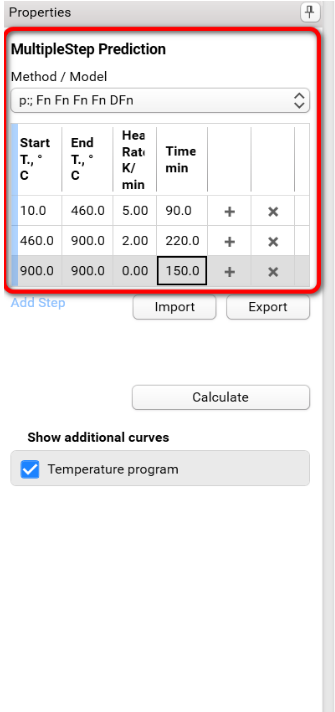

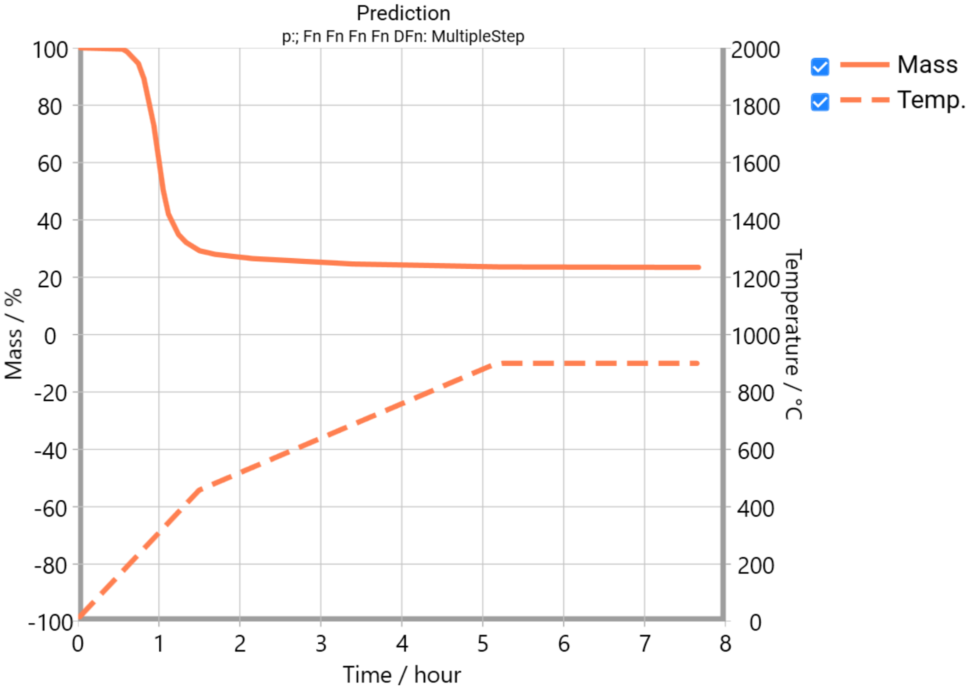

Multiple step prediction of mass change over time under different temperature conditions

Software Demonstration

Step-by-Step Recap

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Materials for pyrolysis

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

Measured data TGA

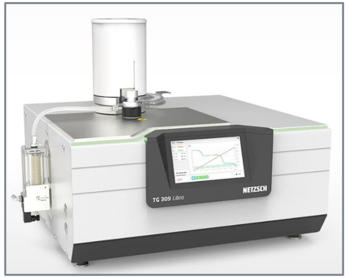
Kinetics Analysis

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

Kinetics Triplet, Prediction and Process Optimization

Validation of kinetic models

TG 309 Libra Classic



KINETICS NEO

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)
- Diffusion control for curing
- Crystallization kinetics
- Kamal model for curing
- Deconvolution analysis (sum of peaks)

ELSEVIER

Thermochimica Acta
Volume 689, July 2020, 178597

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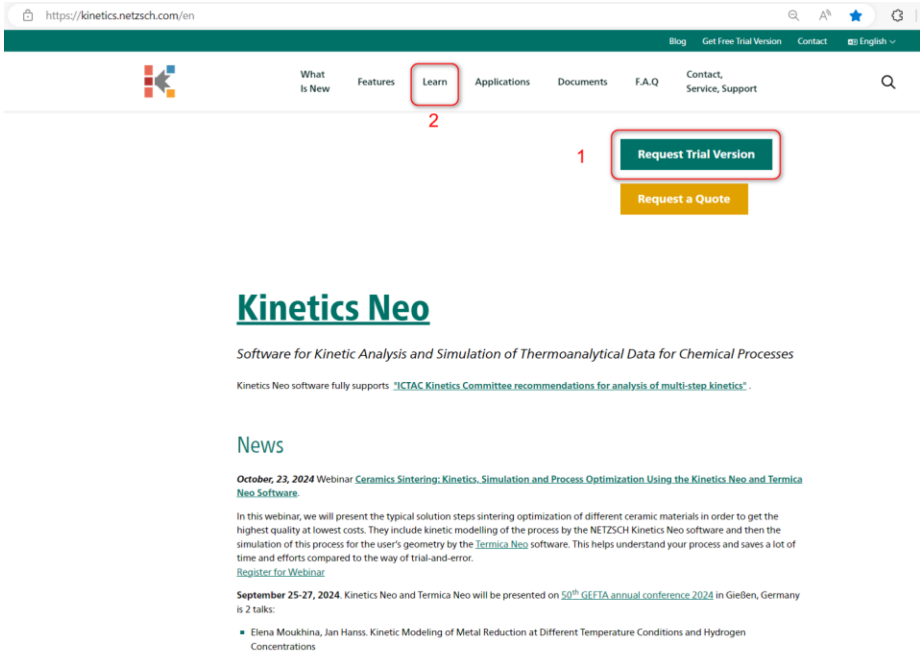
- Go to: https://kinetics.netzsch.com

- *Trial Version 30 days*

kinetics.neo@netzsch.com



Thank you for your attention!

Dr. Mohammed Bouzbib
Chemist

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