



Nordic PhD course in Analytical Techniques in Combustion

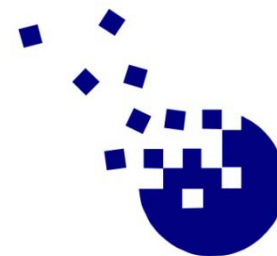
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Introduction to kinetic models for biomass pyrolysis. Part 1.

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What we can overview during 2×50 minutes?

- Pyrolysis is the 1st of the three main steps of combustion. It also has roles in other industrial processes. Pyrolysis modeling is a huge area, however. It includes kinetics, transport processes, product distributions, effects of the mineral matter (as catalysts), effect of the volatile products when their escape is hindered (in close reactors), and so on ...
- Due to our limited time, we shall restrict the treatment for the kinetic part only. Besides we shall treat kinetic models with only a limited number of kinetic equations.
- We shall deal with thermal analysis experiments when the kinetic regime can be well ensured. Mainly TGA.

Definitions:

Definition of thermal analysis:

A sample is subjected to a $T(t)$ temperature program and one or more quantities are measured as function of time or temperature

- ❖ mass, heat flux, mass spectrometric intensities, etc.
- ❖ every sort of time-resolved pyrolysis experiments

Definition of kinetics:

The study of the rate(s) of change(s) in a physical or chemical system

Definition of kinetic control:

When transport processes do not alter the rate(s) of change(s) significantly

Is thermal analysis a marginal topic?

Estimations from the 2005 data of the Science Citation Index:

- ❖ ca. 10 000 papers mentions a thermal analysis technique in title, abstract, or keywords in a year
- ❖ ca. 2 000 papers are based mainly on thermal analysis in a year
- ❖ ca. 25% of the latter group deals with kinetics on some level

Why we need kinetics in thermal analysis?

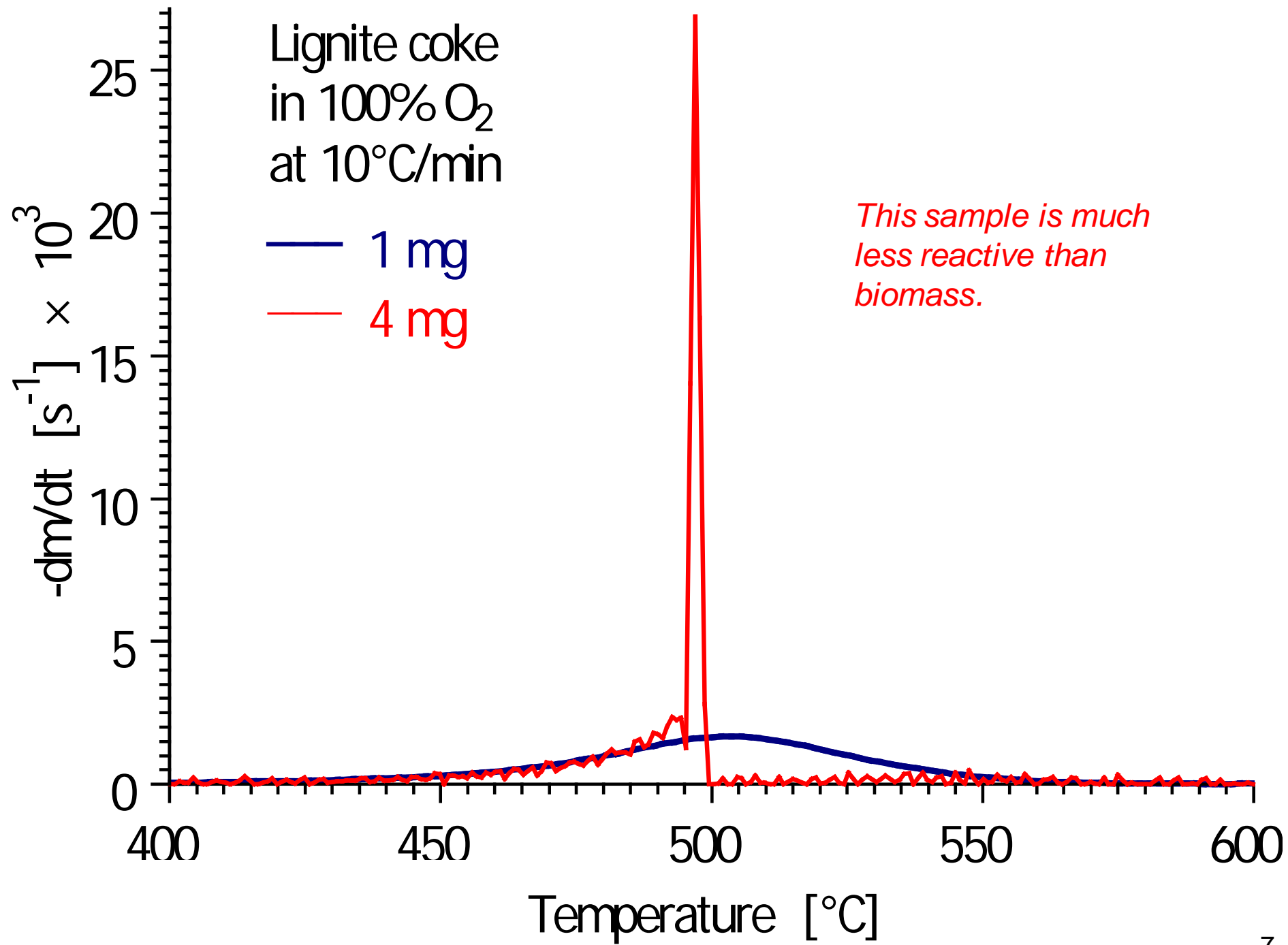
Not for activation energies or preexponential factors!

Why Thermal Analysis? (Why not something else?)

- *A problem:* During a combustion the heating of the fuel is usually very fast. Even tobacco smoothing implies a $30^{\circ}\text{C}/\text{second}$ heating of the tobacco grains. On the other hand, a typical safe heating rate in thermal analysis is $40^{\circ}\text{C}/\text{minute}$. When the reaction heat does not cause problems, we can go up till ca. $100^{\circ}\text{C}/\text{min}$.
- *Are there other techniques that can measure higher heating rates with a high precision in the kinetic regime?* If the sample is in flame, for example, then we have only rough estimation on its true temperature. Besides, the mass measurement has a higher precision than anything else. But we cannot measure the sample mass accurately if a particle burns in a split second.

What limits the heating rate in TGA?

- *(A qualitative reasoning)* If we heat something fast, it will not have time to react at lower temperatures. So the reaction occurs at higher temperatures where the reaction rate is obviously higher. Later we shall see (by simple mathematical deductions as well as on actual experiments) that the reaction rate is nearly proportional with the heating rate.
- In a TGA experiment the sample mass should be at least 0.1 – 0.5 mg, depending on the sensitivity and stability of the apparatus. Usually we put a few grains or a thin layer into a sample pan of ca. \varnothing 6 mm.
- Heat production is proportional to reaction rate \Rightarrow ignition (strong self-heating or even flames).
- So does heat consumption (pyrolysis in inert gas) \Rightarrow self cooling



Experimental conditions needed for a true kinetic control

- Because the reactivity of the samples depends on the chemical and physical properties, we need test experiments for each type of samples: what are the highest amount tolerated without significant self heating or self-cooling. Experiments with different initial sample masses are compared.
- Some examples from our experience:

Cokes & semicokes in 30% O ₂ at 50°C/min (HAS):	0.6 mg
Charcoal powder in air, 25°C/min (HAS):	0.2 mg
Wood-powder in air, 20°C/min (HAS):	0.2 mg
Tobacco from cigarettes in 9% O ₂ , 40°C/min (HAS):	0.4 mg
Charcoal in CO ₂ , 20°C/min (NTNU):	1 mg

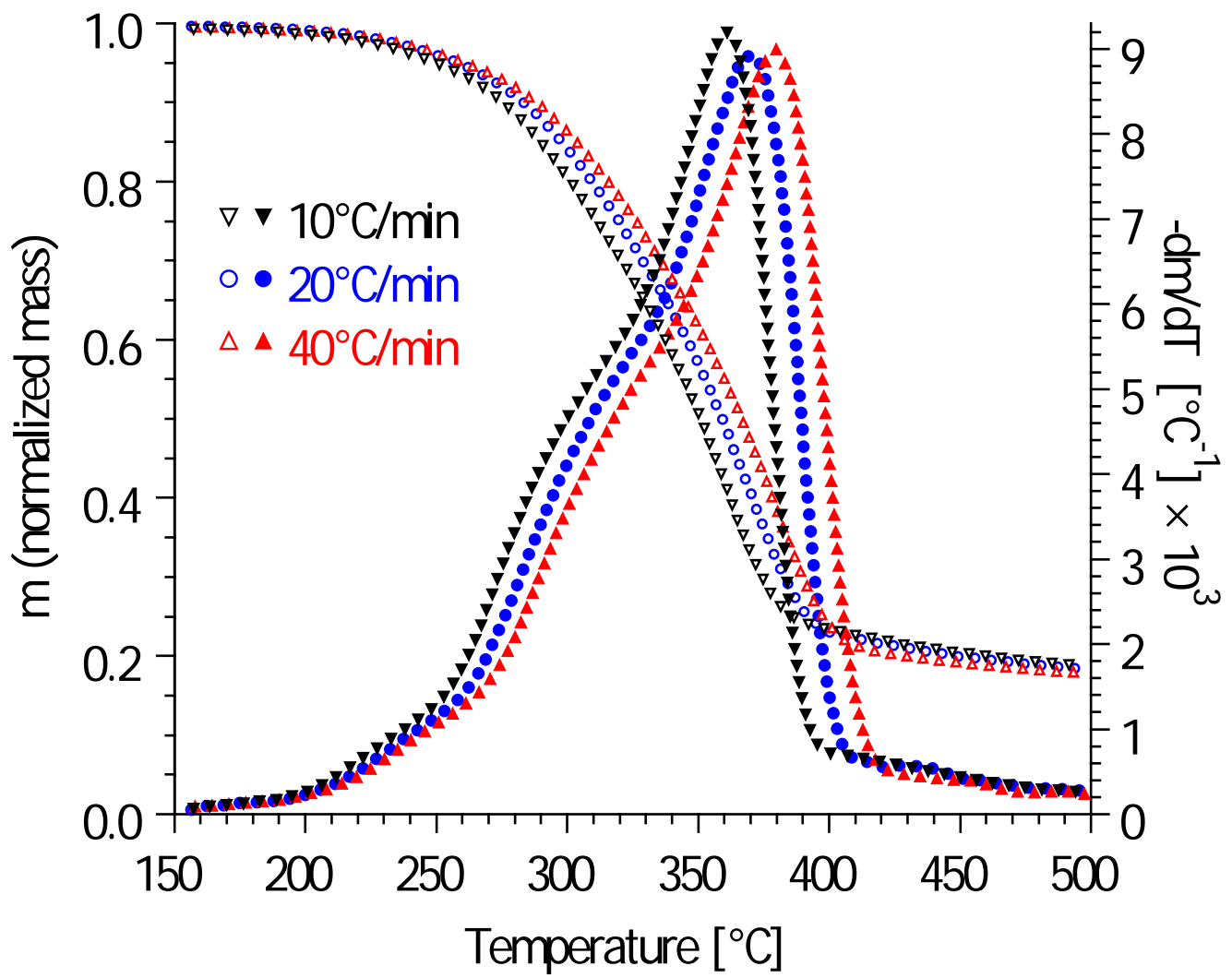
Experimental conditions needed for a true kinetic control

- It is easier in pyrolysis studies, when the reaction is endothermic and the reaction heat has smaller magnitudes. If it is small and the sample has a loose structure, then the sample mass at 40°C/min can be as much as 20 mg as shown by *Mette Stenseng, Anker Jensen and Kim Dam-Johansen* for straws. Which is a rare and lucky situation. It's advisable to carry out a few test experiments at each new type of samples in the given apparatus.

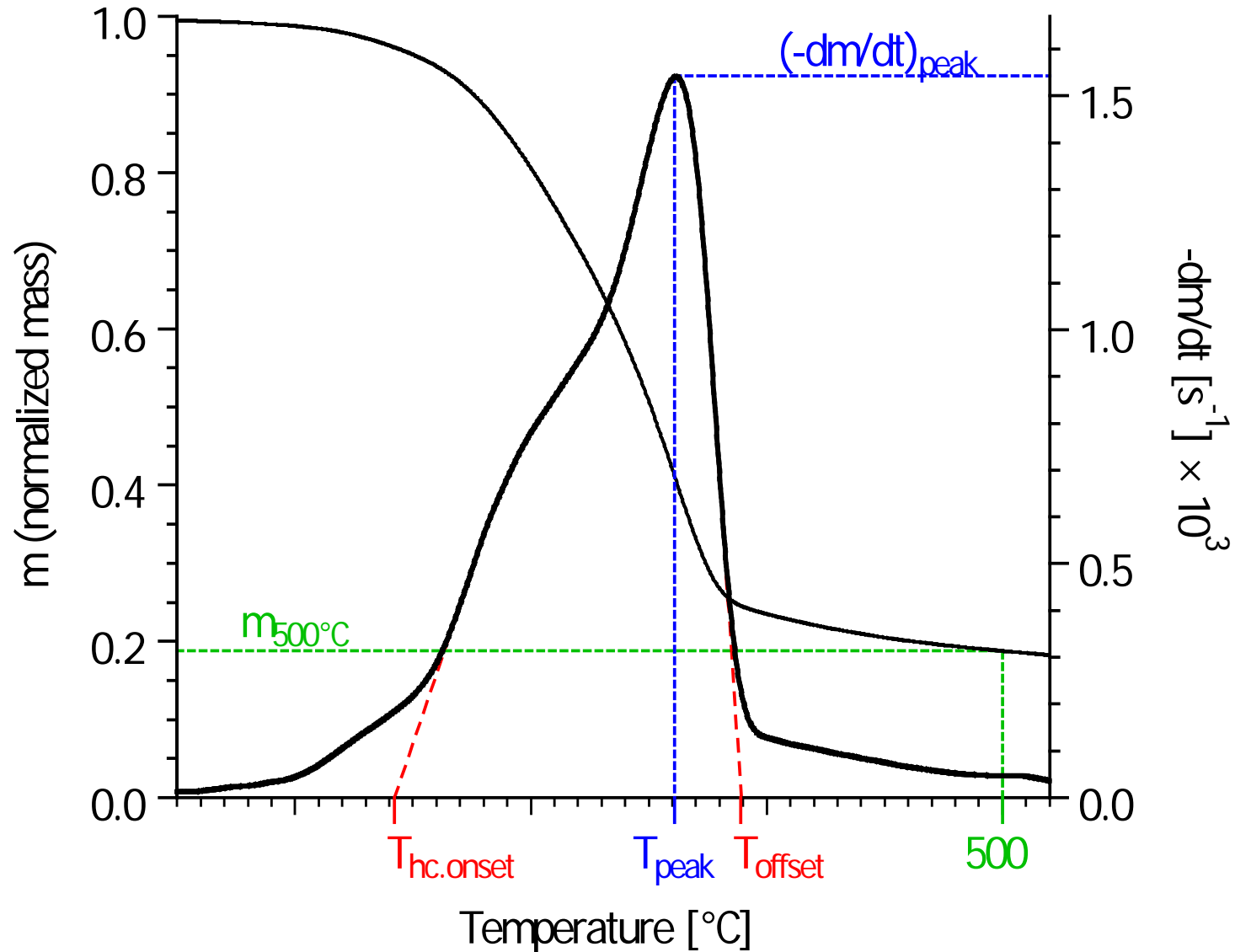
Even a qualitative interpretation may need a kinetic background!

Example: Why do the thermoanalytical curves shift to higher T if we increase the heating rate? Why does their shape change so slightly during this shift in the case of such a complex material as a *wood with its bark*?

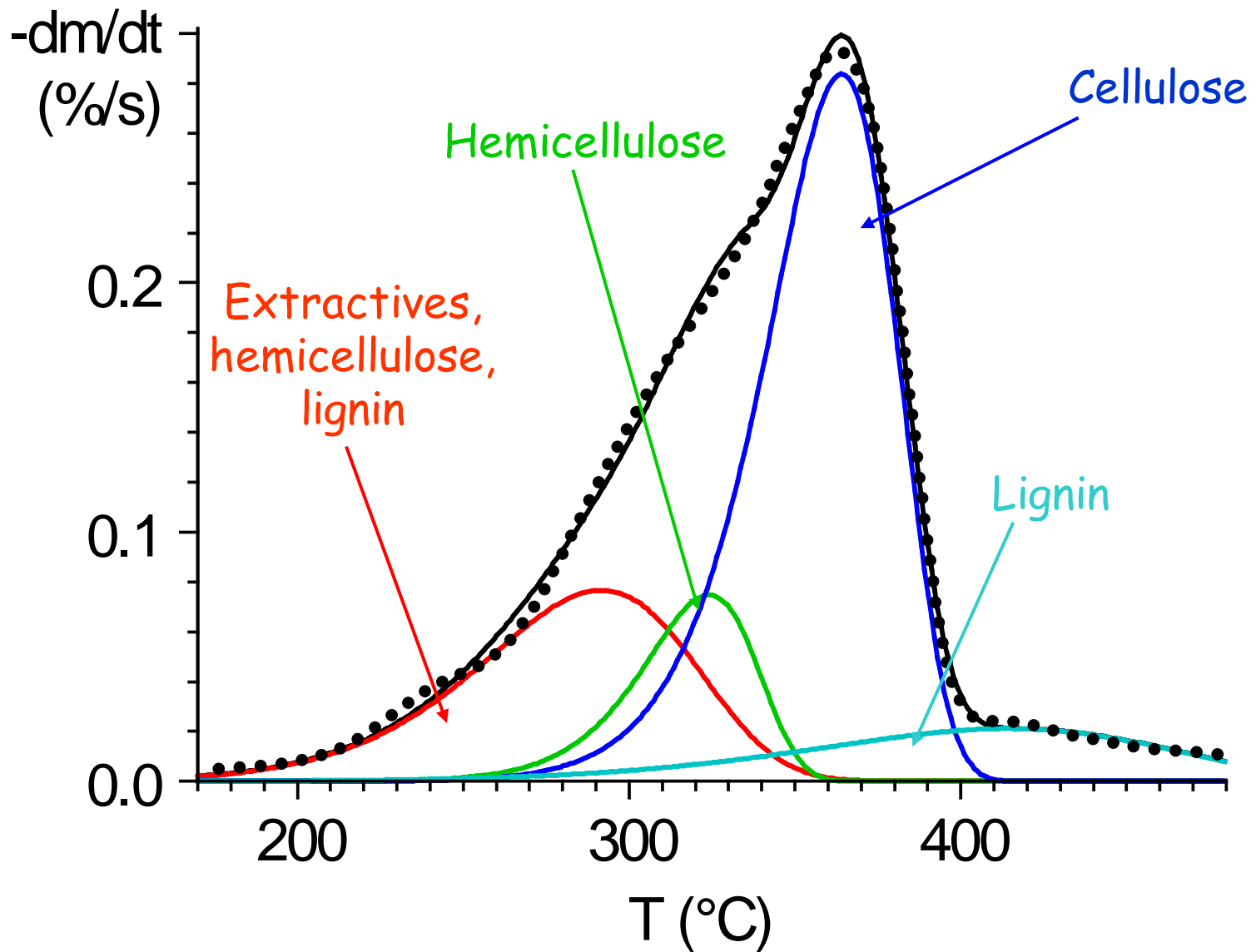
This is a plot as function of T: we plotted $m(T)$ and $-dm/dT$



What quantitative characteristics can be obtained without a kinetic model? *Examples:*



What we expect from a kinetic model?



What we expect from a kinetic model?

- ❖ It should describe the behavior of the samples in a wide range of experimental conditions
- ❖ Predicting the behavior outside of the domain of the given set of observations
- ❖ Characteristics that can reveal similarities and differences between the samples
- ❖ A deeper insight into the processes
- ❖

Three reaction types. 1. First order reactions

We can use this approximation to describe the decomposition of *either* a sample *or* a part of the sample.

Whatever we describe with it, let us denote its reacted fraction by $\alpha(t)$:

$$\alpha(0)=0 \quad \text{and} \quad \alpha(\infty)=1$$

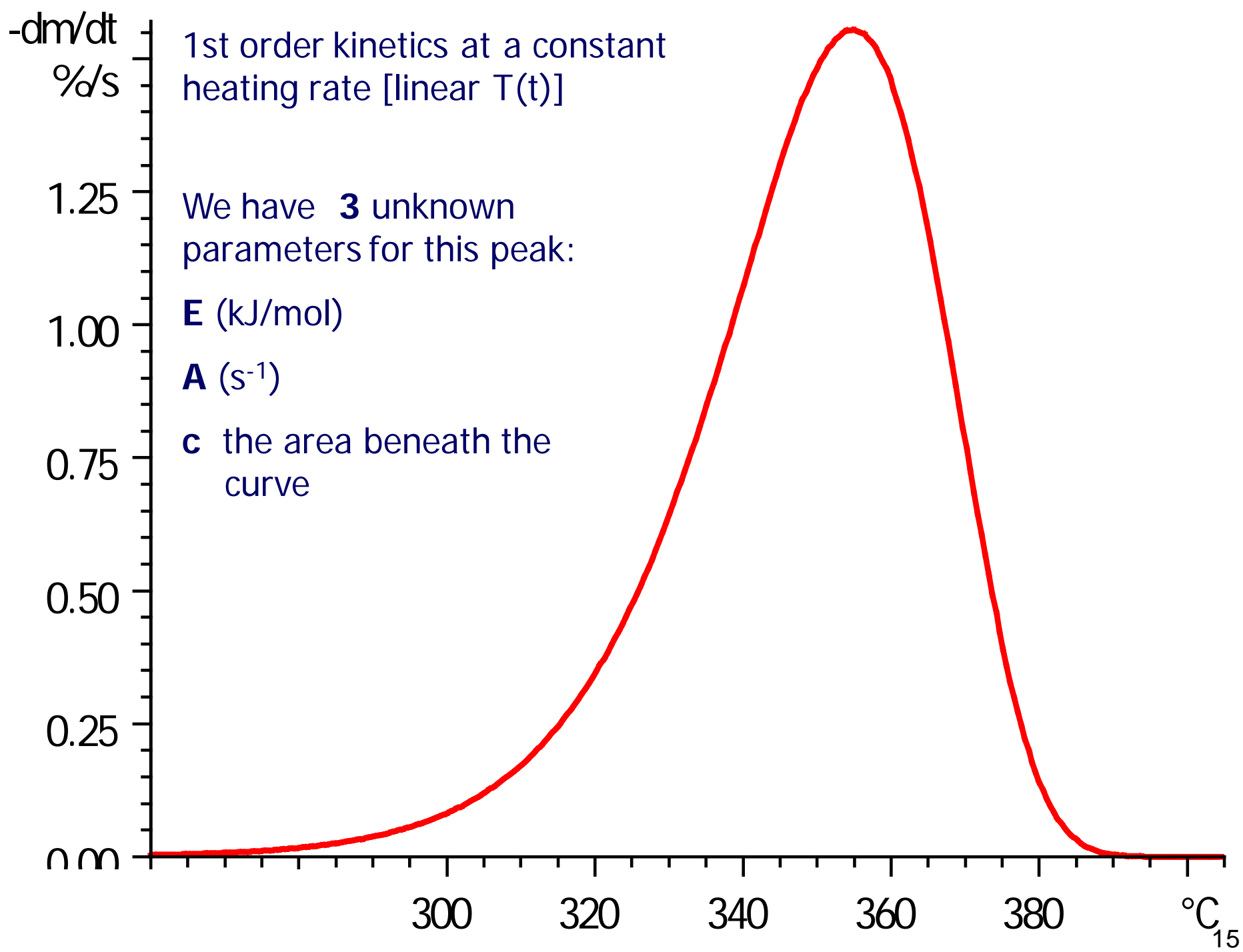
The fraction available for reaction in a given moment is $1-\alpha(t)$.

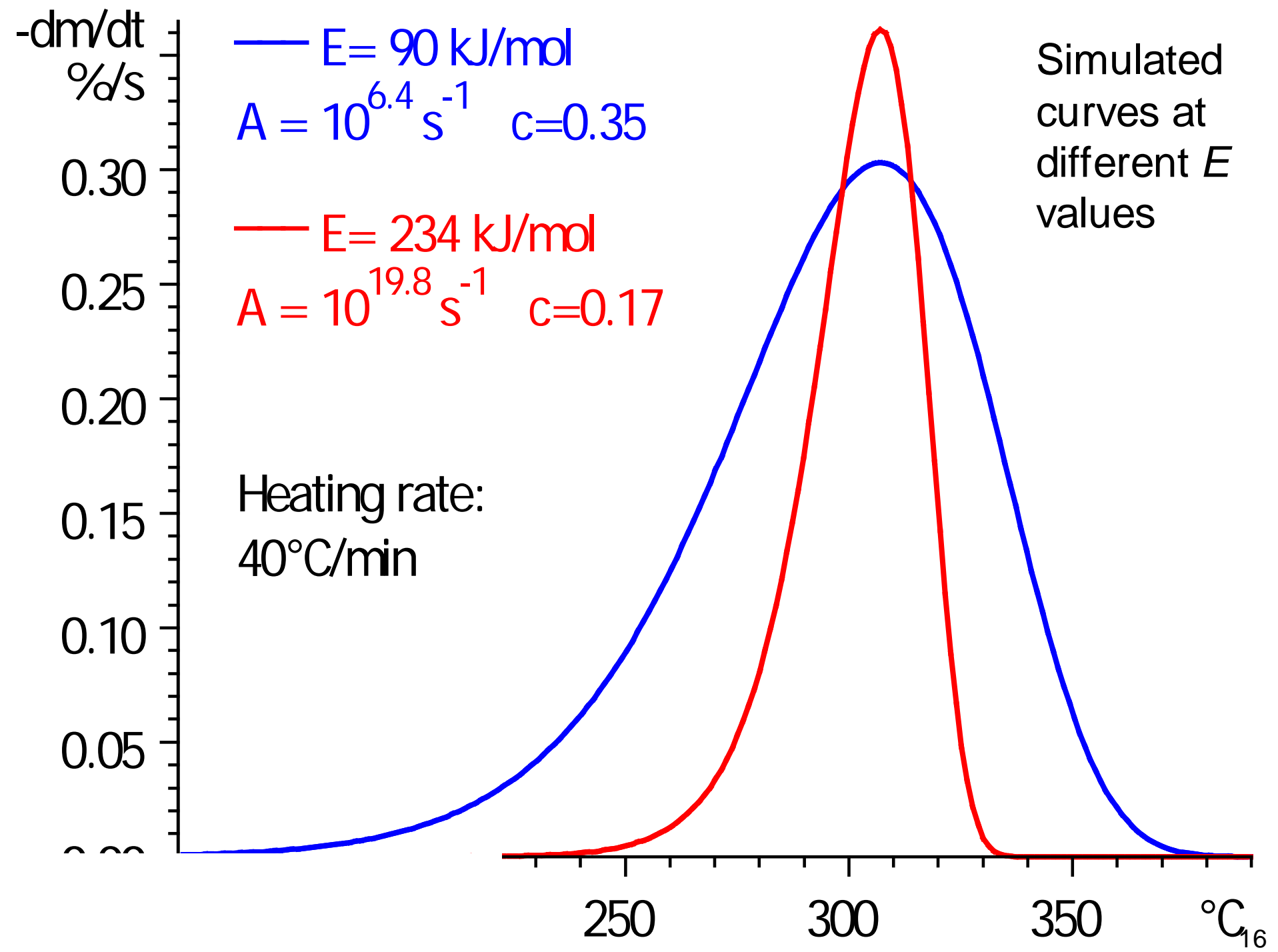
The reaction rate, $d\alpha/dt$ obviously depends on $1-\alpha(t)$. The simplest approximation:

$$d\alpha/dt \cong A e^{-E/RT} [1-\alpha(t)]$$

Let us separate the variables and integrate the equation:

$$\int_0^{\alpha} \frac{d\alpha'}{1-\alpha'} = A \int_0^t e^{-E/RT(t')} dt' \quad \text{or} \quad g(\alpha) = A \int_0^t e^{-E/RT(t')} dt'$$





Three reaction types. 2. A more general type of reactions

$\alpha(0)=0$, $\alpha(\infty)=1$, fraction available for reaction: $1-\alpha(t)$.

There are effects that can alter the kinetics from the first order behavior. E.g. differences between the reacting species. Or the growth of the reaction surface during car burn-off or char gasification:

$$d\alpha/dt \cong A e^{-E/RT} f(\alpha)$$

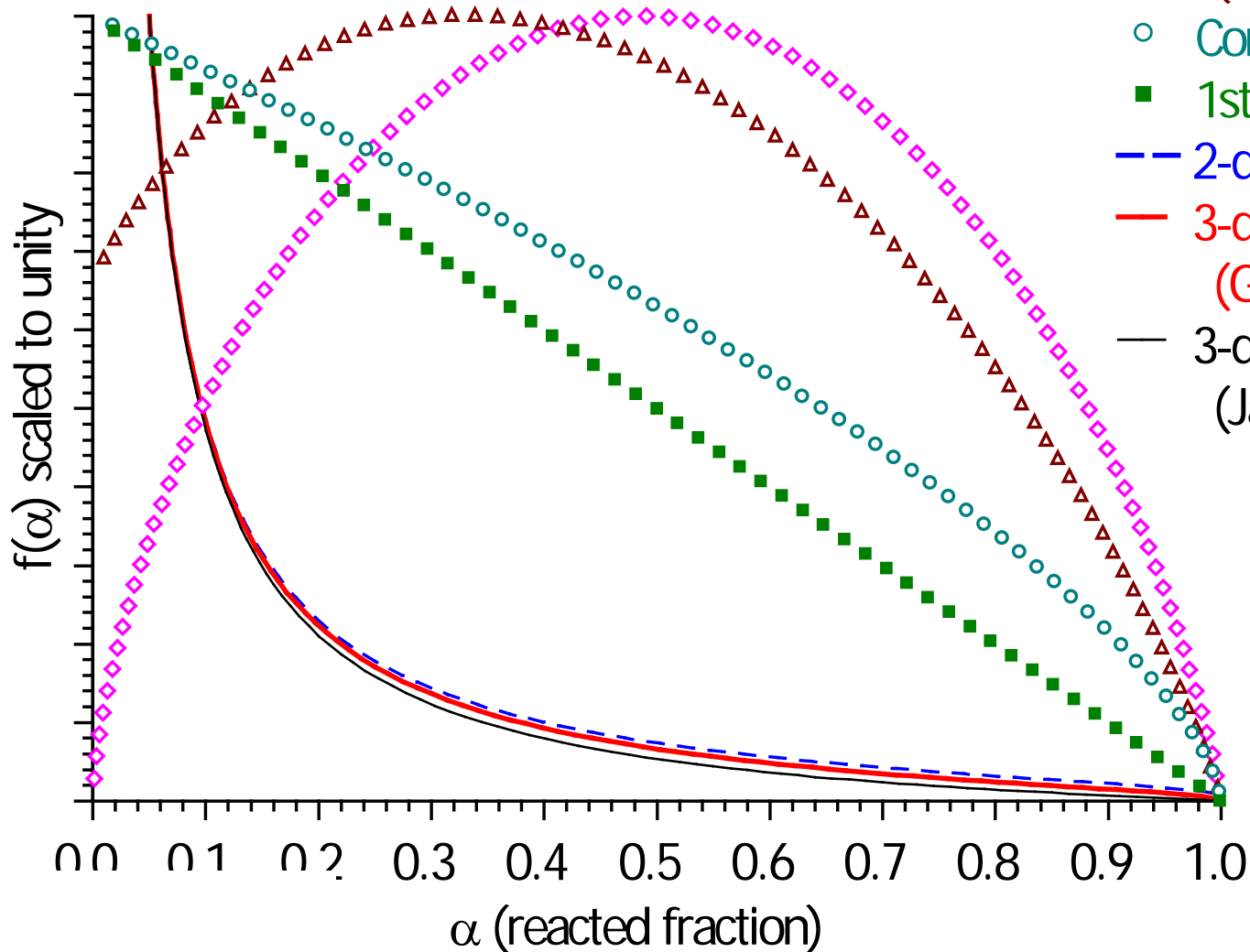
where $f(\alpha)$ is an empirical function

Let us separate the variables and integrate the equation:

$$\int_0^{\alpha} \frac{d\alpha'}{f(\alpha')} = A \int_0^t e^{-E/RT(t')} dt' \quad \text{or} \quad g(\alpha) = A \int_0^t e^{-E/RT(t')} dt'$$

Kinetic equation: $d\alpha/dt = A \exp(-E/RT) f(\alpha)$

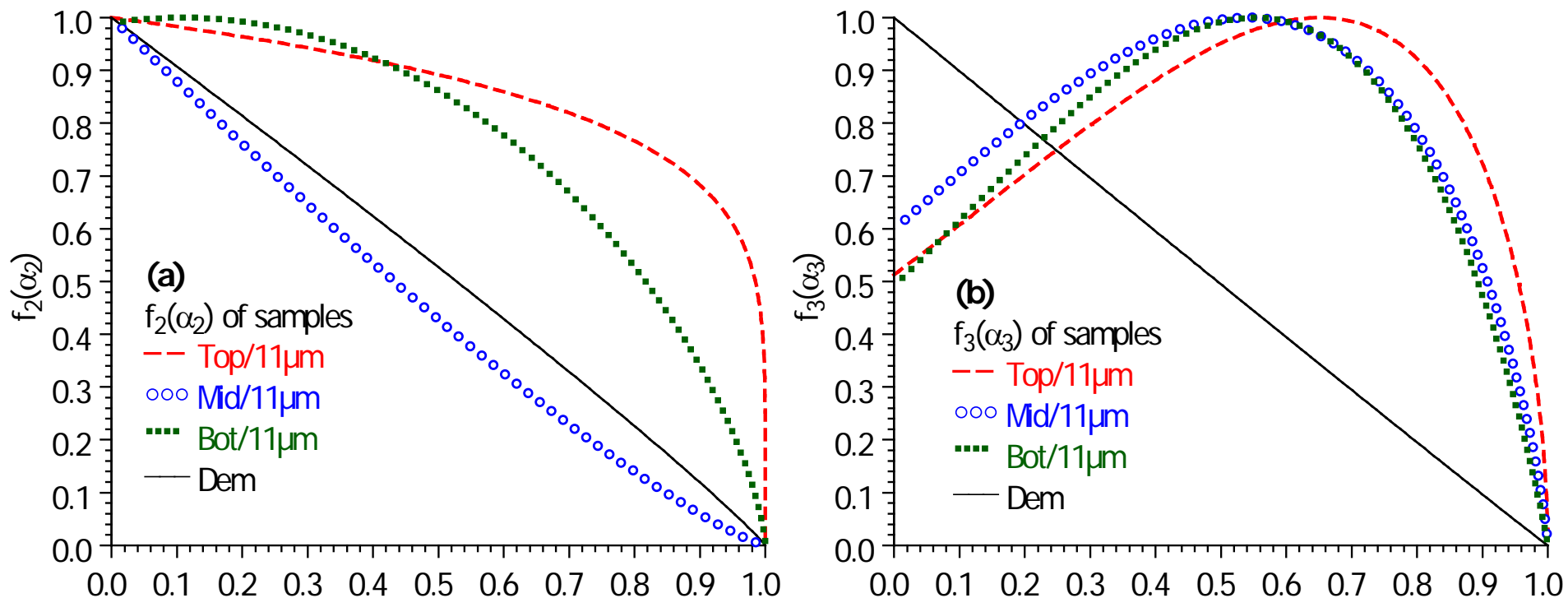
Examples for theoretically derived $f(\alpha)$ functions:



- ◇ 1st order nucleation (Avrami-Erofeev-Mampel)
- △ Random pore theory (Su - Perlmutter)
- Contracting sphere
- 1st order kinetics
- 2-dimensional diffusion
- 3-dimensional diffusion (Ginstling - Brounshtein)
- 3-dimensional diffusion (Jander)

Empirical $f(\alpha)$ functions from a charcoal combustion study

(Várhegyi et al, *Ind. Eng. Chem. Res* 2006)



$f(\alpha) \cong \text{const} (\alpha + z)^a (1 - \alpha)^n$ where a , n and z are parameters. This function can also describe reactions that accelerate at isothermal conditions.

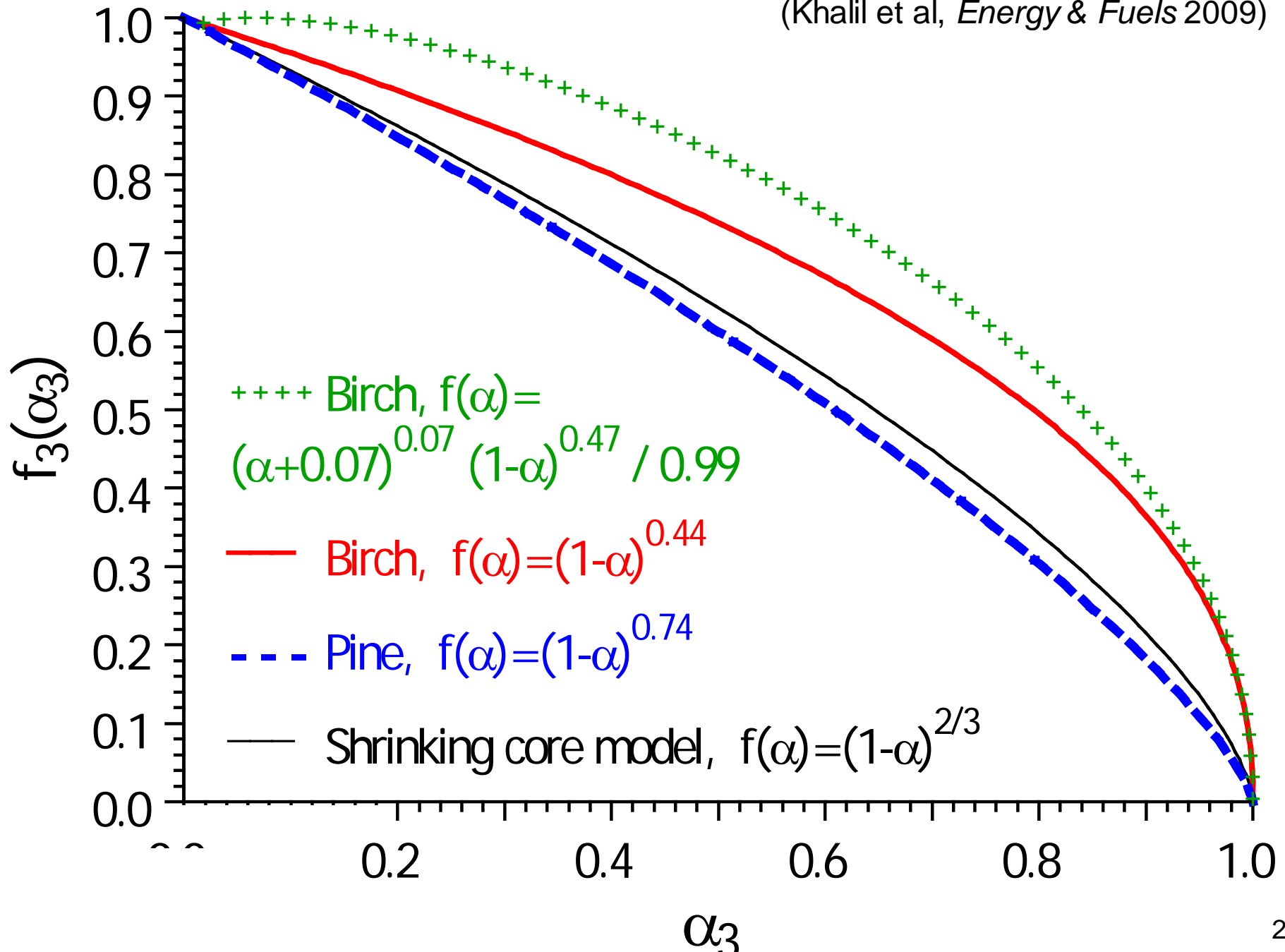
Tomorrow we shall use only the rightmost part of this formula:

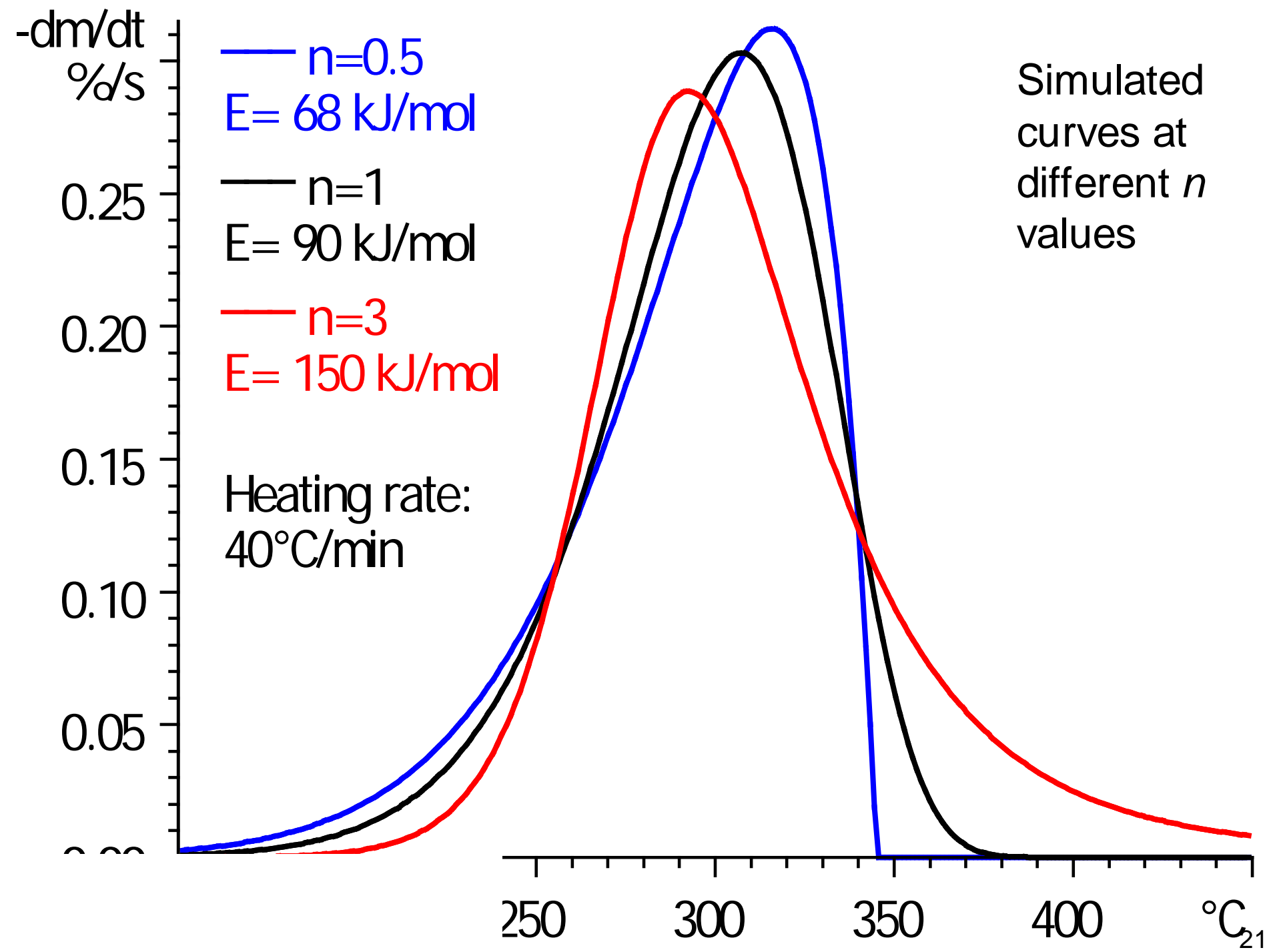
$f(\alpha) \cong (1 - \alpha)^n$ where n is the reaction order: any number between 0 and an upper limit chosen by us.

Name of the $(1 - \alpha)^n$ approximation: Power-law kinetics or n -order kinetics

Empirical $f(\alpha)$ functions from a charcoal gasification study

(Khalil et al, *Energy & Fuels* 2009)





The Coats – Redfern linearization from 1964

$$g(\alpha) = A \int_0^t e^{-E/RT(t')} dt' \quad \text{where} \quad g(\alpha) = \int_0^\alpha \frac{d\alpha'}{f(\alpha')} d\alpha'$$

$$\ln g(\alpha) \cong \ln \frac{AR}{\beta E} - \frac{E}{RT} + 2 \ln T \quad \text{where } \beta \text{ is the heating rate in K/s.}$$

It shows why the DTG curves are similar at different heating rates (β) when plotted as function of T . Example: Let us define a width as the T difference between the points $\alpha=2/3$ and $\alpha=1/3$ and let us neglect the slow change of the last term, $2 \ln T$. Then we have:

$$\ln g(2/3) - \ln g(1/3) \approx -\frac{E}{RT_{2/3}} + \frac{E}{RT_{1/3}}$$

On a $1/T$ scale the width ($1/T_{2/3} - 1/T_{1/3}$) is independent of β in this approximation. On a T scale it is not so, but the change of $T_{2/3} - T_{1/3}$ is not big.

Typical T values in biomass TGA: $T_{\text{peak}} \approx 500 - 800$ K, and its shift by a 10x increase of β is around 30K.

Distributed activation energy model (DAEM)

Biomasses usually have very complex chemical and physical structure. A further complication comes from the mineral matter.

So we have a wide range of species differing in reactivity. In DAEM the different reactivity of the species are described by different E .

Let us look for those species that have a given E value in this model and let us apply a first order kinetics for their behavior. Let $\alpha(t, E)$ be their reacted fraction: $\alpha(0, E) = 0$ and $\alpha(\infty, E) = 1$.

$$d\alpha(t, E)/dt = A e^{-E/RT} [1 - \alpha(t, E)]$$

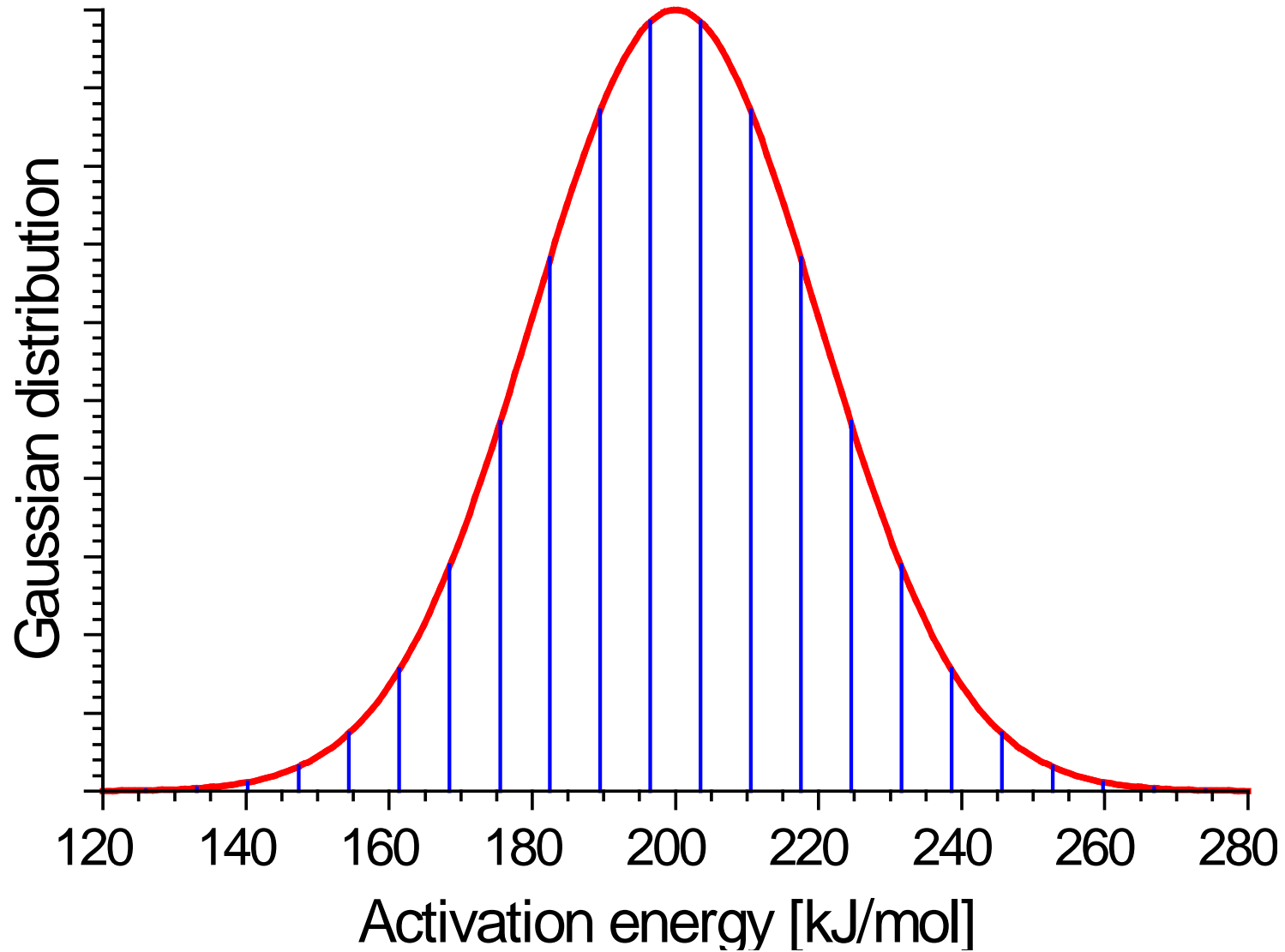
The overall reacted fraction, $\alpha(t)$ is the integral of $\alpha(t, E)$ terms taking into account that the different E values occur with different frequency:

$$\alpha(t) = \int_0^{\infty} D(E) \alpha(t, E) dE$$

Here $D(E)$ is a density function. Usually it is approximated by a Gaussian:

$$D(E) = (2\pi)^{-1/2} \sigma^{-1} \exp[-(E - E_0)^2 / 2\sigma^2]$$

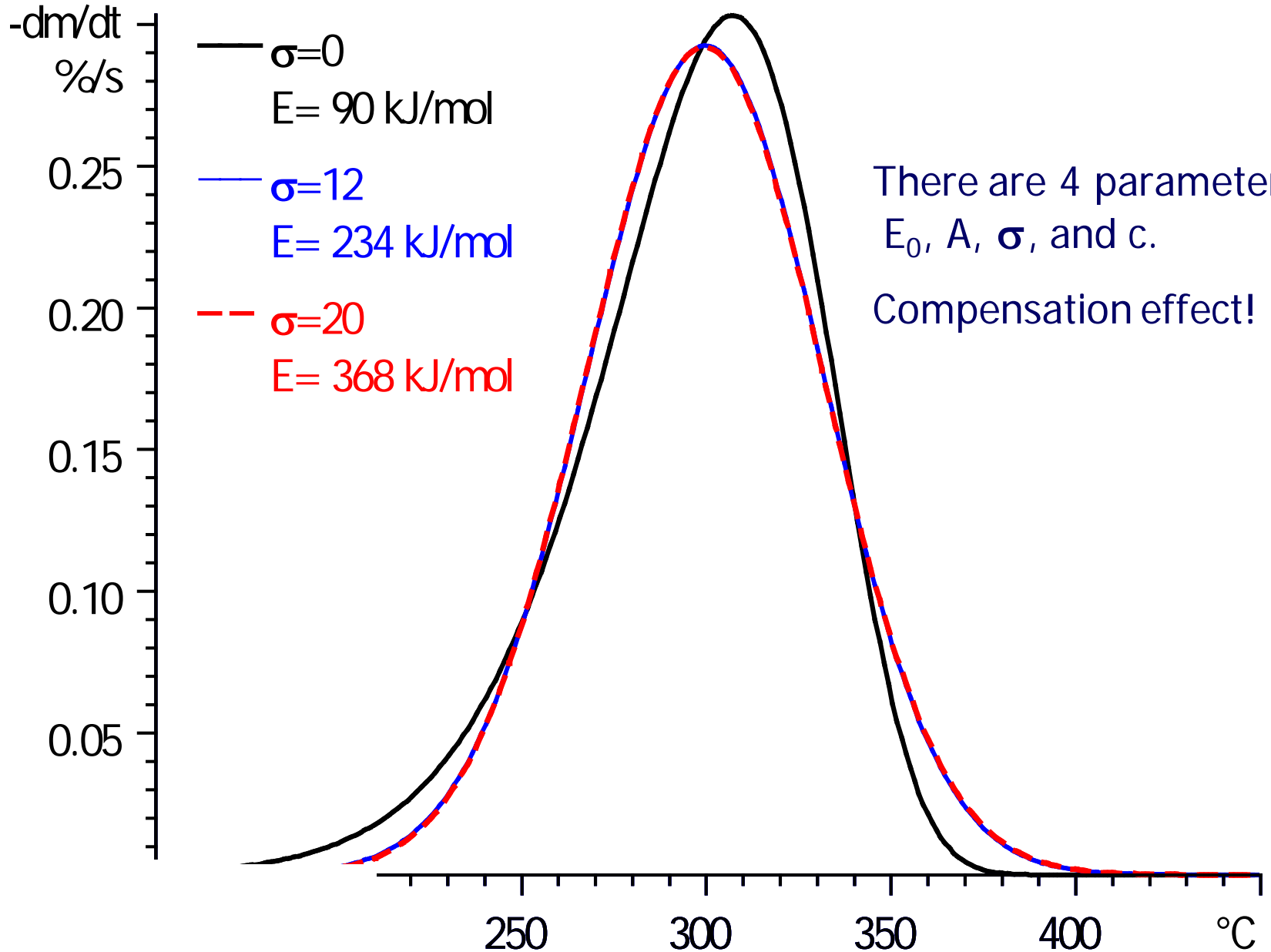
Numerical integration by E at a normal distribution:



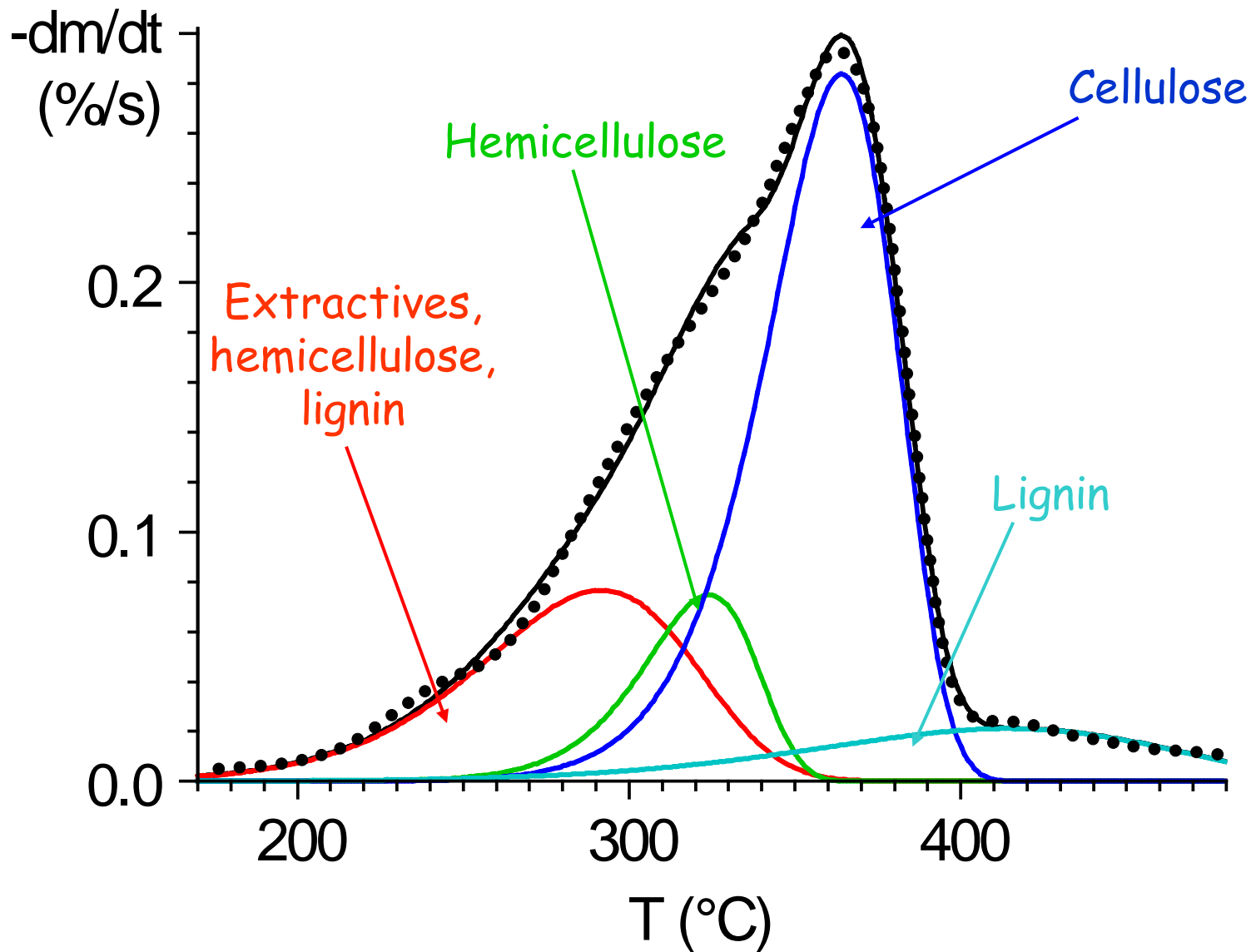
Blue lines indicate the points where we actually solve the 1st order kinetic equations in a numerical integration by a Gauss – Hermite quadrature. I use 150 quadrature points.

Reaction rates at different σ values at a linear T(t)

(These curves approximate the same experimental data)



Multicomponent models: An example of simple, 1st order partial reactions.



A multicomponent model:

Let we have M components and let α_j be the reacted fraction of the j th component:

$$-dm/dt = \sum_{j=1}^M c_j d\alpha_j / dt$$

$$m(t) = 1 - \sum_{j=1}^M c_j \alpha_j(t)$$

$c_j = (\text{concentration})_j$ (amount of volatiles) _{j}

$$c_j \geq 0$$

either

$$d\alpha_j/dt = A_j \exp(-E_j/RT) f(\alpha_j)$$

or

$d\alpha_j/dt$ is defined by a DAEM model.

The method of the least squares:

$$S_N = \sum_{k=1}^N \sum_{i=1}^{N_k} \frac{[X_k^{obs}(t_i) - X_k^{calc}(t_i)]^2}{N_k h_k^2} = \min$$

Why?

- ❖ A good model describe the experimental data in a wide range of experimental conditions
- ❖ We do not know yet other general criteria for the goodness of a model*
- ❖ Accordingly, we should prefer evaluation techniques that directly aim at this criterion
- ❖ The evaluation of a large series of experiments by the method of least squares is a straightforward tool for this purpose.

A measure of the fit quality on a group of N experiments:

$$fit_N (\%) = 100 S_N^{0.5}$$

* The laws of the mathematical statistics do no offer help since the most important experimental errors are not random in thermal analysis.

Pseudocomponents

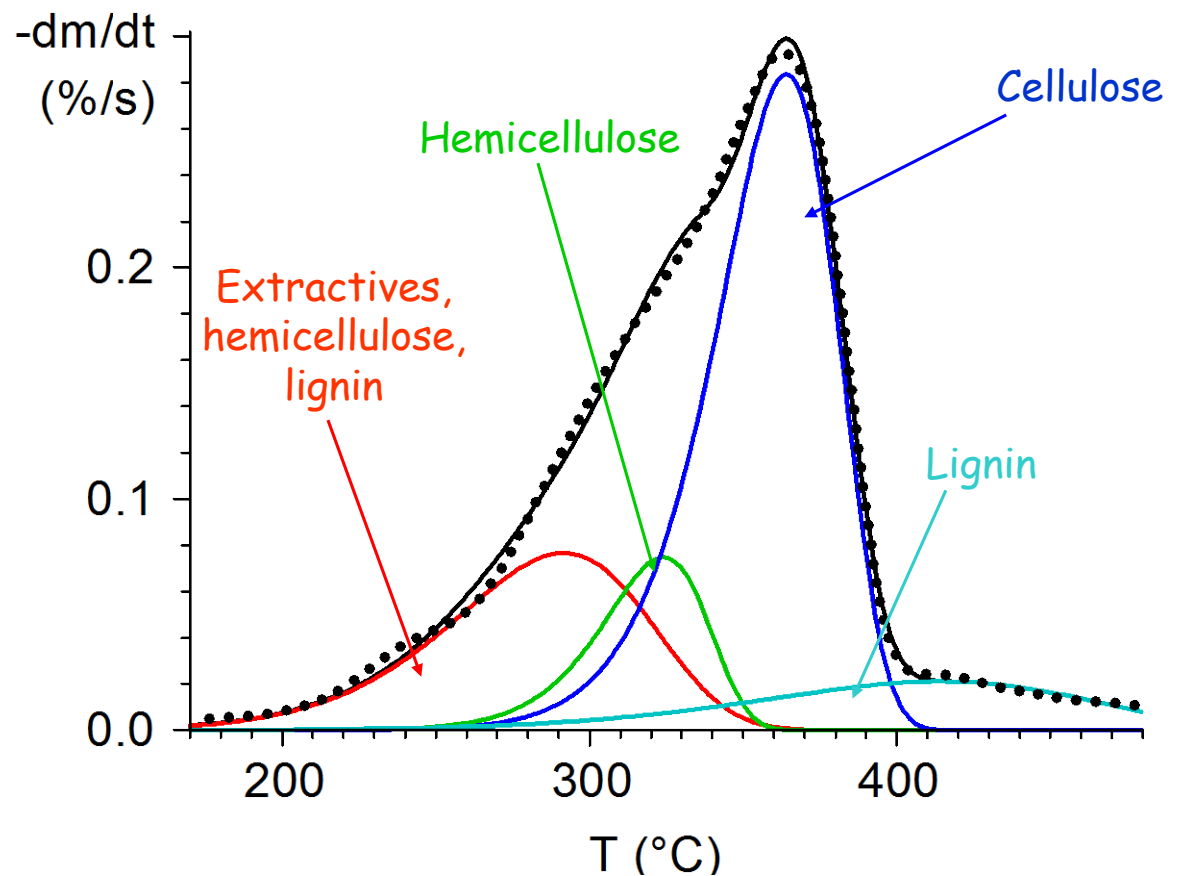
How should a least squares evaluation recognize what part of the decomposition is due hemicelluloses, celluloses, lignin, etc.?

(MS or FTIR offer little help here due to the similarities of the main decomposition products.)

No solution at this

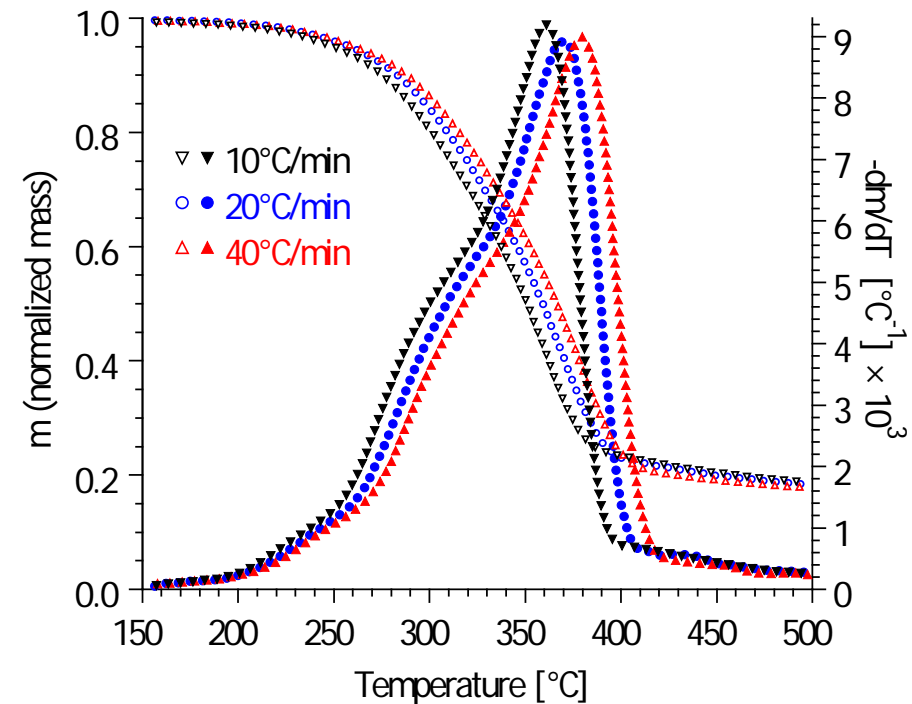
moment: ***Kinetics cannot reveal the true chemical components.*** We get “pseudocomponents” that we can interpret *afterward* based on our knowledge from other sources. (E.g. “mainly lignin decomposition”.)

A ***pseudocomponent*** is the totality of those decomposing species which can be described by the same reaction kinetic parameters in the given model.



Sufficient amount of experimental information is needed for complex models

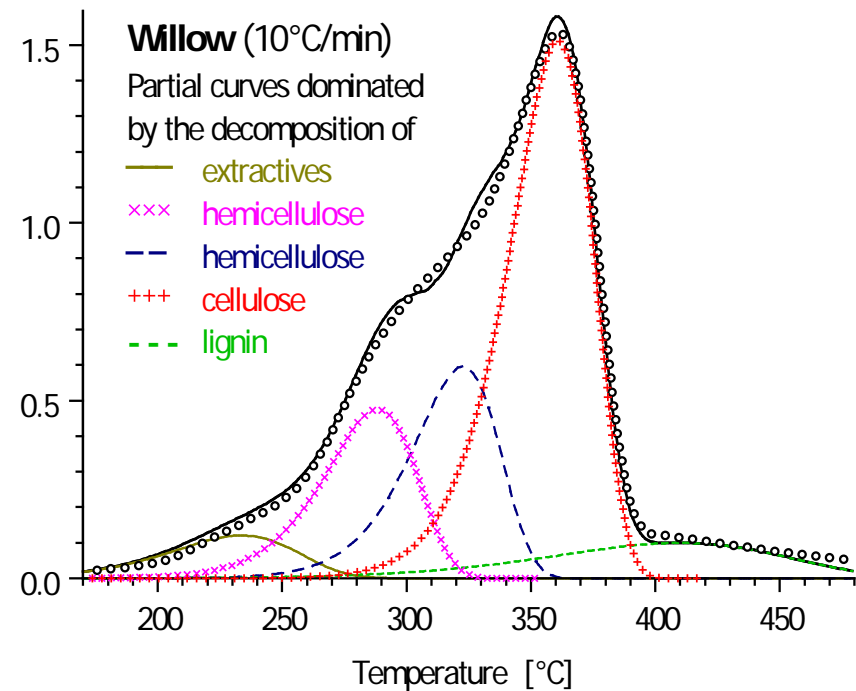
An example from the study of a wood in inert atmosphere:*



?



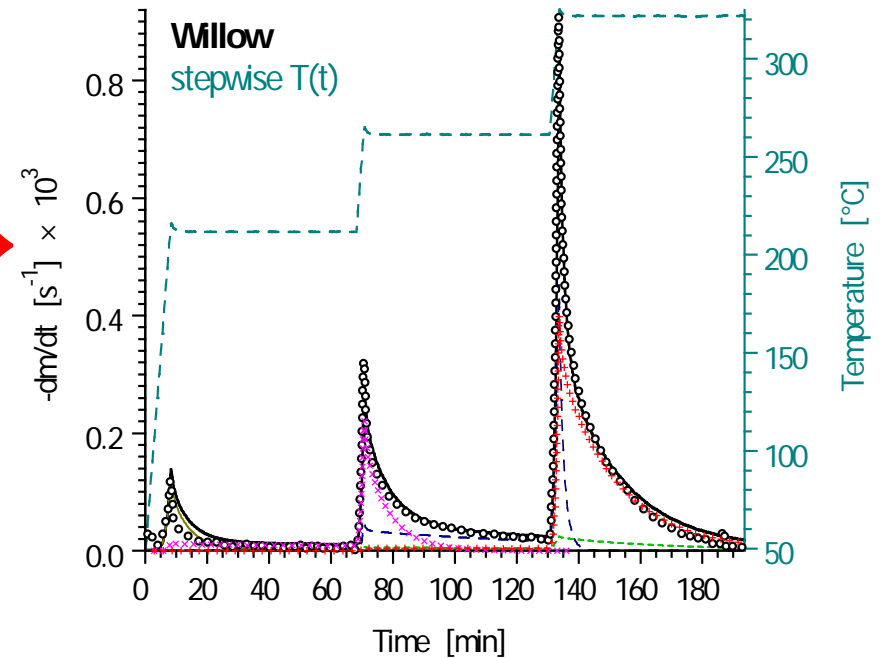
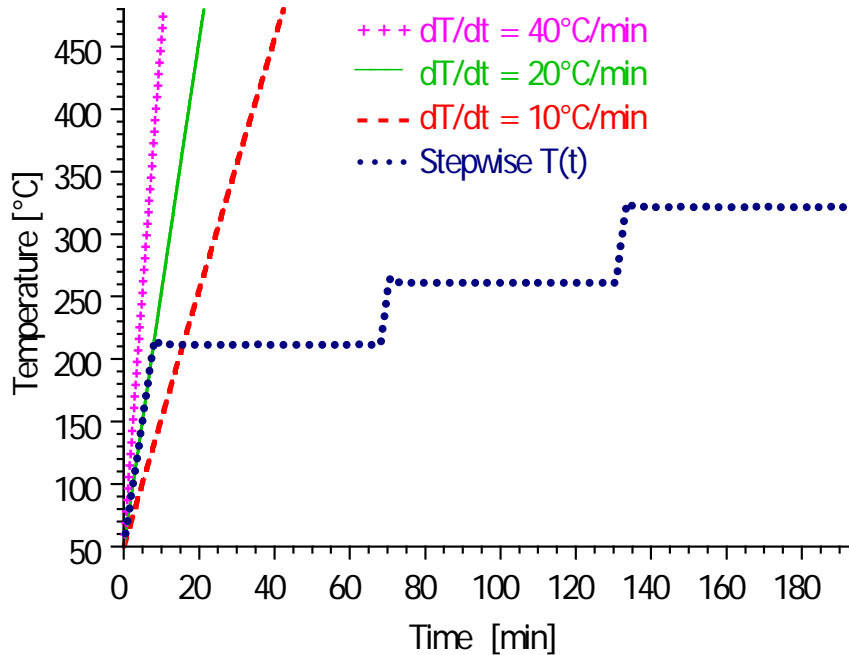
$-\frac{dm}{dt} [\text{s}^{-1}] \times 10^3$



* Mészáros et al, *Energy & Fuels* 2004.

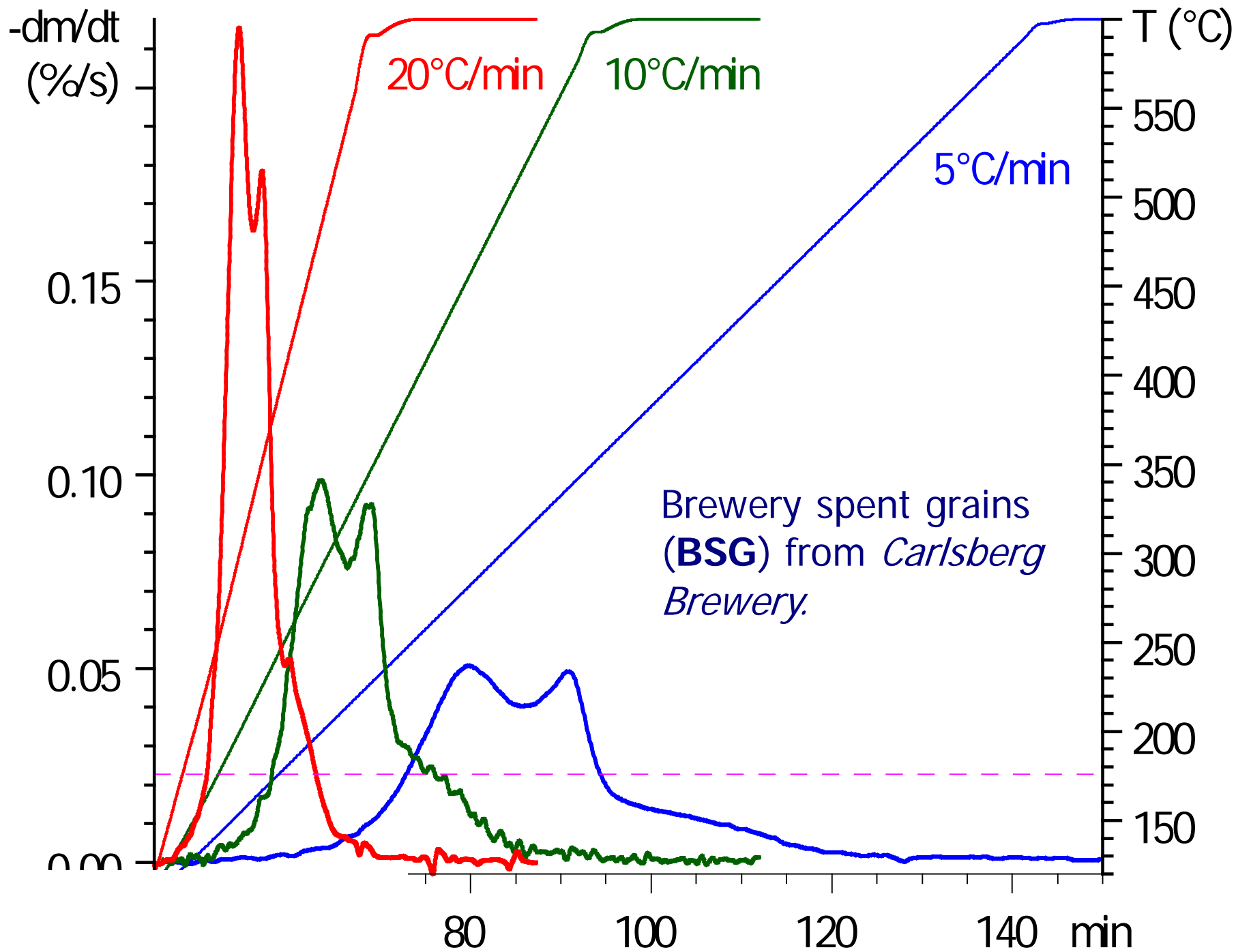
Sufficient amount of experimental information is needed for complex models

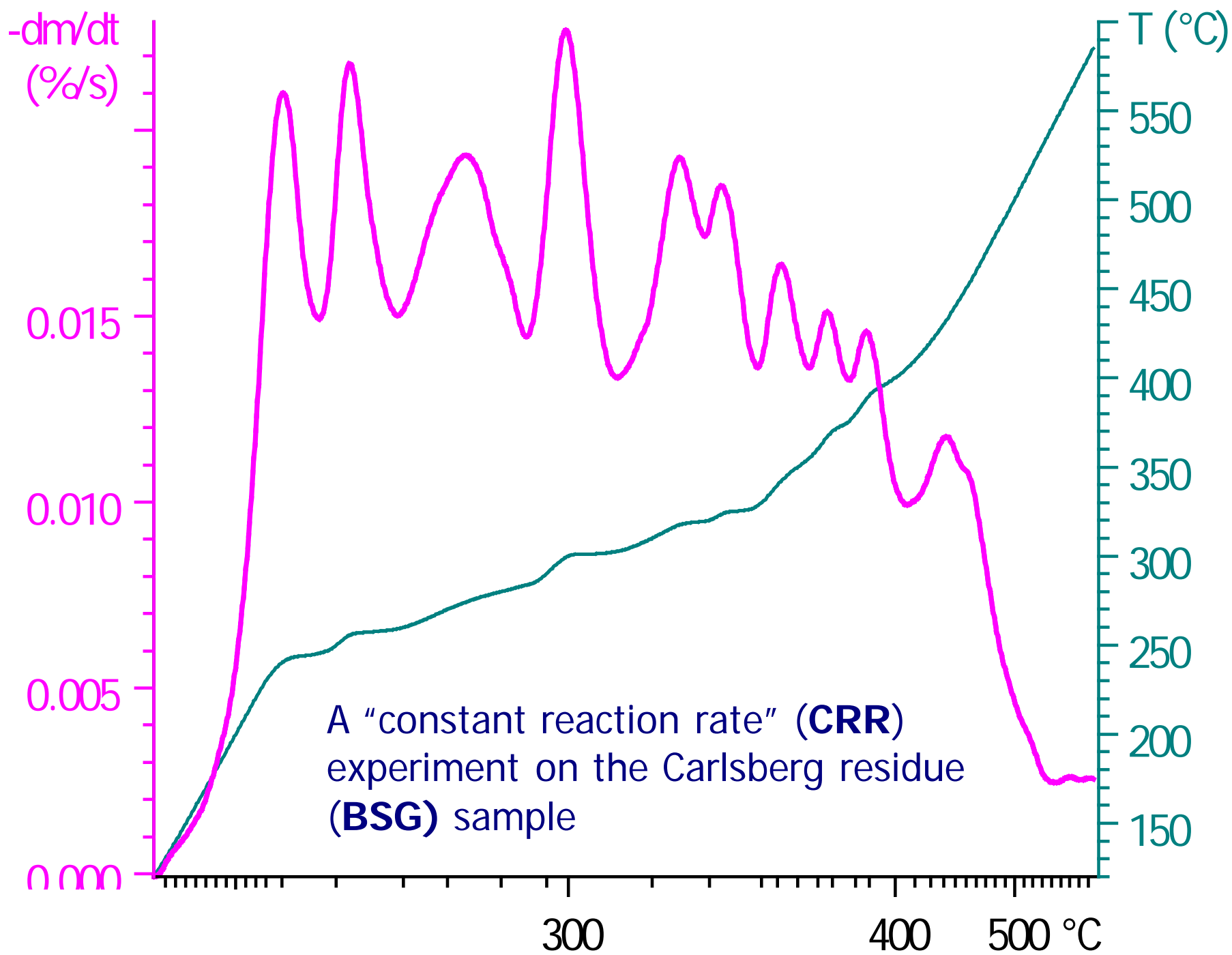
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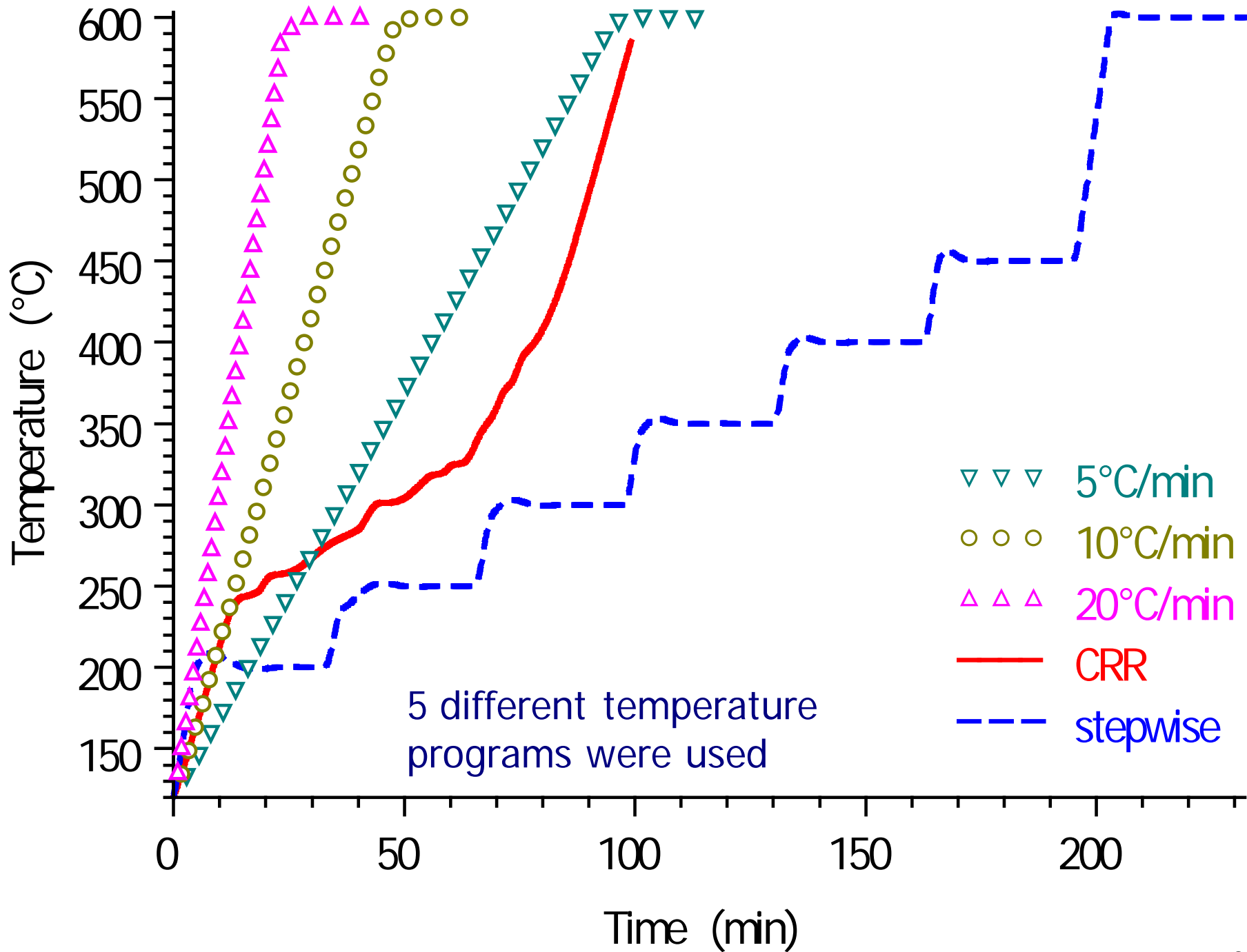


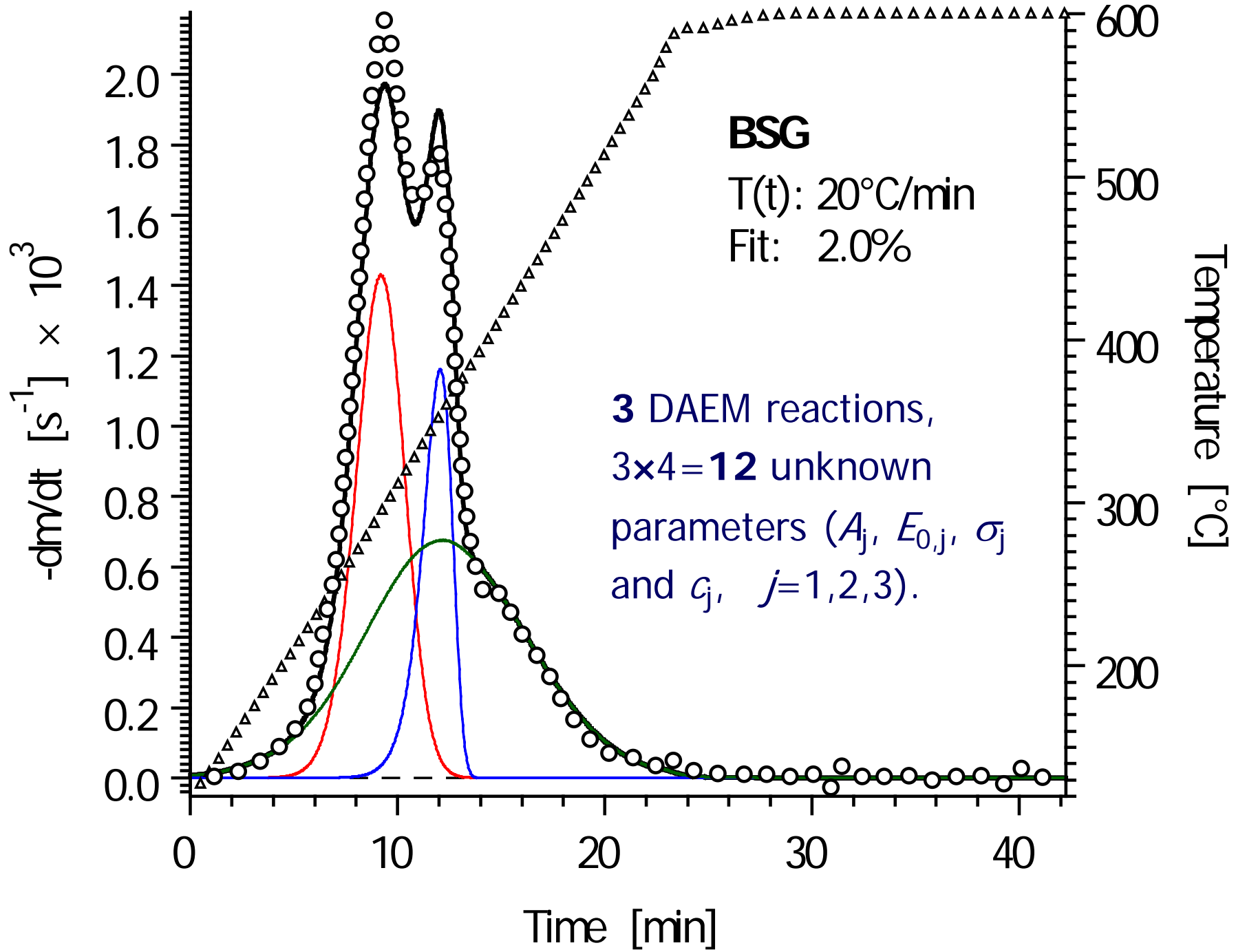
Examples from this work:

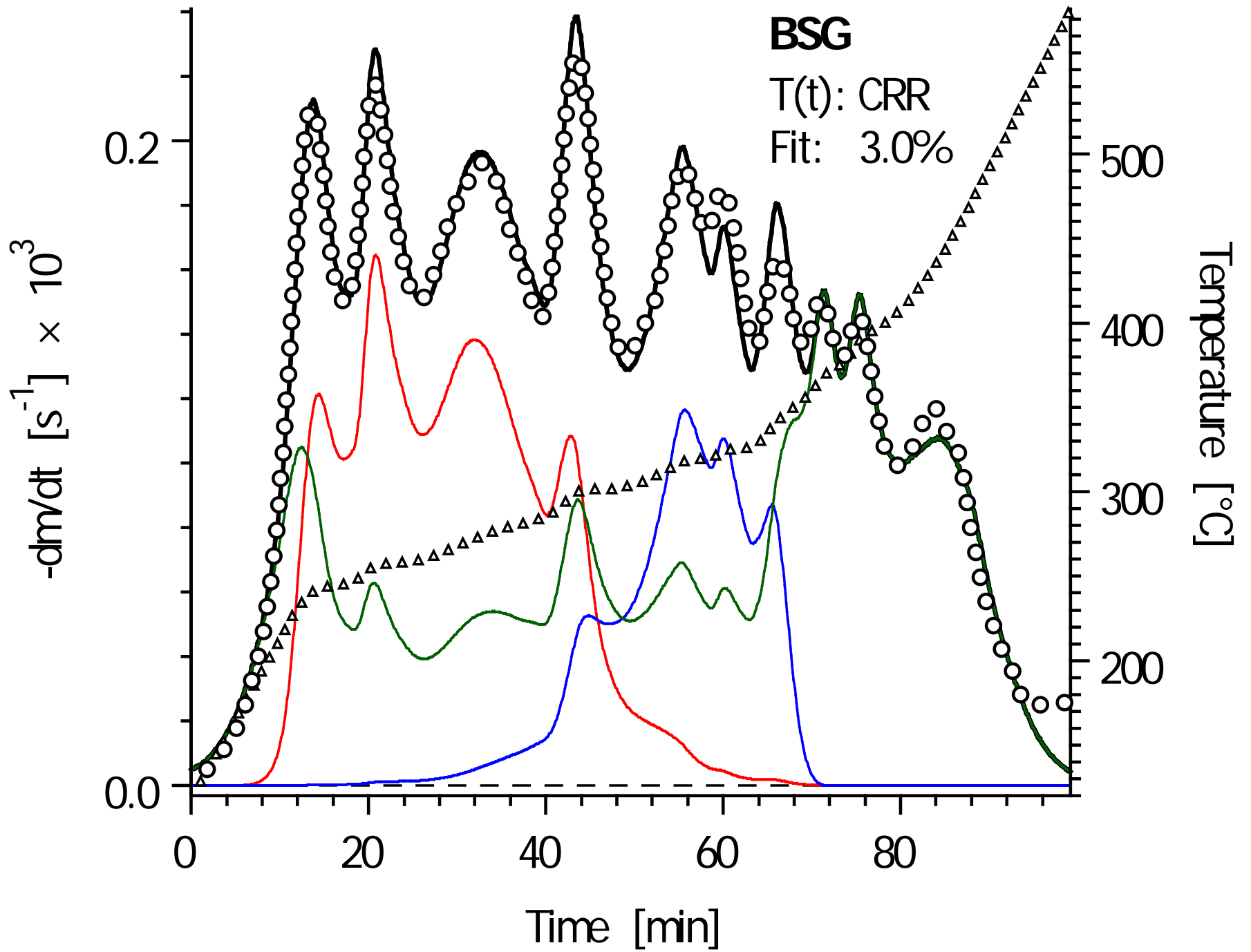
M. Becidan, G. Várhegyi, J. E. Hustad, Ø. Skreiberg:
Thermal decomposition of biomass wastes. A kinetic study.
Ind. Eng. Chem. Res. 46 (2007) 2428-2437

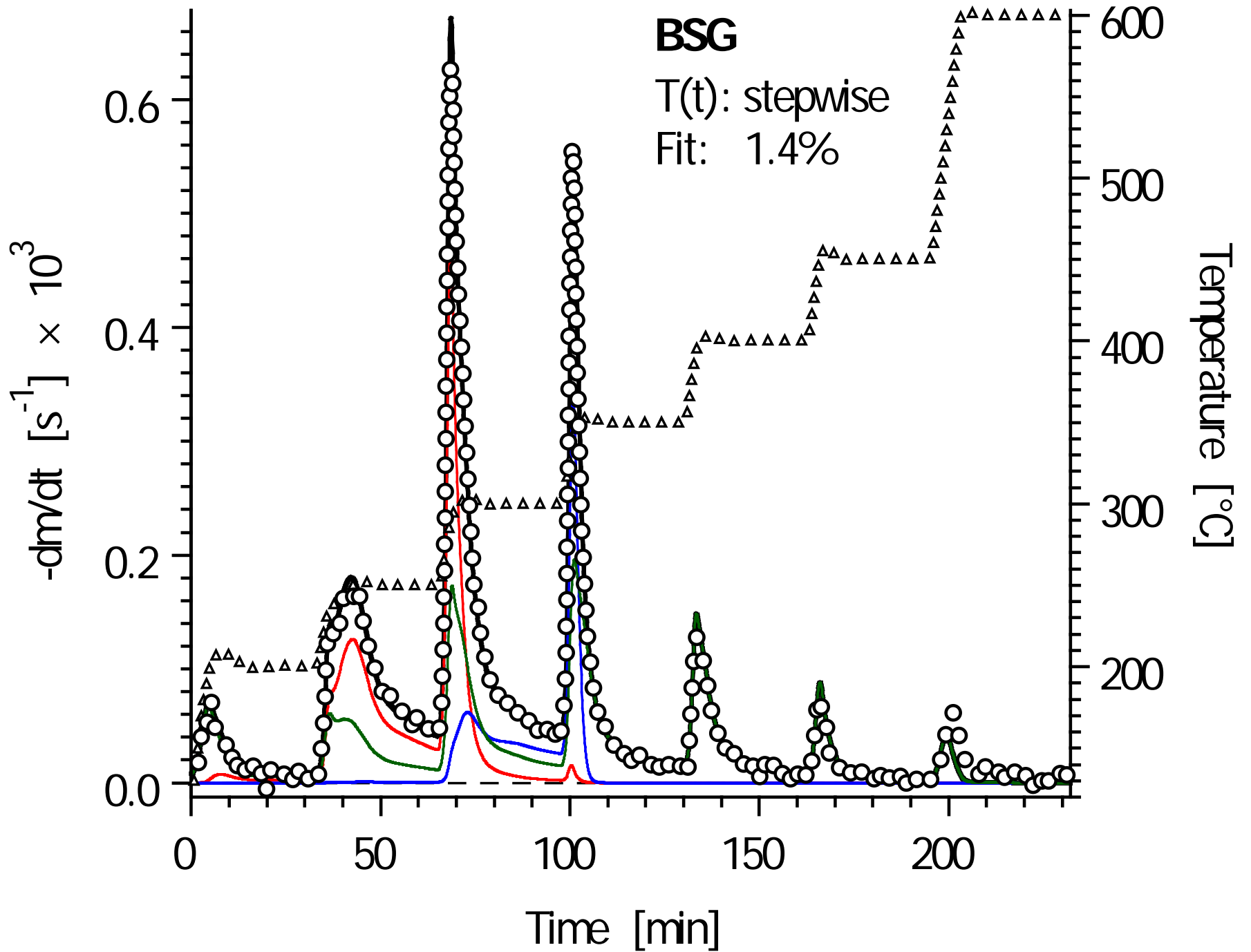


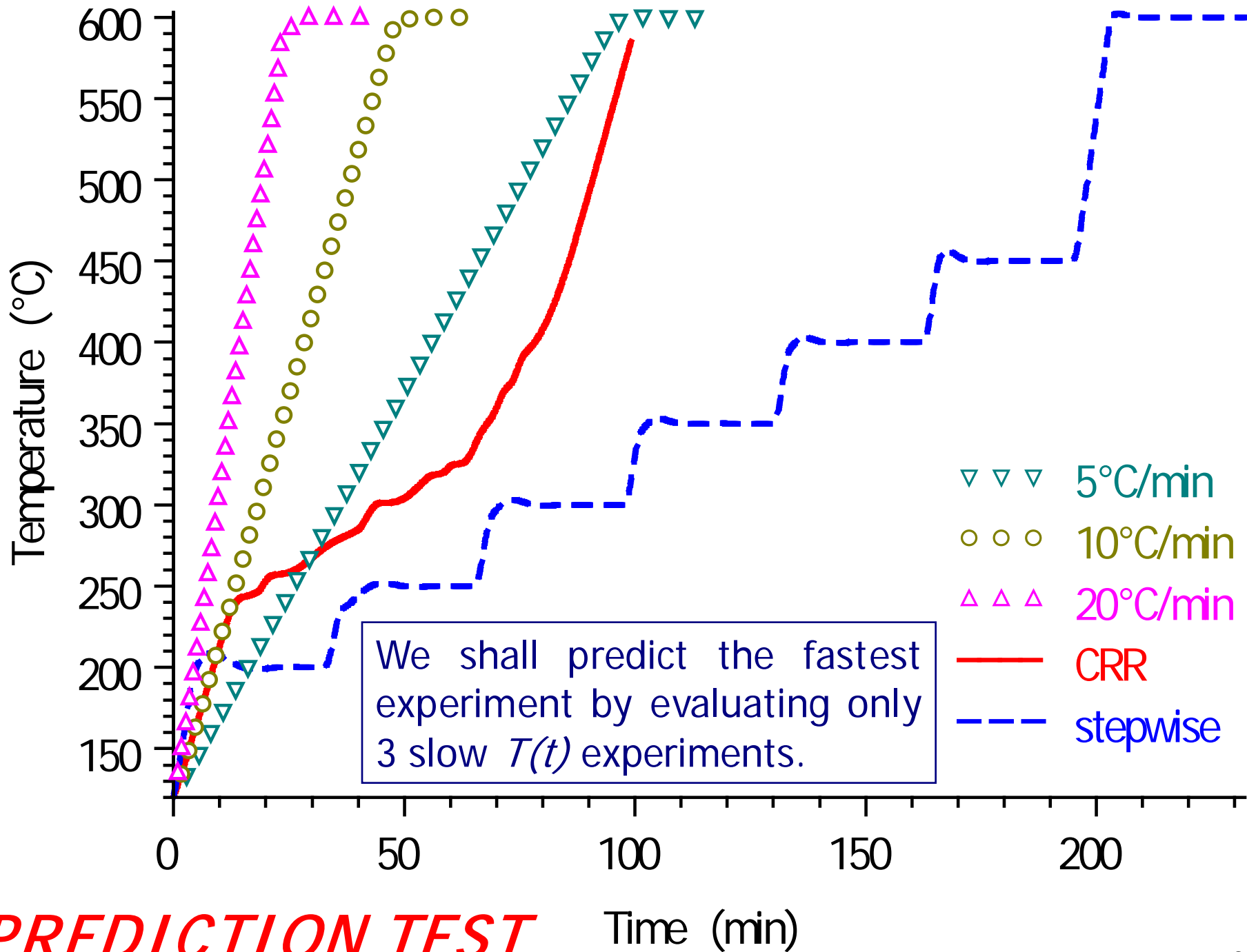




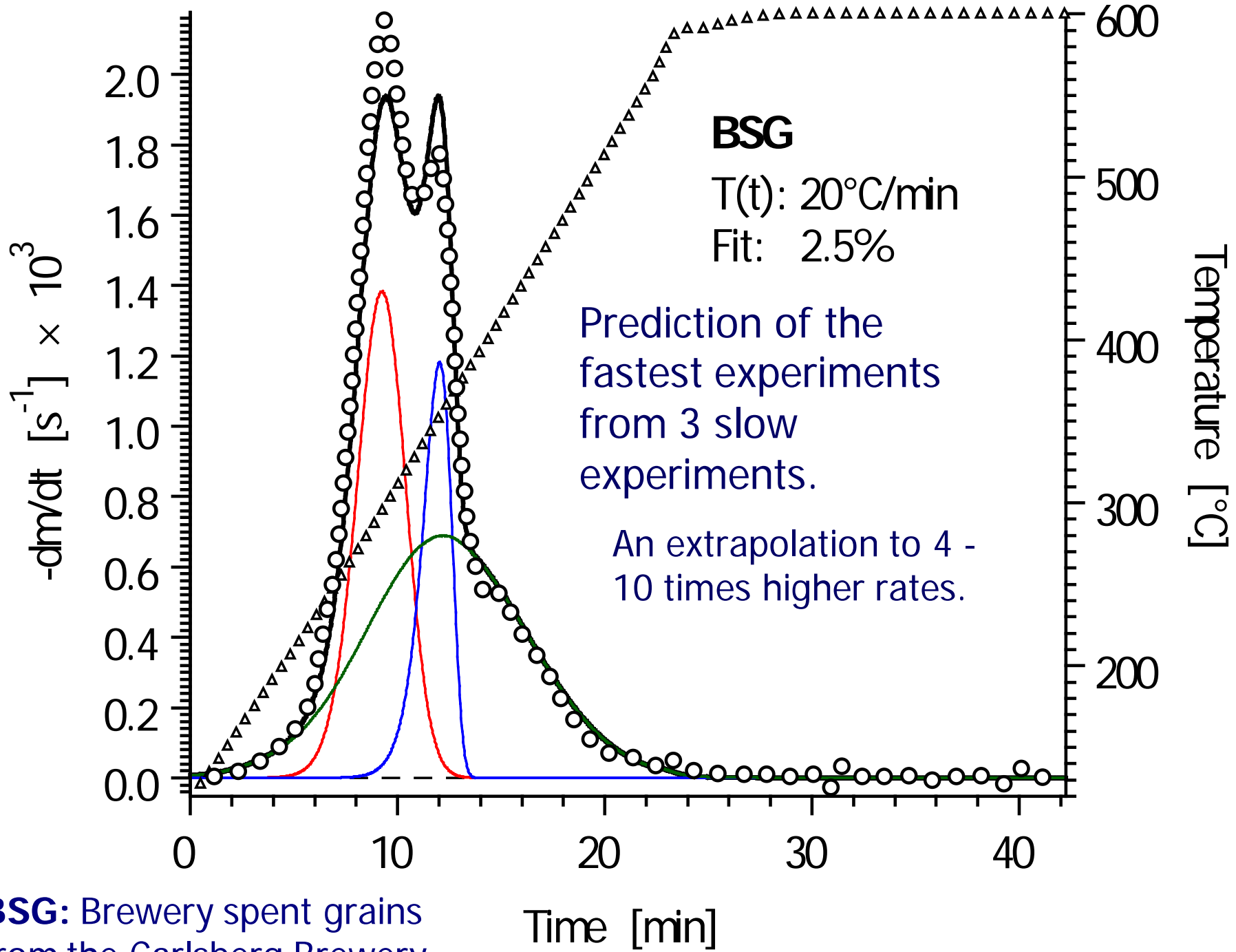




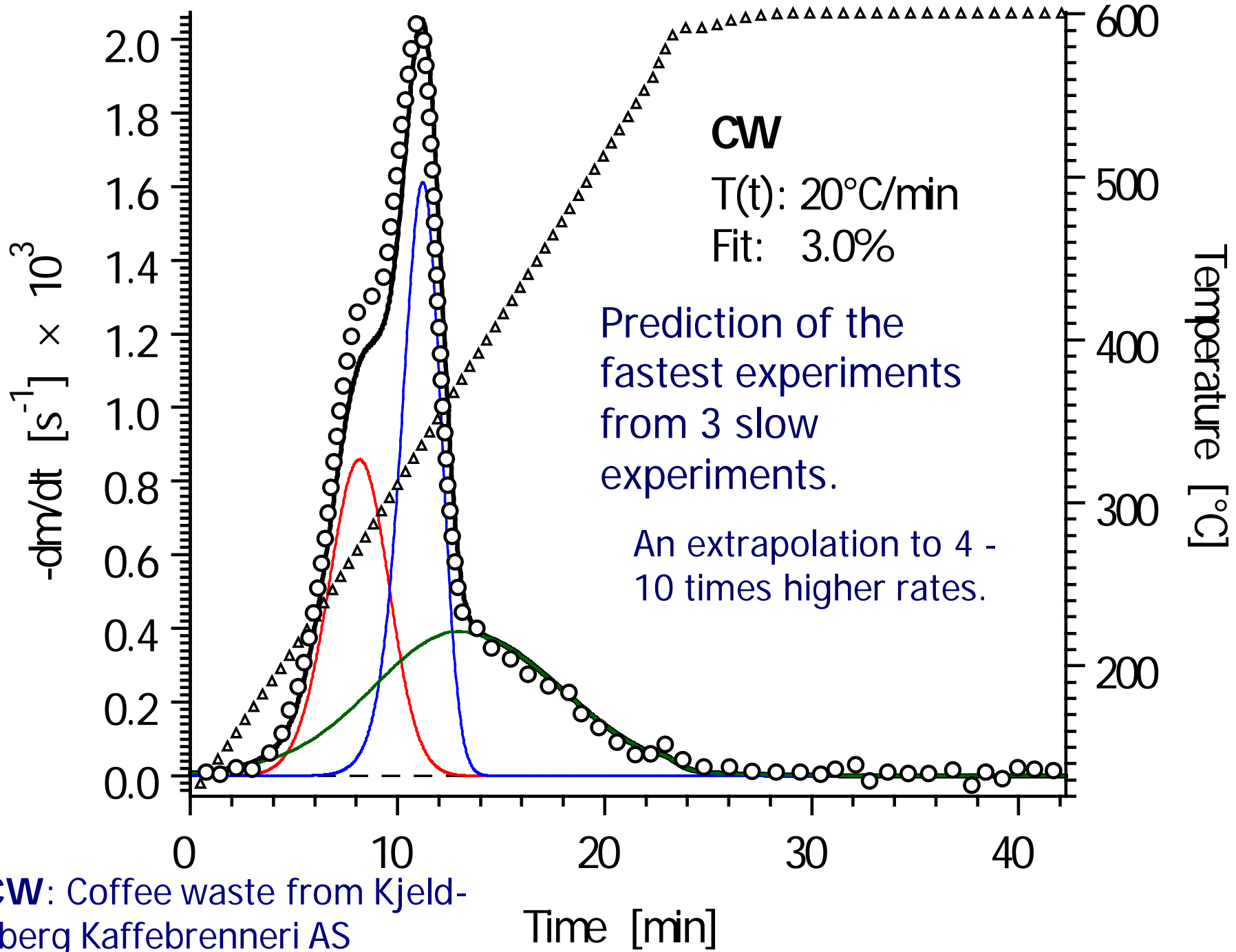


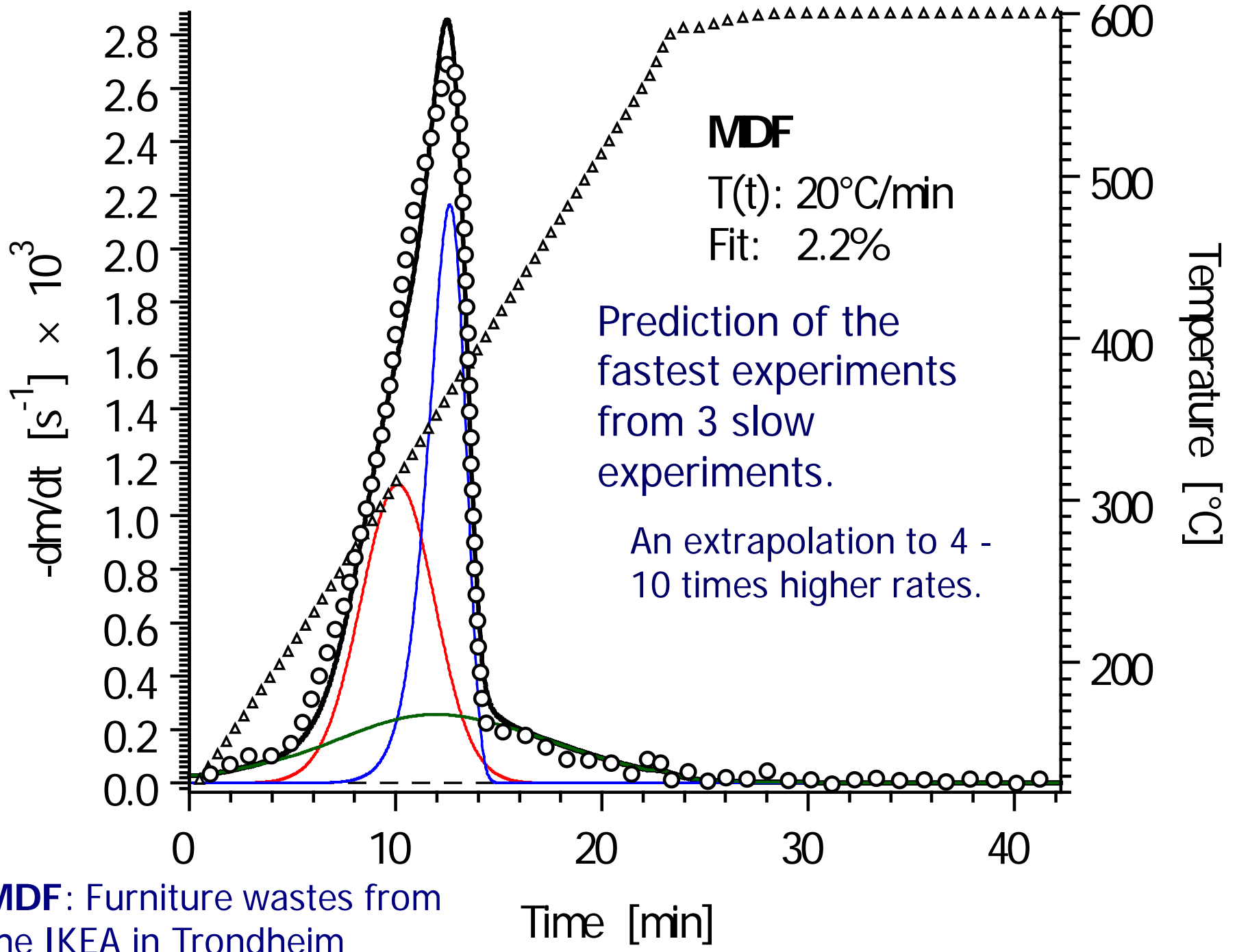


PREDICTION TEST



BSG: Brewery spent grains from the Carlsberg Brewery.





End of the Introduction.

Thanks for your attention. 😊

But we have not finished yet all ... 😞



