Kinetic Analysis of Biomass Pyrolysis with a Peak Temperature Method

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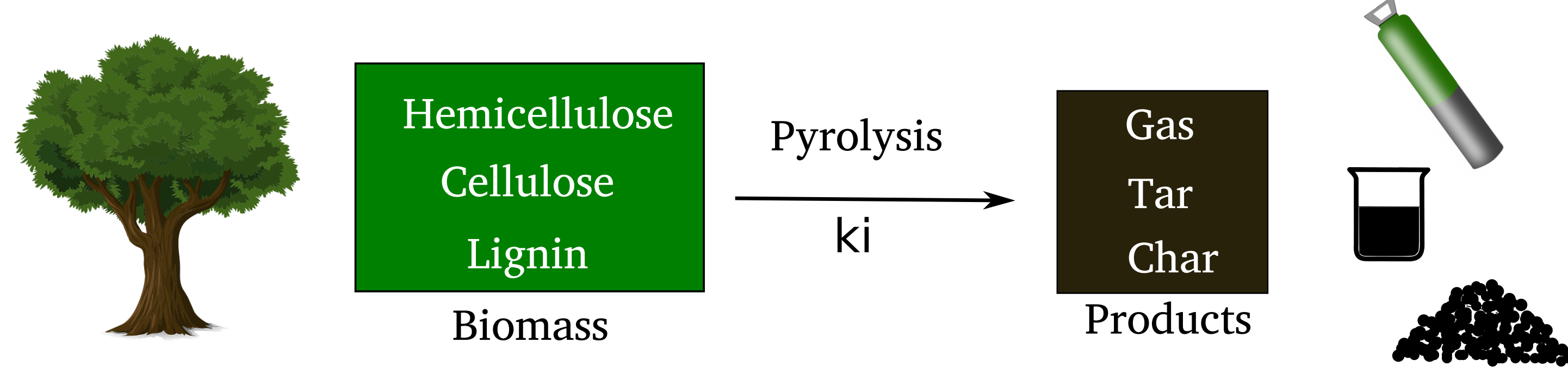University of Strathclyde Engineering

1. Introduction

Biomass pyrolysis consists of heating an organic material in the absence of oxygen in order to obtain a range of valuable products.

Biomass: Hemicellulose, Cellulose, Lignin → Pyrolysis k_i → Products: Gas, Tar, Char

In this a study, a multi-component mechanism, consisting of three paralel first order and single-step reactions, is considered, and non-isothermal conditions with a constant heating rate (β) are applied. The decomposition rate (dm/dt) features an Arrhenius temperature dependence (Eq. 2), where A is the pre-exponential factor (1/s), E the activation energy (kJ/mol), R the gas constant and T is the biomass temperature.

$$\frac{dm_i}{dt} = -k_i\, m_i \quad (1) \qquad k_i = A_i\, e^{\frac{-E_i}{RT}} \quad (2)$$

The aim of this study is to develop a straightforward method to perform a kinetic analysis of the biomass pyrolysis, applying a developed peak temperature method to the experimental thermogravimetric data. When performing a non-linear fit to the experimental data, initial values of the parameters to fit, are required. With this peak temperature method, the initial values can be estimated by direct observation of the differential thermogravimetric curves (DTG), which should nott present any difficulty and it will help to achieve convergence more quickly.

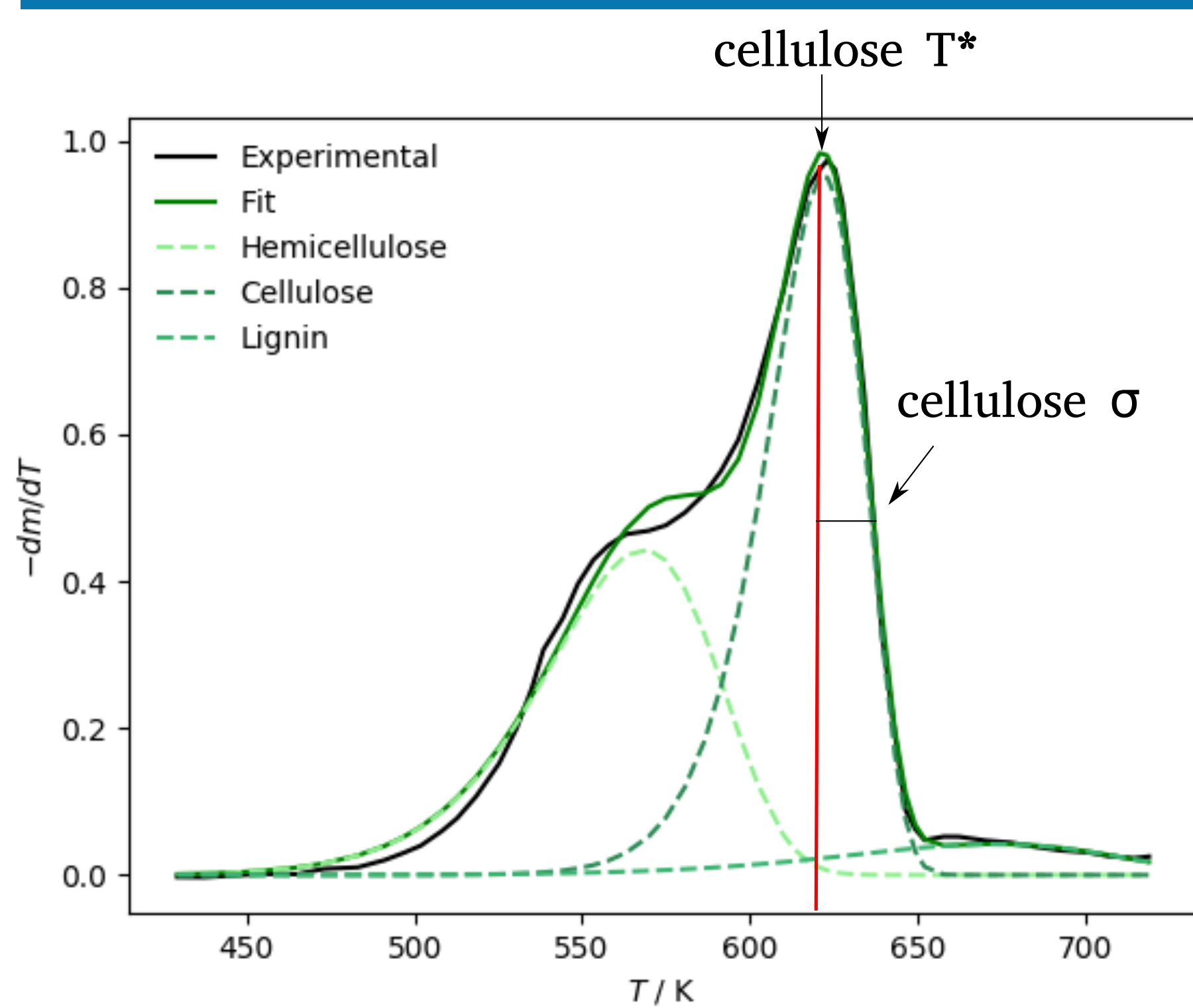## 3. Single Fitting of a DTG curve

cellulose T*

Fig. 2. Deconvolution of a DTG curve (normalized to unity) of beech wood at 5 K/min[1].

Deconvolution of a DTG curve has been performed with traditional Arrhenius and with the peak temperature method. The initial values for the peak temperature method have been estimated only by direct observation of the DTG curve, and the initial values for the kinetic parameters with traditional Arrhenius, have been taken from the literature [2]. In both cases, as initial composition a standard 1:1:1 has been chosen.

Table 1. Parameters initial values

	Hemicellulose	Cellulose	Lignin
E/ $kJ\, mol^{-1}$	147	193	181
A/ s^{-1}	$2.5 \cdot 10^{11}$	$1.38 \cdot 10^{14}$	$2.2 \cdot 10^{12}$
T*/ K	550	620	655
σ/ K	20	20	100

In order to reduce the convergence time, a part from good initial values, parameters bounds could be applied, in the case of the peak temperature, narrow bounds could be set depending on the level of overlapping of the individual curves.

The kinetic parameters, are calculated with the following expressions according to the peak temperature method:

$$E = R\, \frac{(T^*)^2}{\sigma} \quad (4) \qquad A = \frac{\beta}{\sigma}\, e^{\frac{T^*}{\sigma}} \quad (5)$$

Both methods give very similar results in terms of kinetic parameters and composition. However, the difference remains in how easy is to estimate the parameters initial values in order to perform a non-linear fit and quickly achieve convergence.

Table 2. Resulting kinetic parameters

		Hemicellulose	Cellulose	Lignin
Traditional Arrhenius	E/kJ mol^{-1}	99.89 ± 3.4	216.07 ± 6.8	$102.21 \pm 59.9\%$
	A/s^{-1}	$4.73 \cdot 10^6 \pm 3.7 \cdot 10^6$	$7.88 \cdot 10^{15} \pm 1.1 \cdot 10^{16}$	$1.66 \cdot 10^5 \pm 1.8 \cdot 10^6$
	Composition	42.1	52.2	5.7
Peak Temperature Method	T*/K	568.2 ± 1.1	621.9 ± 0.4	675 ± 1.1
	σ/K	26.9 ± 1.0	14.8 ± 0.5	40.7 ± 25.7
	E/kJ mol^{-1}	99.79	216.83	93.09
	A/s^{-1}	$4.62 \cdot 10^6$	$9.15 \cdot 10^{15}$	$3.28 \cdot 10^4$
	Composition	42.1	51.9	6.0

2. Peak Temperature Method

The peak temperature method is derived from the traditional Arrhenius equation, and the resulting reparameterized equation is similar to a Gauss model in terms of the main parameters to fit, which are the peak temperature (T*) and the standard deviation (σ).

Fig. 1. Gaussian (dashed line) versus peak temperature method (solid line) at different standard deviations.

From the second derivative of the rate of reaction and a Taylor-series expansion at the peak temperature, the already introduced reparameterized equation is obtained:

$$\frac{dm}{dT} = -\left(\frac{T^*}{\sigma}\right)^2 \frac{\sigma\, m}{(T^*)^2}\, exp\left[\frac{T^*}{\sigma} - \frac{(T^2)^2}{\sigma\, T} - \left(\frac{T^*}{\sigma}\right)^2 e^{\frac{T^*}{\sigma}}\, p(y)\right] \quad (3)$$

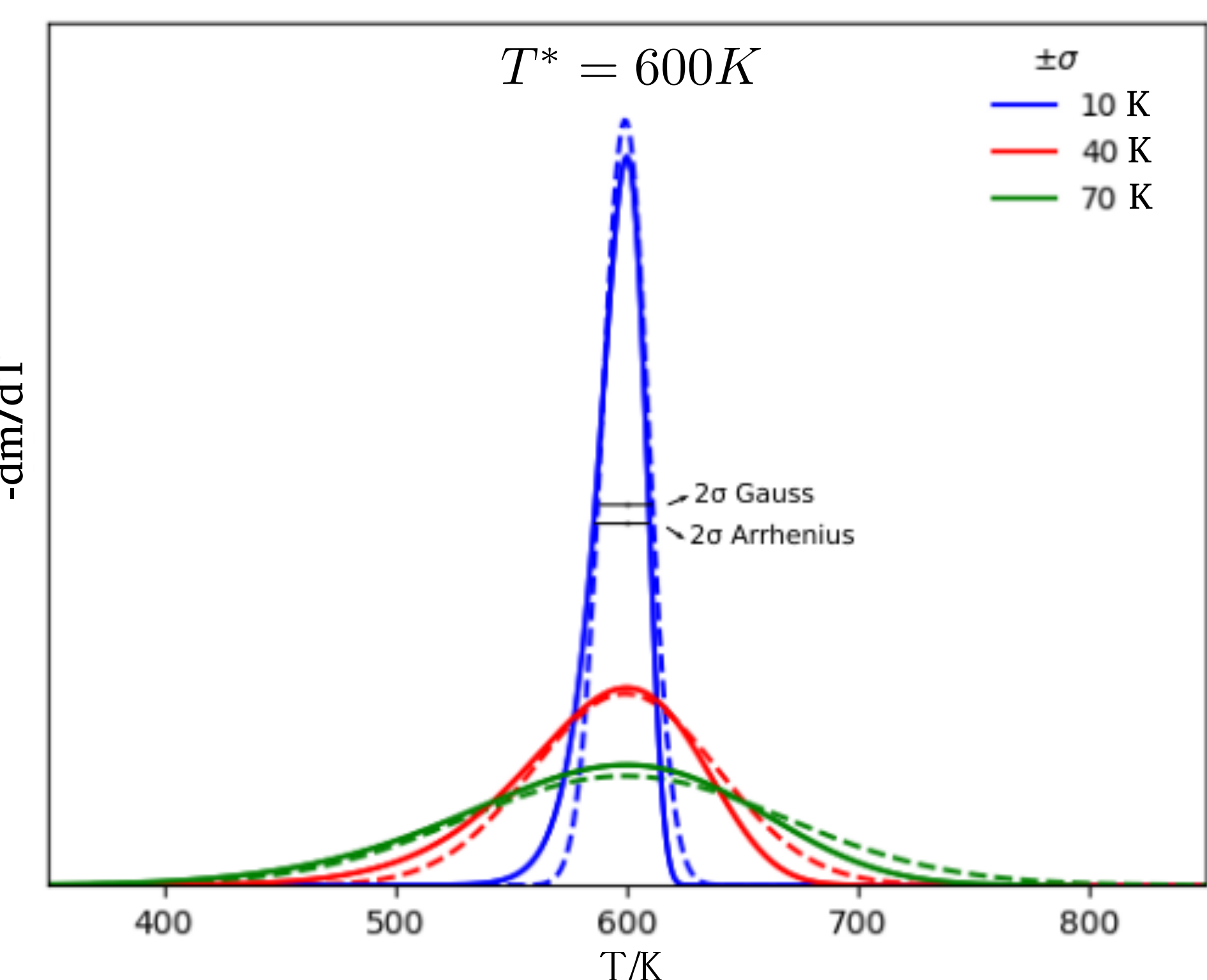Where $p(y) = \int_{y_0}^{y} e^{-y} y^{-2} dy$ and $y = \frac{E}{RT}$.

4. Simultaneous Fitting at different Heating Rates

From the peak temperature expression for the activation energy, an expression that relates the peak temperature with the heating rate for a specific activation energy can be derived, where the subscript zero refers to a chosen reference curve. As can be observerd from Fig. 3, the peak temperature increase with heating rate, is approximately twice the width increase.

Fig 3. Activation energy curves derived from the peak temperature method, cellulose experimental data points from the literature: [3][4][5][6][7][8][9][10][11] and simulation points ✗ ✗ ✗ from Fig. 4 for the sake of clarity.

$$-\ln\frac{\beta}{\beta_0} = \frac{E}{RT_0^*}\left(\frac{T_0^*}{T^*} - 1\right) + 2\ln\frac{T_0^*}{T^*} \quad (6)$$

A single set of kinetic parameters and a single biomass composition have been determined from several thermogravimetric analysis at different heating rates, in order to obtain results more generalizable to different operating conditions.
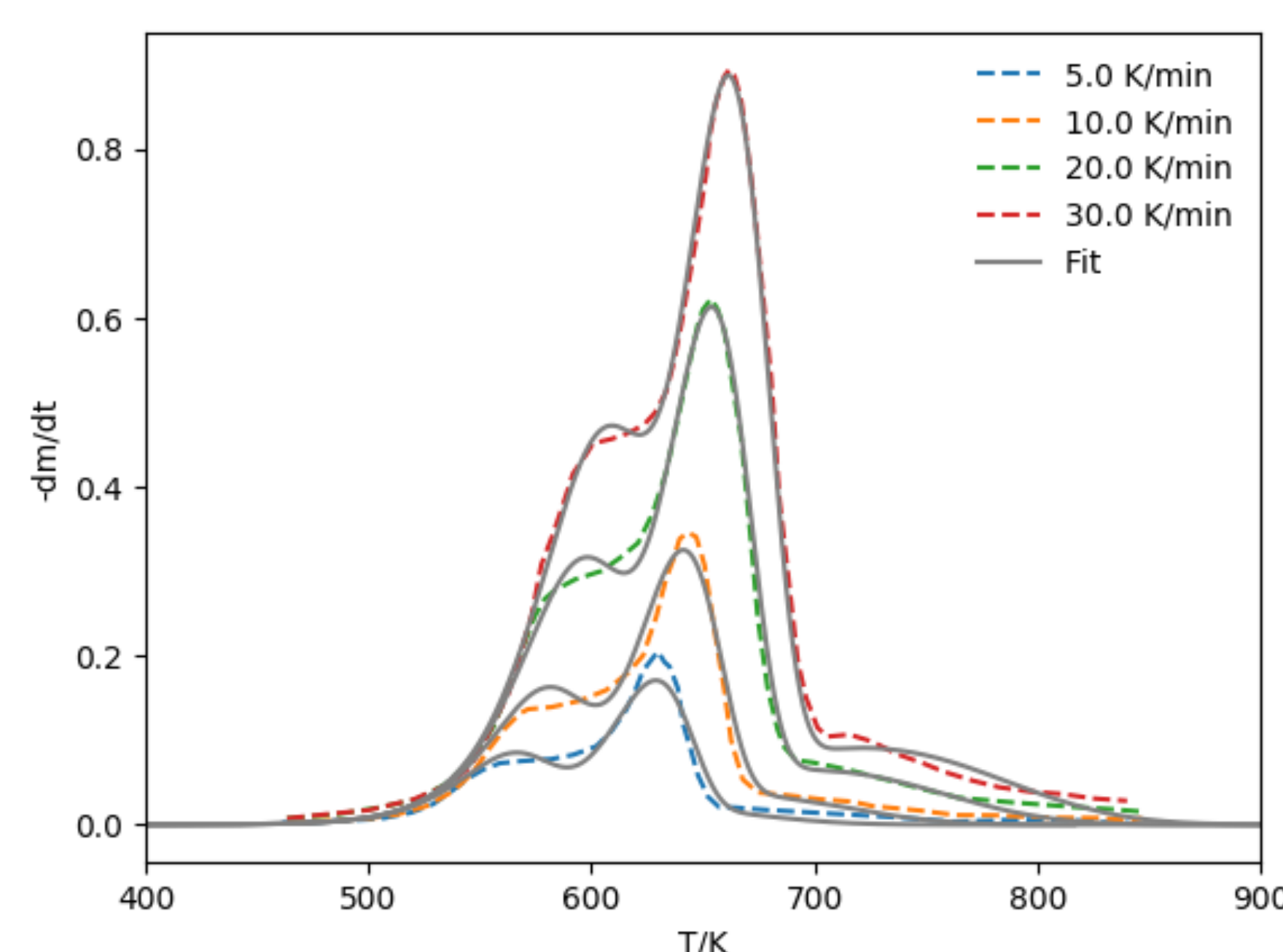

Fig. 5. Simultaneous fitting at different heating rates. Dashed lines: experimental, solid line: fit.

Fig 4. DTG simulation curves at 100 kJ/mol derived from Eq. 6 at different heating rates.

Experimental data[12] for 5, 10, 20 and 30 K/min of nutshell have been simultaneously fitted using one of them as a reference curve (10), in order to apply the previous expression that relates the peak temperature with the heating rate.

5. Conclusions

- The developed peak temperature method allows the easy estimate of the parameters initial values when performing a fit of thermogravimetric data.
- Depending on the degree of the curves overlapping, narrow bounds could be applied to the parameters in order to reduce the convergence time or improve the fit.
- The peak temperature method can also be used to determine the activation energy and pre-exponential factor without fitting the DTG curves, only from the peak temperatures and corresponding heating rates of each component. When experimental data show a certain degree of deviation from the ideal results, at least a range of activation energies can be defined.
- Finally, the developed method is also suitable for simultaneous evaluation of several DTG curves at different heating rates, allowing to obtain a single biomass composition and a single set of kinetic parameters. In order to improve the fit, a modified Arrhenius with extra kinetic parameters to fit could be considered.
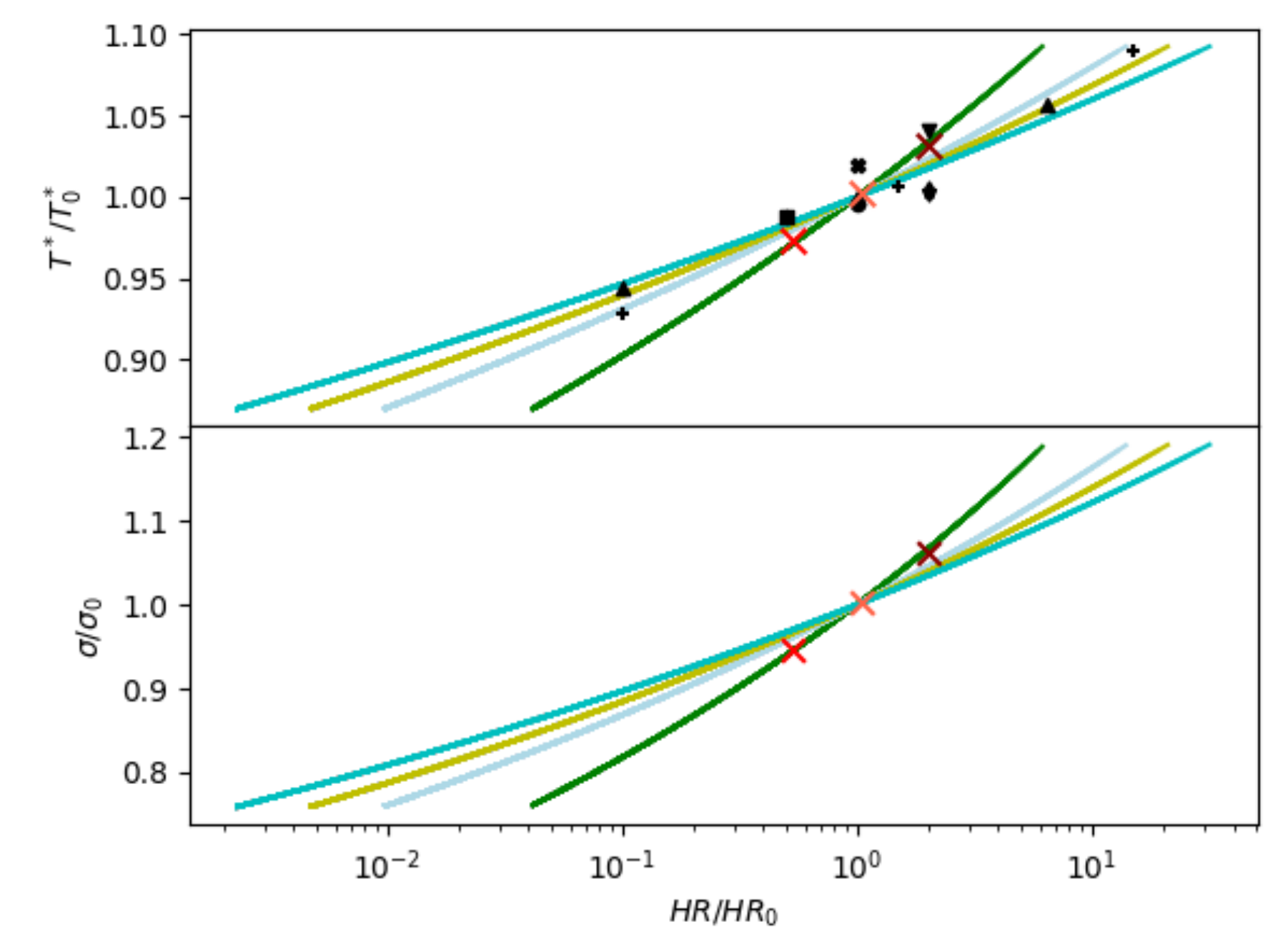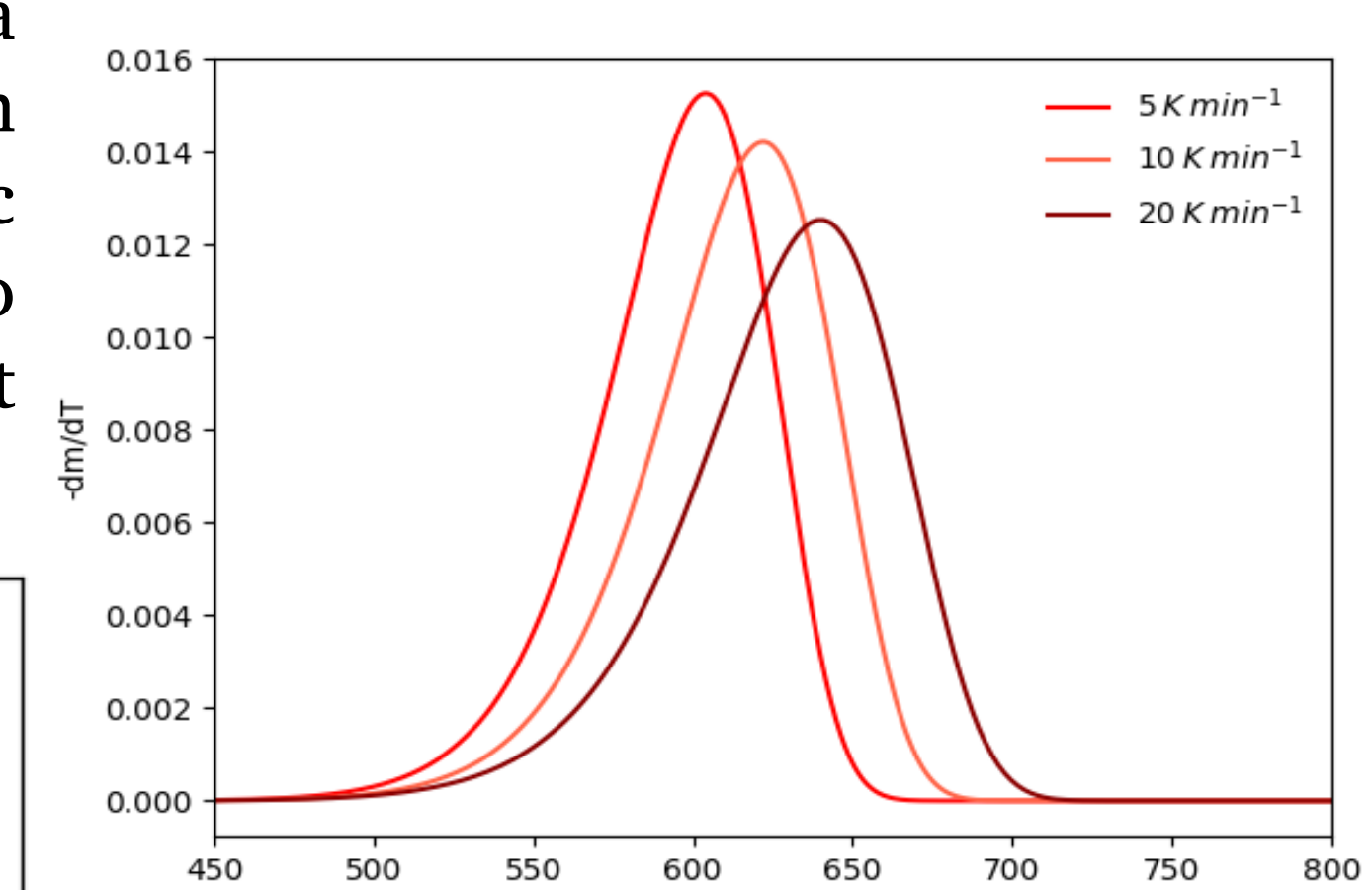
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