Supporting Information for Article

Empirical Kinetic Models for the Combustion of Charcoals and Biomasses in the Kinetic Regime

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Scope of this Document: Models are presented for the combustion of 6 charcoals, a straw sample, and a willow sample. The performance of the models was tested by the reevaluation of TGA experiments belonging to earlier publications. Herewith we present figures that show the calculated and experimental data. 38 TGA experiments were reevaluated by the method of least squares as described in the paper. Approach II was used, meaning that an identical E value was determined for the charcoals and another E value was determined for the biomasses.

Notation in the Figures: $(d\alpha/dt)^{calc}$**: blue lines**; $(d\alpha/dt)^{obs}$**: thick gray lines**; $T(t)$, when present: thin green lines.

There is some textual information beneath each figure. The first line of the text gives the name or abbreviated name of the given sample and summarizes the experimental conditions. Here $\mathbf{G_0}$ denotes the initial sample mass. This line is set in boldface. Two further lines show data about the fit quality.

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About the Employed Model

Here the modelling is summarized. The employed empirical model:

$$d\alpha/dt = A(\alpha)f(\alpha)\exp(-\frac{E}{RT}) \tag{S1}$$

where α is the reacted fraction (dimensionless), while *[A(α)f(α)]* / s^{-1} is an empirical function.

In a rearranged form:

$$d\alpha/dt = \tilde{A}(\alpha)(1-\alpha)\exp(-\frac{E}{RT}) \tag{S2}$$

where the term (1-*α*) ensures that dα/dt would be 0 at *α*=1. $\tilde{A}(\alpha)=A(\alpha)f(\alpha)/(1-\alpha)$ when *α*<1. (Obviously, the division by (1-*α*) is not possible at the *α*=1 point. There, however, $\tilde{A}(\alpha)$ may have any finite value so that $\tilde{A}(\alpha)(1-\alpha)$ would be zero at *α*=1.)

A further rearrangement yields:

$$d\alpha/dt = (1-\alpha)\exp(\ln\tilde{A}(\alpha)-\frac{E}{RT}) \tag{S3}$$

To obtain flexible approximations with limited numbers of unknowns, $\ln\tilde{A}(\alpha)$ is approximated by polynomials. For this purpose, the variable **$x=2\alpha-1$** is introduced which varies from -1 till +1 as α varies from 0 to 1. The results will be presented as the following example shows:

$$\log_{10}\tilde{A}(x)= 8.6276385 -0.100983T_1(x) +0.2155345T_2(x) -0.106734T_3(x) +0.0321649T_4(x) -0.011974T_5(x) +0.0083596T_6(x) -0.000487T_7(x) -0.001529T_8(x) +0.0040258T_9(x) \tag{S4}$$

Here $T_1(x)$, $T_2(x)$, … are Chebyshev polynomials of the first kind. See the next section for their simple computer evaluation. $\log_{10}\tilde{A}(x)$ is reported instead of $\ln\tilde{A}(x)$ for an easier survey of the magnitudes.
[Note that $\ln\tilde{A}(x) = \ln 10 \log_{10}\tilde{A}(x)$]

Simple Computer Code Examples for the Calculations with the Results

The calculations with the by Chebyshev polynomials of the first kind are fast and simple. Their values can be calculated by a recurrence relationship at any *x*:

$T_0 = 1;$

$T_1 = x;$

$T_2 = 2 x T_1 - T_0;$

…

$T_n = 2 x T_{n-1} - T_{n-2};$

A small C/C++ function to evaluate the polynomials in the results:

```
// Calculation of p(x) = c0+c1T1(x)+c2T2(x)+... +cnTn(x)
// where T1, T2, ... Tn are Chebyshev polynomials of the 1st kind.
// x=2α-1;
// c is the array for the coefficients: c[0], c[1] ... c[n];
// n is the polynomial order, n≤13.
double p(double x, double *c, int n)
{
	// T is an array for Chebyshev polynomial values up to order 13:
	// T[0], T[1], ... T[13]
	double T[14];
	// The result will be formed in variable “result”:
	double result;
	T[0]=1;
	T[1]=x;
	result=c[0]+c[1]*T[1];
	for(int i=2; i<=n; i++)
	{
		T[i]=2*x*T[i-1]-T[i-2];
		result=result+c[i]*T[i];
	}
	return result;
}
```

A Fortran version of the same code:

```
! In Fortran, "real(8)" denotes floating point with 8-byte (64-bit) precision:
real(8) function p( x, c, n )
      integer n
      real(8) x
      ! c is the array of the coefficients: c(0), c(1) ... c(n):
      real(8) c(0:n)
      ! T is an array for Chebyshev polynomial values up to order 13:
      ! T(0), T(1), ... T(13)
      real(8) T(0:13)
      integer i
      ! The calculations follow:
      T(0)=1
      T(1)=x
      p=c(0)+c(1)*T(1)
      do i=2, n
            T(i)=2*x*T(i-1)-T(i-2)
            p=p+c(i)*T(i)
      end do
end function p
```

S1. Charcoal Samples from Spruce Wood and from a Forest Residue

The experiments belong to this work:

[S1] Wang, L.; Várhegyi, G.; Skreiberg, Ø.; Li, T.; Grønli, M.; Antal, M. J.: Combustion characteristics of biomass charcoals produced at different carbonization conditions. A kinetic study. *Energy Fuels* **2016**, *30*, 3186-3197. *doi:* 10.1021/acs.energyfuels.6b00354 Supporting Info Repository

TGA experiments with linear, modulated, and constant reaction rate (CRR) experiments were employed for each charcoal. Letters **S** and **R** in the names of the samples stand for spruce and forest residue, respectively, while substrings “500-1” and “500-8” denote preparations in a macro TGA at 1 and 8 bar pressures. A third preparation method, identified by substring “fc-8”, employed a flash carbonization process.

S1.1. Spruce Charcoal “S500-1”

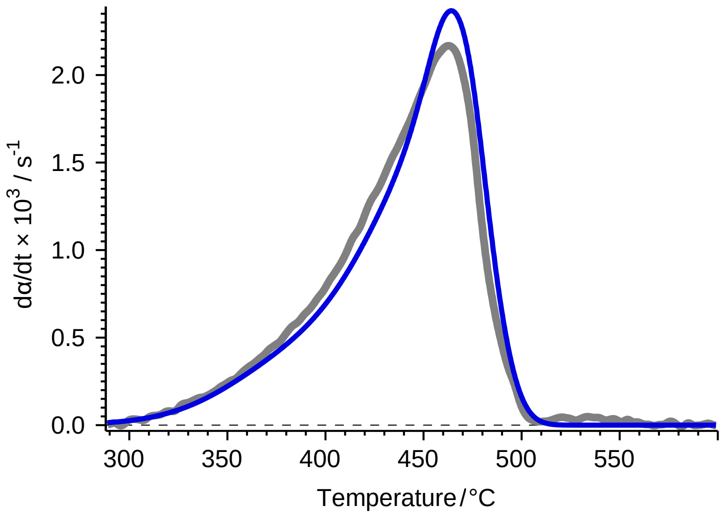
Model:

$x=2\alpha-1$

$E = 150$ kJ/mol

$$\log_{10}\tilde{A}(x) = 8.6276385 - 0.100983T_1(x) + 0.2155345T_2(x) - 0.106734T_3(x) + 0.0321649T_4(x) - 0.011974T_5(x) + 0.0083596T_6(x) - 0.000487T_7(x) - 0.001529T_8(x) + 0.0040258T_9(x)$$

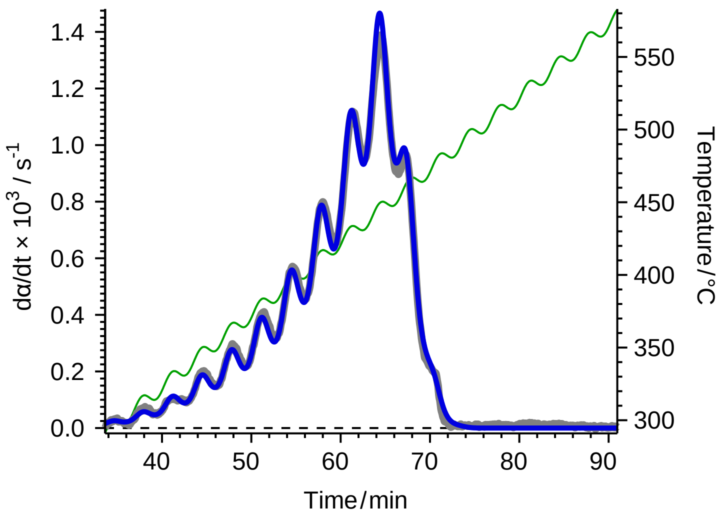
(Input file: "S500_1__0,9_150kJ_mol.par")



Char "S500-1" 10°C/min [O_2]=0.20 G_0=0.20mg

Relative deviation: 5.05%, Deviation: 0.021 µg/s

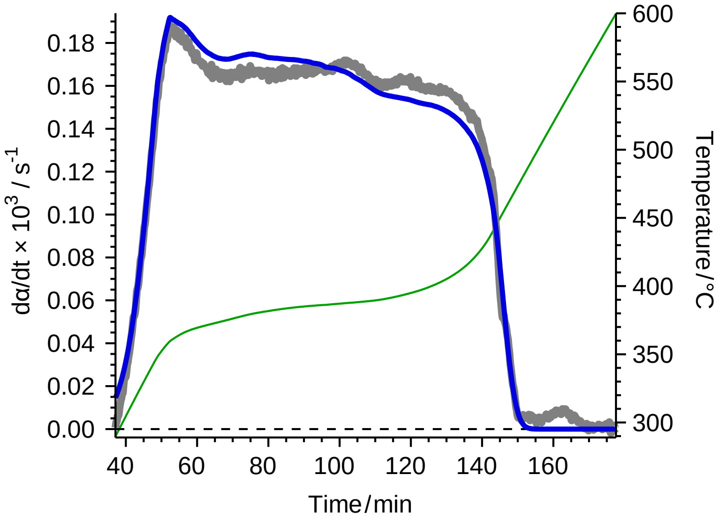
rms rel. dev. of 3 experiments: 3.60%



Char "S500-1" modulated T(t) (5°C/min) [O_2]=0.20 G_0=0.5mg

Relative deviation: 1.37%, Deviation: 0.0097 µg/s

rms rel. dev. of 3 experiments: 3.60%



Char "S500-1" CRR T(t) [O_2]=0.20 G_0=1.0mg

Relative deviation: 3.41%, Deviation: 0.0065 µg/s

rms rel. dev. of 3 experiments: 3.60%

S1.2. Spruce Charcoal "S500-8"

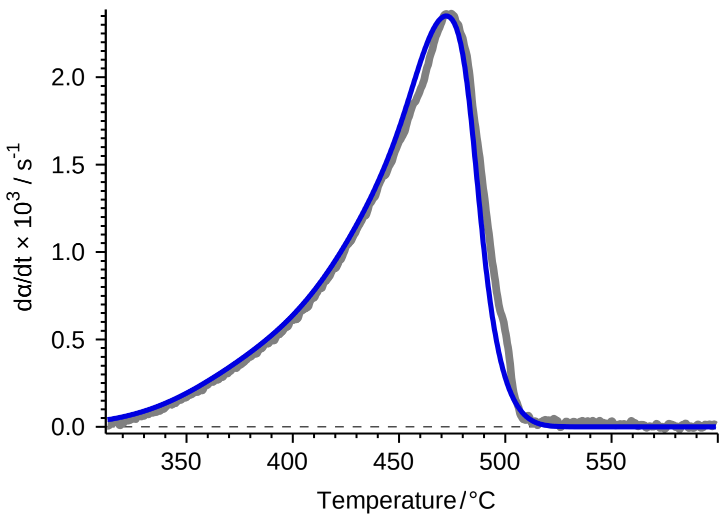
Model:

$x = 2\alpha - 1$

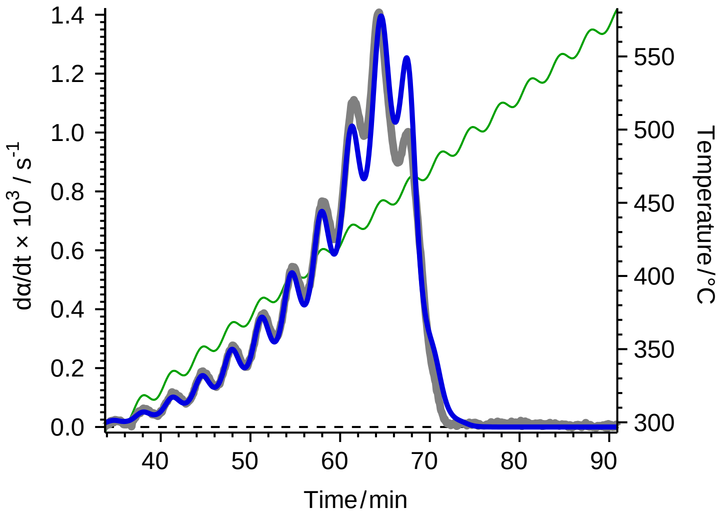
E= 150 kJ/mol

$\log_{10}\tilde{A}(x) = 8.5556654 - 0.088356T_1(x) + 0.2151246T_2(x) - 0.110181T_3(x) + 0.0094049T_4(x) - 0.028439T_5(x) - 0.005718T_6(x) - 0.006718T_7(x) - 0.003527T_8(x) + 0.0018759T_9(x)$

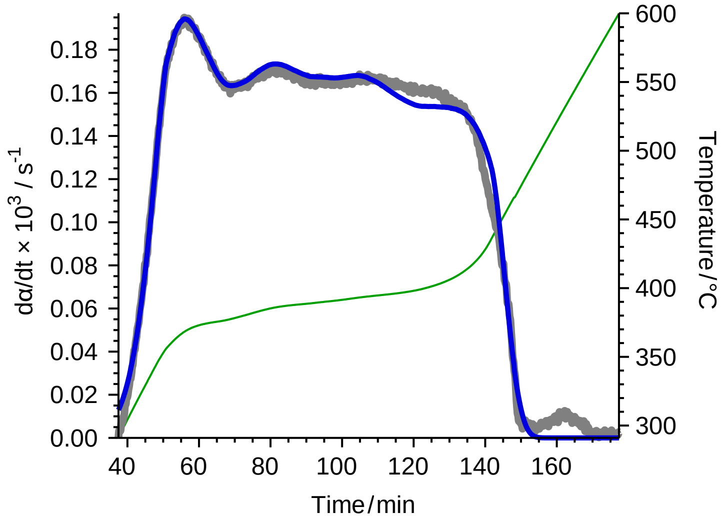
(Input file: "S500_8__0,9_150kJ_mol.par")



Char "S500-8" 10°C/min [O_2]=0.20 G_0=0.20mg
Relative deviation: 3.50%, Deviation: 0.016 µg/s
rms rel. dev. of 3 experiments: 3.40%



Char "S500-8" modulated T(t) (5°C/min) [O_2]=0.20 G_0=0.5mg
Relative deviation: 3.95%, Deviation: 0.028 µg/s
rms rel. dev. of 3 experiments: 3.40%



Char "S500-8" CRR T(t) [O_2]=0.20 G_0=1.0mg
Relative deviation: 2.61%, Deviation: 0.0051 µg/s
rms rel. dev. of 3 experiments: 3.40%

S1.3. Spruce Charcoal "Sfc-8"

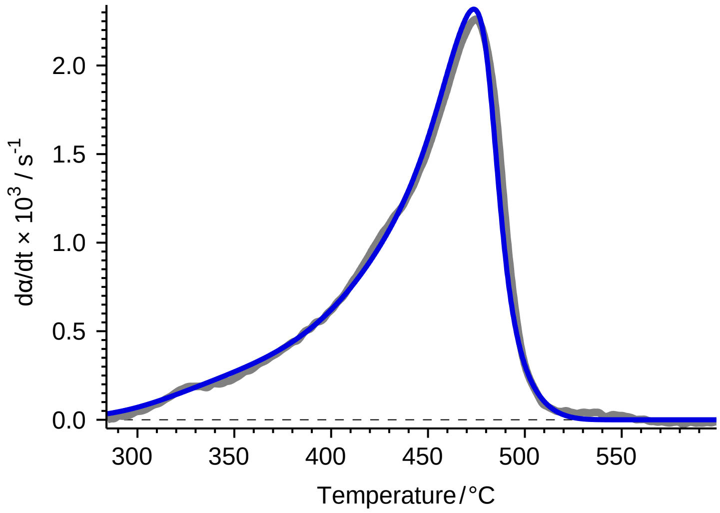
Model:

$x=2\alpha-1$

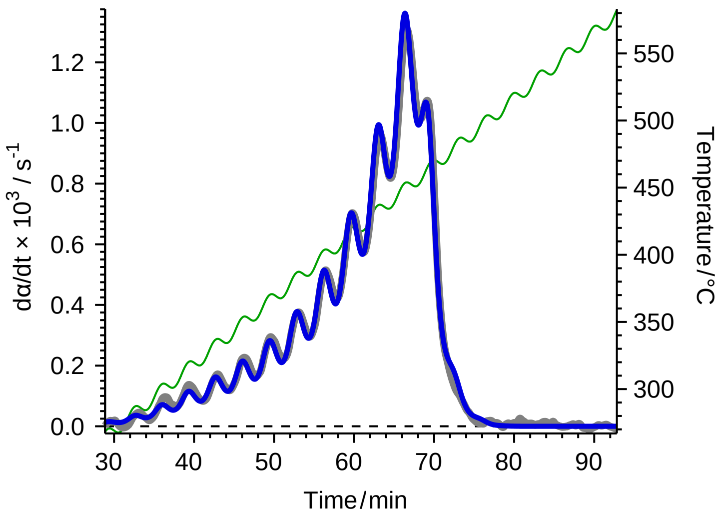
E= 150 kJ/mol

$$\log_{10}\tilde{A}(x)= 8.6246704 -0.321914T_1(x) +0.3229788T_2(x) -0.237484T_3(x) +0.0333173T_4(x) -0.073142T_5(x) +0.0035167T_6(x) -0.016629T_7(x) -0.000105T_8(x) +0.0001471T_9(x)$$

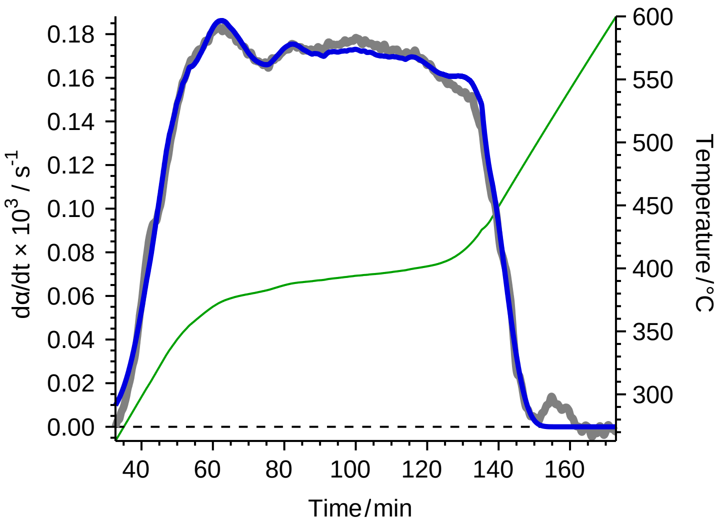
(Input file: "Sfc__8__0,9_150kJ_mol.par")



Char "Sfc-8" 10°C/min [O_2]=0.20 G_0=0.21mg
Relative deviation: 2.29%, Deviation: 0.010 µg/s
rms rel. dev. of 3 experiments: 2.22%



Char "Sfc-8" modulated T(t) (5°C/min) [O_2]=0.20 G_0=0.5mg
Relative deviation: 1.76%, Deviation: 0.011 µg/s
rms rel. dev. of 3 experiments: 2.22%



Char "Sfc-8" CRR T(t) [O_2]=0.20 G_0=0.5mg
Relative deviation: 2.54%, Deviation: 0.0024 µg/s
rms rel. dev. of 3 experiments: 2.22%

S1.4. Forest Residue Charcoal "R500-1"

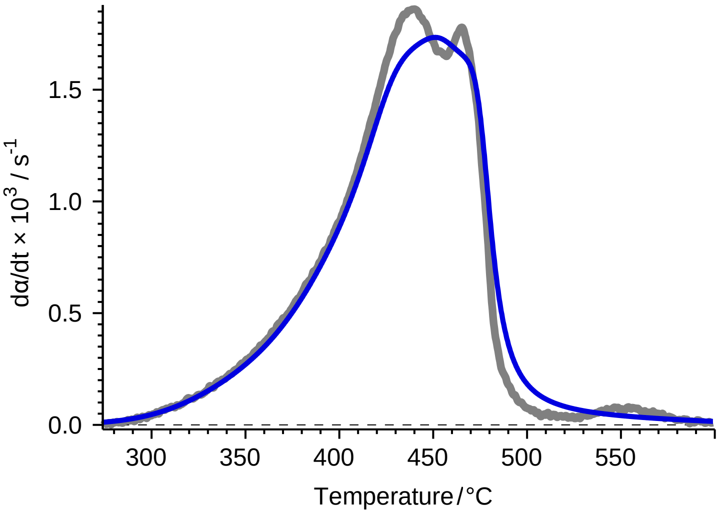
Model:

$x=2\alpha-1$

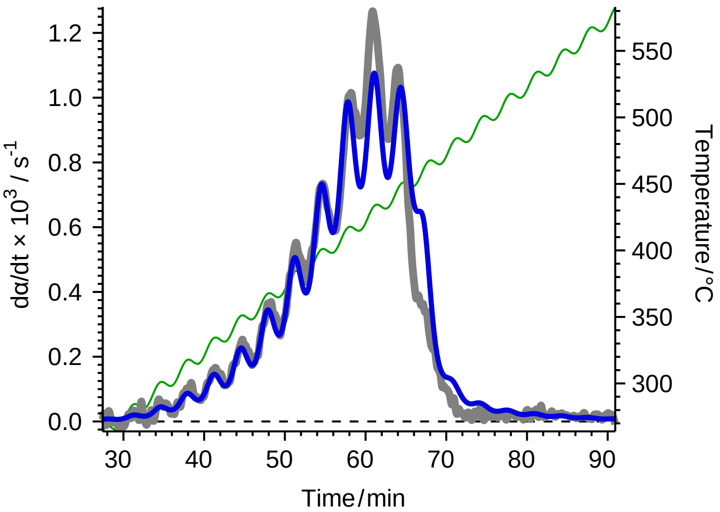
E= 150 kJ/mol

$\log_{10}\tilde{A}(x)= 8.4959156 -0.663436T_1(x) -0.153737T_2(x) -0.38119T_3(x) -0.175869T_4(x) -0.219272T_5(x) -0.103289T_6(x) -0.079101T_7(x) -0.027103T_8(x) -0.018519T_9(x)$

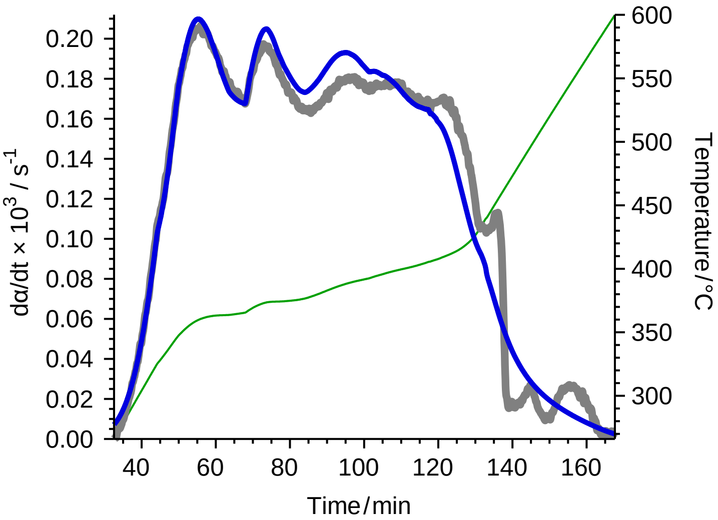
(Input file: "R500_1__0,9_150kJ_mol.par")



Char "R500-1" 10°C/min [O_2]=0.20 G_0=0.29mg
Relative deviation: 4.26%, Deviation: 0.021 µg/s
rms rel. dev. of 3 experiments: 5.41%



Char "R500-1" modulated T(t) (5°C/min) [O_2]=0.20 G_0=0.4mg
Relative deviation: 5.64%, Deviation: 0.027 µg/s
rms rel. dev. of 3 experiments: 5.41%



Char "R500-1" CRR T(t) [O_2]=0.20 G_0=1.0mg
Relative deviation: 6.15%, Deviation: 0.012 µg/s
rms rel. dev. of 3 experiments: 5.41%

S1.5. Forest Residue Charcoal "R500-8"

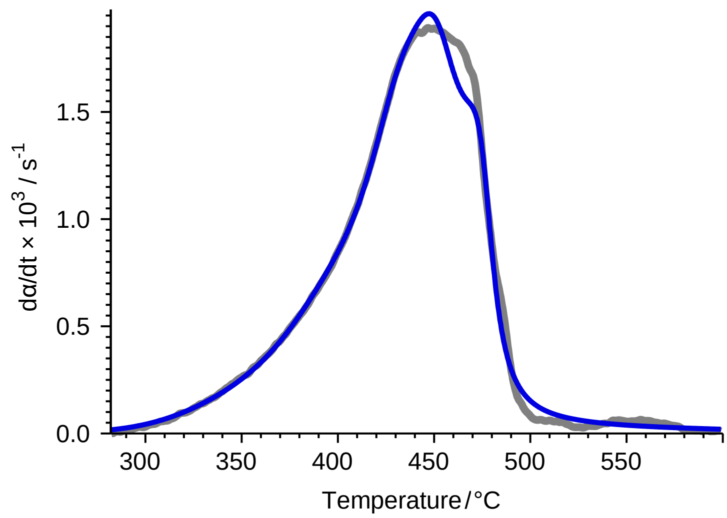
Model:

$x=2\alpha-1$

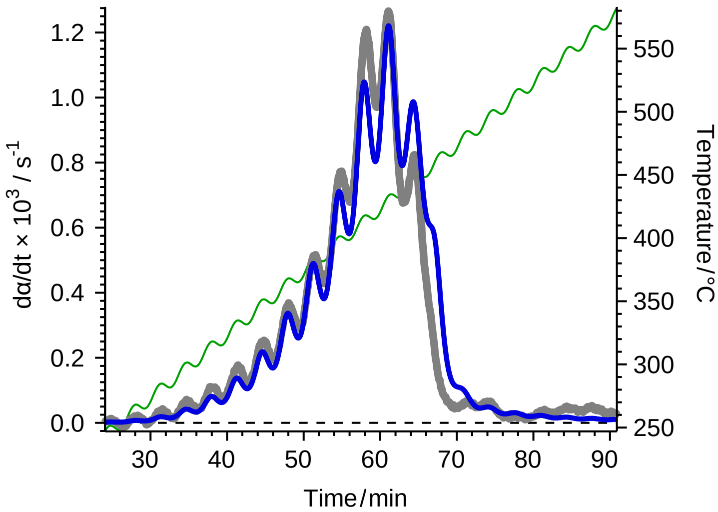
E= 150 kJ/mol

$\log_{10}\tilde{A}(x)= 8.4570496 -0.705757T_1(x) -0.24949T_2(x) -0.459354T_3(x) -0.224129T_4(x) -0.260085T_5(x) -0.150565T_6(x) -0.117868T_7(x) -0.04664T_8(x) -0.029742T_9(x)$

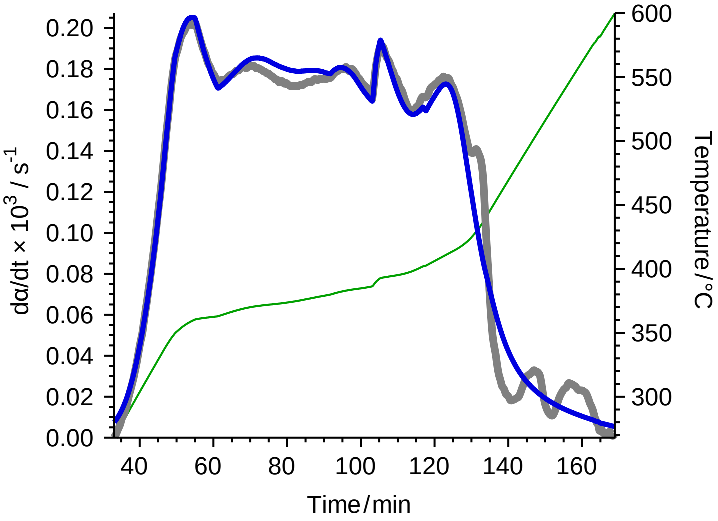
(Input file: "R500_8__0,9_150kJ_mol.par")



Char "R500-8" 10°C/min [O_2]=0.20 G_0=0.36mg
Relative deviation: 2.43%, Deviation: 0.016 µg/s
rms rel. dev. of 3 experiments: 4.72%



Char "R500-8" modulated T(t) (5°C/min) [O_2]=0.20 G_0=0.5mg
Relative deviation: 6.28%, Deviation: 0.037 µg/s
rms rel. dev. of 3 experiments: 4.72%



Char "R500-8" CRR T(t) [O_2]=0.20 G_0=1.0mg
Relative deviation: 4.63%, Deviation: 0.0089 µg/s
rms rel. dev. of 3 experiments: 4.72%

S1.6. Forest Residue Charcoal "Rfc-8"

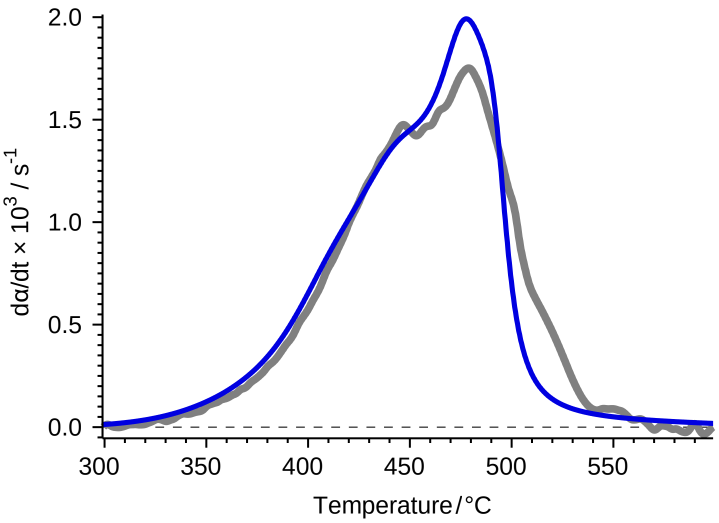
Model:

$x=2\alpha-1$

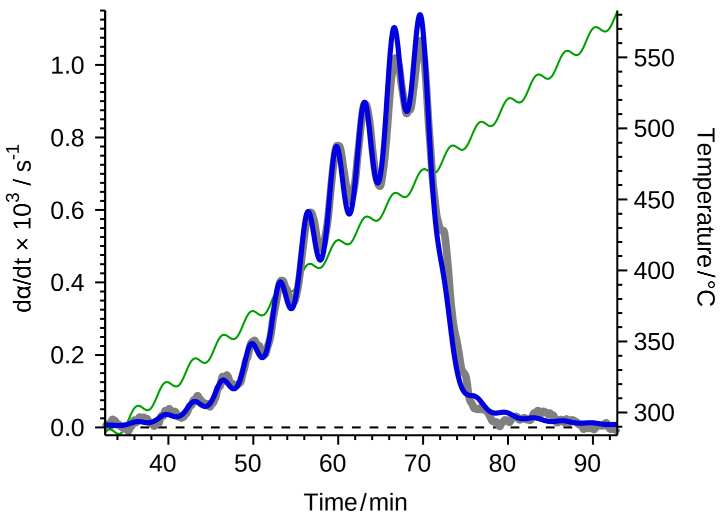
$E = 150$ kJ/mol

$\log_{10}\tilde{A}(x) = 8.2235222 - 0.481624T_1(x) - 0.166208T_2(x) - 0.311307T_3(x) - 0.230806T_4(x) - 0.194783T_5(x) - 0.096607T_6(x) - 0.086906T_7(x) - 0.03685T_8(x) - 0.02896T_9(x)$

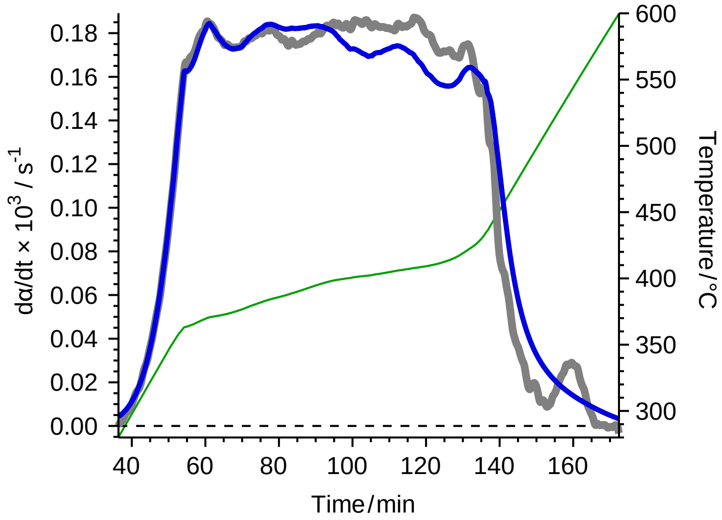
(Input file: "Rfc__8__0,9_150kJ_mol.par")



Char "Rfc-8" 10°C/min [O_2]=0.20 G_0=0.21mg
Relative deviation: 8.23%, Deviation: 0.028 µg/s
rms rel. dev. of 3 experiments: 6.14%



Char "Rfc-8" modulated T(t) (5°C/min) [O_2]=0.20 G_0=0.5mg
Relative deviation: 3.01%, Deviation: 0.016 µg/s
rms rel. dev. of 3 experiments: 6.14%



Char "Rfc-8" CRR T(t) [O_2]=0.20 G_0=0.5mg
Relative deviation: 6.03%, Deviation: 0.0056 µg/s
rms rel. dev. of 3 experiments: 6.14%

S2. Wheat Straw and Willow Samples

The experiments belong to this work:

[S2] Várhegyi, G.; Sebestyén, Z.; Czégény, Z.; Lezsovits, F.; Könczöl, S.: Combustion kinetics of biomass materials in the kinetic regime. *Energy Fuels* **2012**, *26*, 1323-1335. *doi:* 10.1021/ef201497k Supporting Info Repository

Two lignocellulosic samples, a wheat straw as an agricultural byproduct and a willow sample from an energy farm were reevaluated. The TGA experiments were carried out in gas flows of nitrogen−oxygen mixtures with 4 and 20% (v/v) oxygen. Three linear and two stepwise temperature programs were employed in each case. Altogether 20 TGA experimental was evaluated in four groups, as shown below.

S2.1. Wheat Straw in a gas flow of 4% O_2

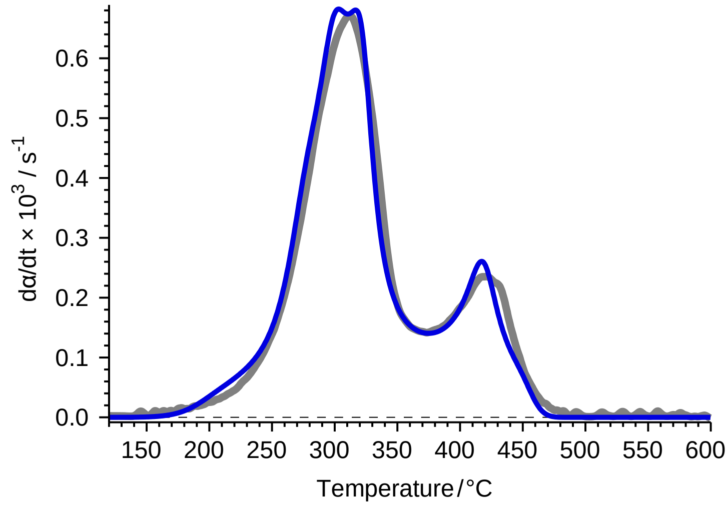
Model:

x=2α-1

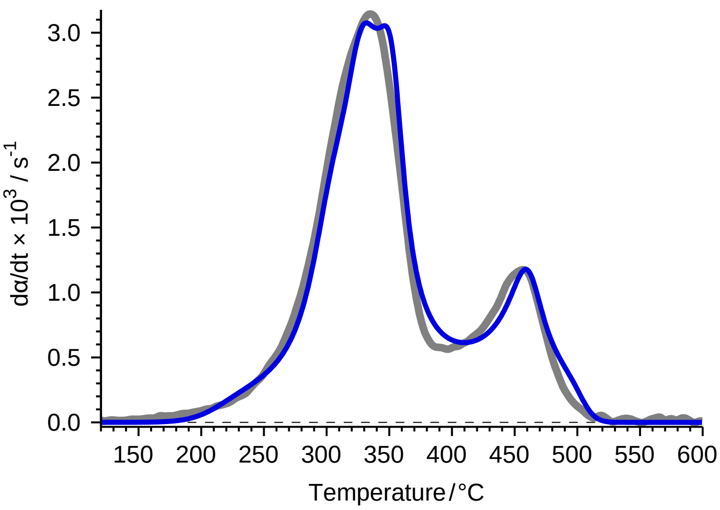
E= 153 kJ/mol

$\log_{10}\tilde{A}(x)$= 10.440113 -1.627885$T_1(x)$ -0.026341$T_2(x)$ -0.080844$T_3(x)$ +0.3494592$T_4(x)$ -0.045439$T_5(x)$ +0.0335689$T_6(x)$ -0.143619$T_7(x)$ +0.023736$T_8(x)$ +0.0174925$T_9(x)$ +0.0675341$T_{10}(x)$ +0.0201545$T_{11}(x)$

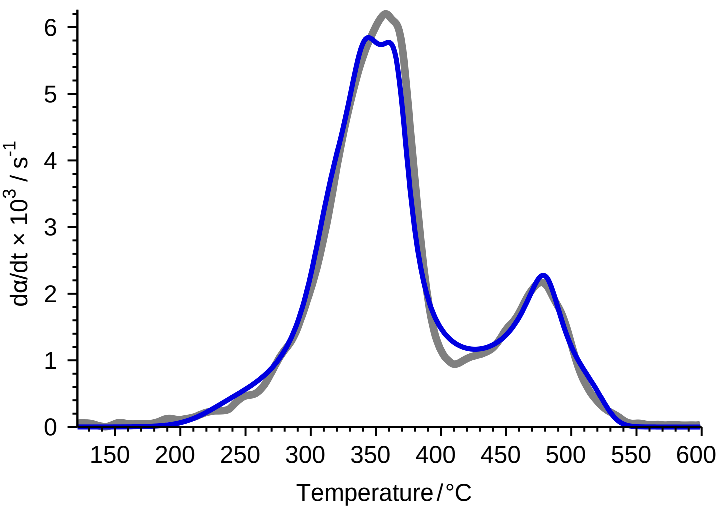
(Input file: "B_o04_0,b_153kJ_mol.par")



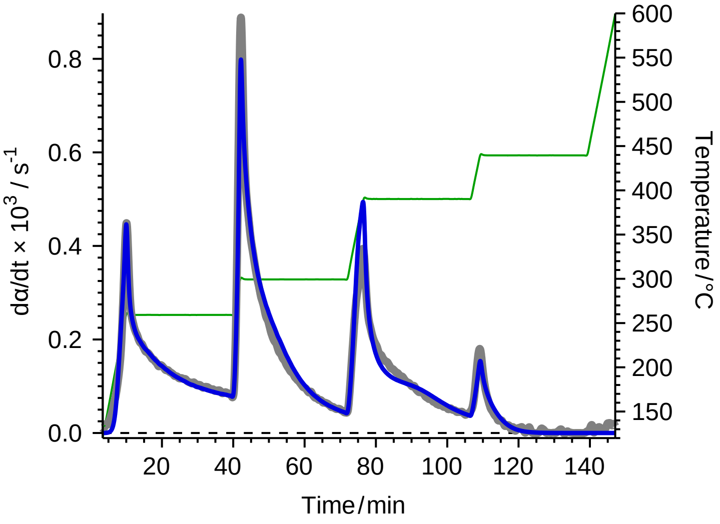
Wheat straw G_0=1.5mg 4°C/min $[O_2]$=0.04 (4.05kPa)
Relative deviation: 3.24%, Deviation: 0.030 µg/s
rms rel. dev. of 5 experiments: 3.11%



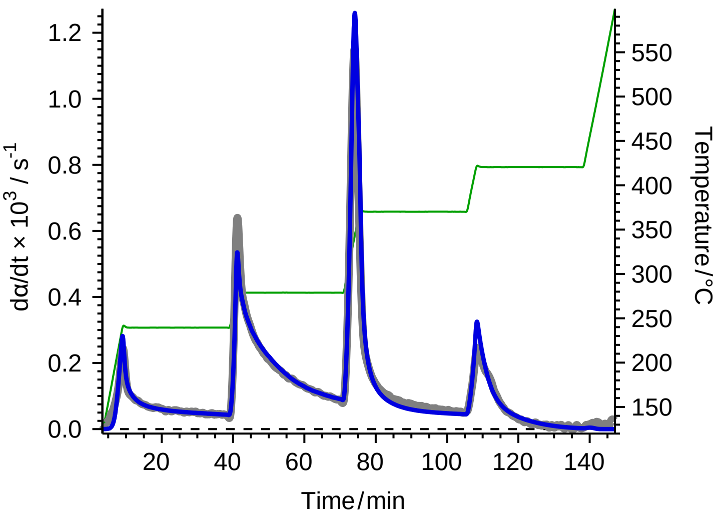
Wheat straw G_0=0.5mg 20°C/min $[O_2]$=0.04 (4.05kPa)
Relative deviation: 3.67%, Deviation: 0.055 µg/s
rms rel. dev. of 5 experiments: 3.11%



Wheat straw G_0=0.3mg 40°C/min $[O_2]$=0.04 (4.05kPa)
Relative deviation: 3.58%, Deviation: 0.055 µg/s
rms rel. dev. of 5 experiments: 3.11%



Wheat straw G_0=1.5mg stepwise T(t) 1 [O_2]=0.04 (4.05kPa)
Relative deviation: 2.32%, Deviation: 0.029 µg/s
rms rel. dev. of 5 experiments: 3.11%



Wheat straw G_0=1.5mg stepwise T(t) 2 [O_2]=0.04 (4.05kPa)
Relative deviation: 2.46%, Deviation: 0.040 µg/s
rms rel. dev. of 5 experiments: 3.11%

S2.2. Wheat Straw in a gas flow of 20% O_2

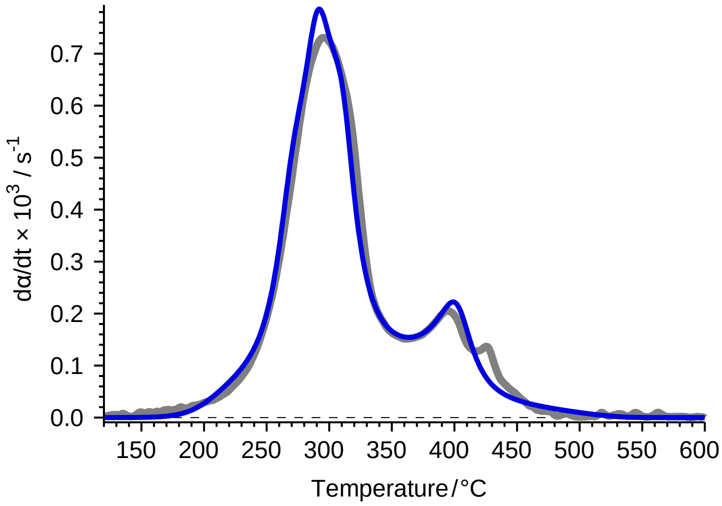
Model:

x=2α-1

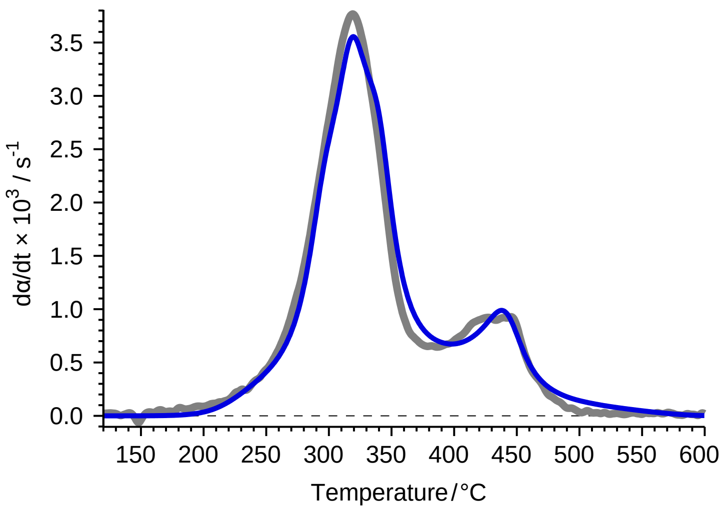
E= 153 kJ/mol

$\log_{10}\tilde{A}(x)$= 10.518558 -1.778785$T_1(x)$ -0.410628$T_2(x)$ -0.231094$T_3(x)$ +0.1042788$T_4(x)$ -0.142556$T_5(x)$ -0.07001$T_6(x)$ -0.174368$T_7(x)$ -0.031119$T_8(x)$ -0.015971$T_9(x)$ +0.0410428$T_{10}(x)$ +0.0190159$T_{11}(x)$

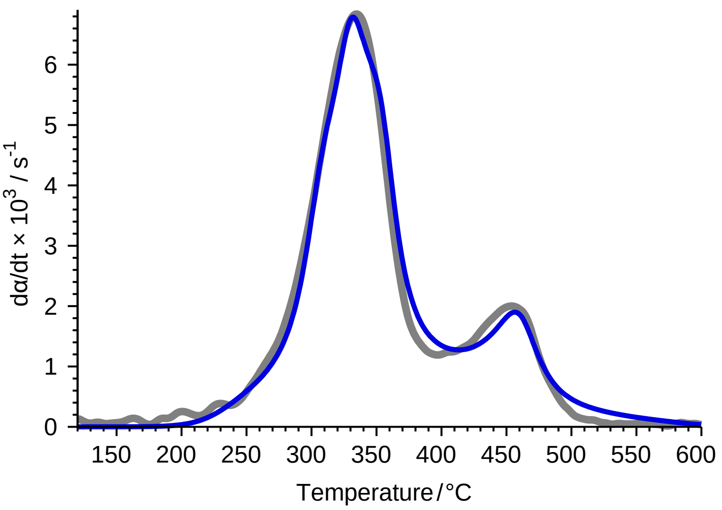
(Input file: "B_o20_0,b_153kJ_mol.par")



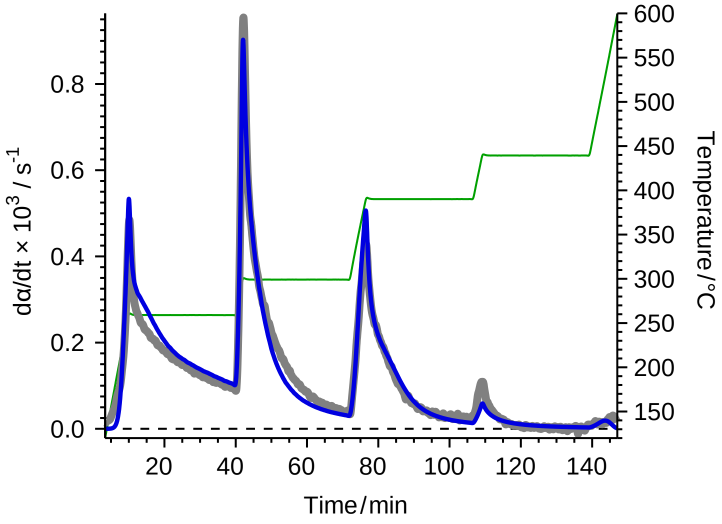
Wheat straw G_0=1.4mg 4°C/min $[O_2]$=0.2 (20.3kPa)
Relative deviation: 3.03%, Deviation: 0.029 µg/s
rms rel. dev. of 5 experiments: 3.08%



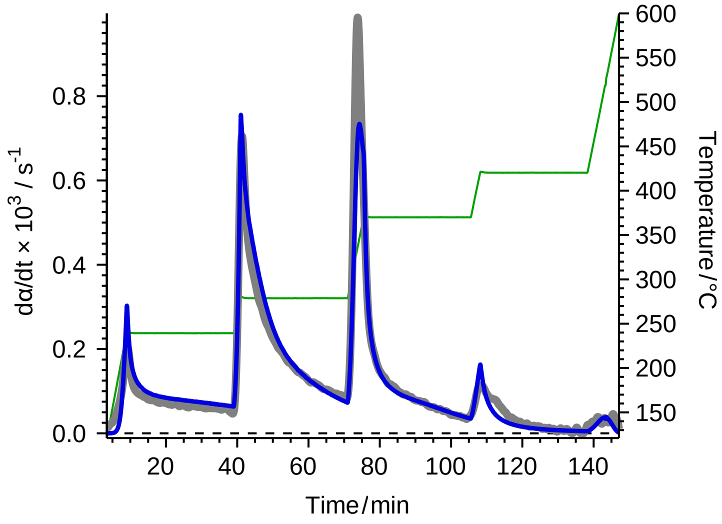
Wheat straw G_0=0.5mg 20°C/min $[O_2]$=0.2 (20.3kPa)
Relative deviation: 3.39%, Deviation: 0.060 µg/s
rms rel. dev. of 5 experiments: 3.08%



Wheat straw G_0=0.3mg 40°C/min $[O_2]$=0.2 (20.3kPa)
Relative deviation: 2.91%, Deviation: 0.047 µg/s
rms rel. dev. of 5 experiments: 3.08%



Wheat straw G_0=0.8mg stepwise T(t) 1 [O_2]=0.2 (20.3kPa)
Relative deviation: 2.39%, Deviation: 0.018 µg/s
rms rel. dev. of 5 experiments: 3.08%



Wheat straw G_0=1.2mg stepwise T(t) 2 [O_2]=0.2 (20.3kPa)
Relative deviation: 3.55%, Deviation: 0.040 µg/s
rms rel. dev. of 5 experiments: 3.08%

S2.3. Willow in a gas flow with 4% O_2

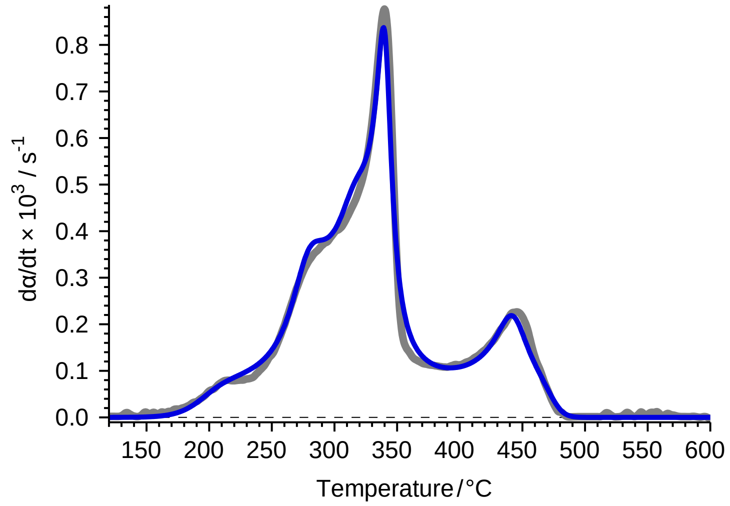
Model:

$x=2\alpha-1$

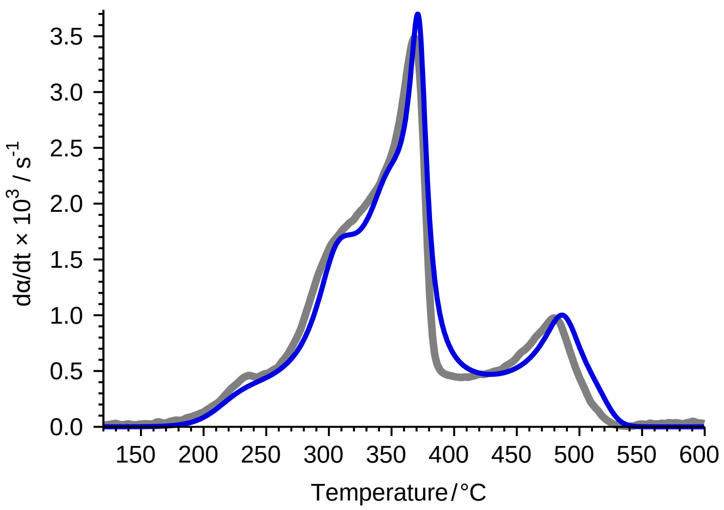
E= 153 kJ/mol

$\log_{10}\tilde{A}(x)= 10.309506 -1.805318T_1(x) +0.0990735T_2(x) -0.243139T_3(x) +0.3542406T_4(x) +0.0852029T_5(x) +0.0986523T_6(x) -0.151094T_7(x) -0.06444T_8(x) -0.000098T_9(x) +0.0381346T_{10}(x) +0.0624258T_{11}(x)$

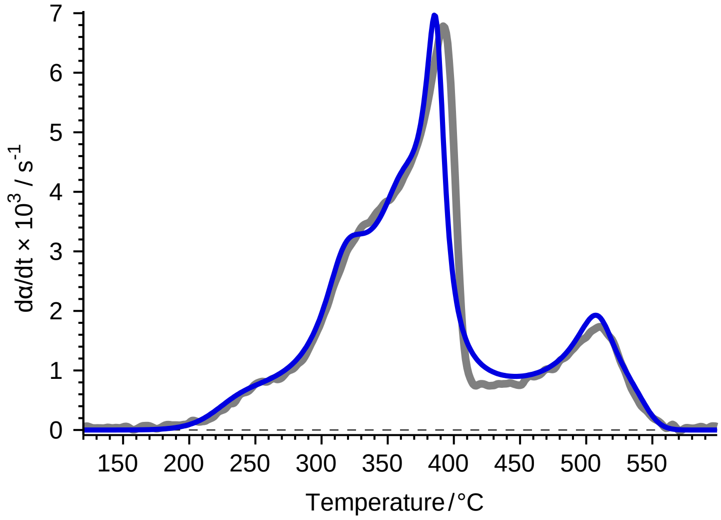
(Input file: "F_o04_0,b_153kJ_mol.par")



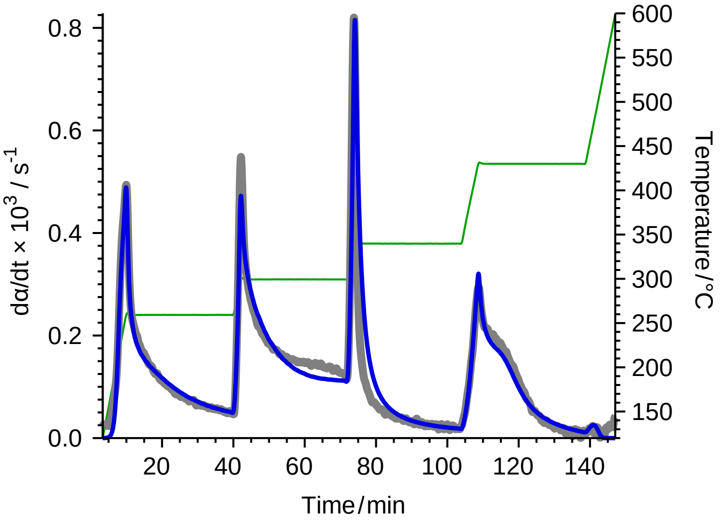
Willow G_0=1.5mg 4°C/min [O_2]=0.04 (4.05kPa)
Relative deviation: 2.21%, Deviation: 0.028 µg/s
rms rel. dev. of 5 experiments: 4.34%



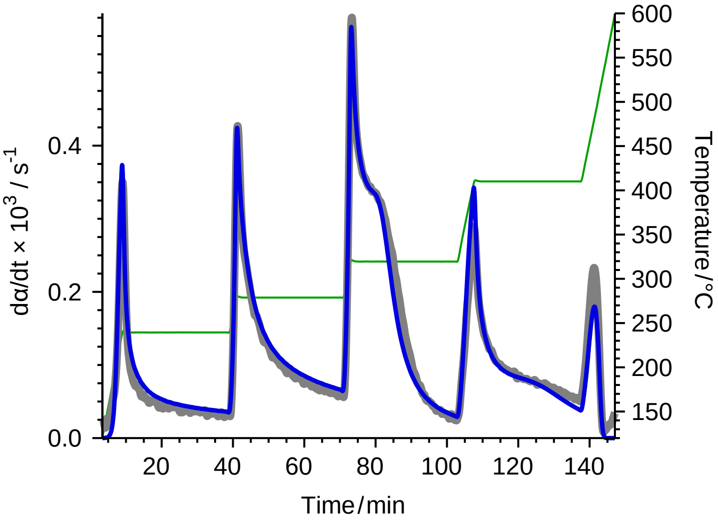
Willow G_0=0.5mg 20°C/min [O_2]=0.04 (4.05kPa)
Relative deviation: 4.87%, Deviation: 0.083 µg/s
rms rel. dev. of 5 experiments: 4.34%



Willow G_0=0.3mg 40°C/min [O_2]=0.04 (4.05kPa)
Relative deviation: 6.39%, Deviation: 0.10 µg/s
rms rel. dev. of 5 experiments: 4.34%



Willow G_0=1.5mg stepwise T(t) 1 [O_2]=0.04 (4.05kPa)
Relative deviation: 4.08%, Deviation: 0.048 µg/s
rms rel. dev. of 5 experiments: 4.34%



Willow G_0=1.5mg stepwise T(t) 2 [O_2]=0.04 (4.05kPa)
Relative deviation: 2.82%, Deviation: 0.024 µg/s
rms rel. dev. of 5 experiments: 4.34%

S2.4. Willow in a gas flow of 20% O_2

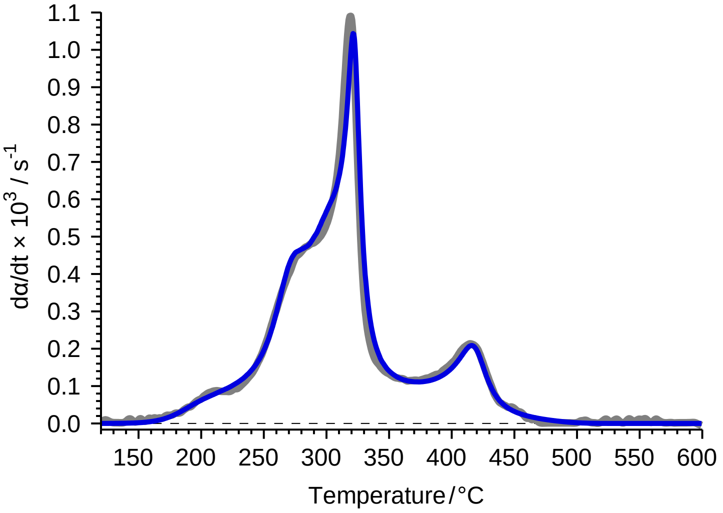
Model:

$x=2\alpha-1$

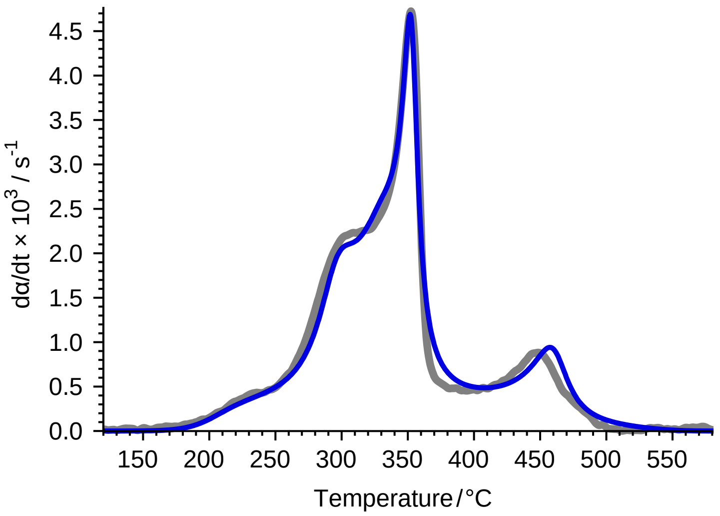
E= 153 kJ/mol

$\log_{10}\tilde{A}(x)= 10.642866 -1.807515T_1(x) -0.121268T_2(x) -0.407472T_3(x) +0.2370154T_4(x) -0.002711T_5(x) +0.0748104T_6(x) -0.210938T_7(x) -0.118066T_8(x) -0.06705T_9(x) -0.000739T_{10}(x) +0.0348312T_{11}(x)$

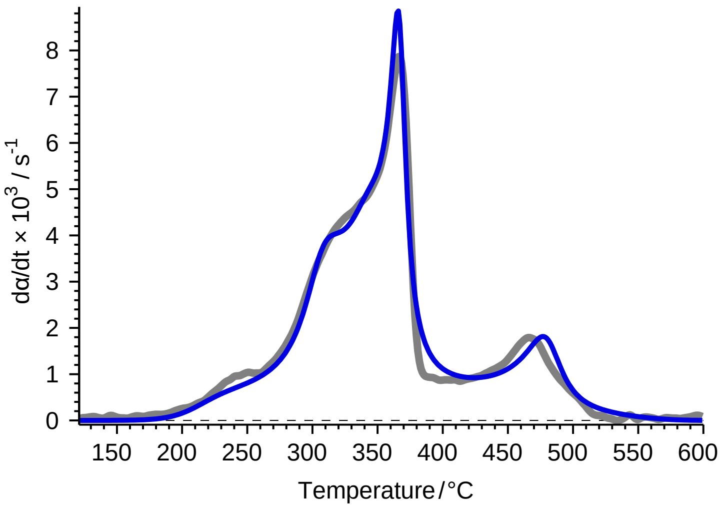
(Input file: "F_o20_0,b_153kJ_mol.par")



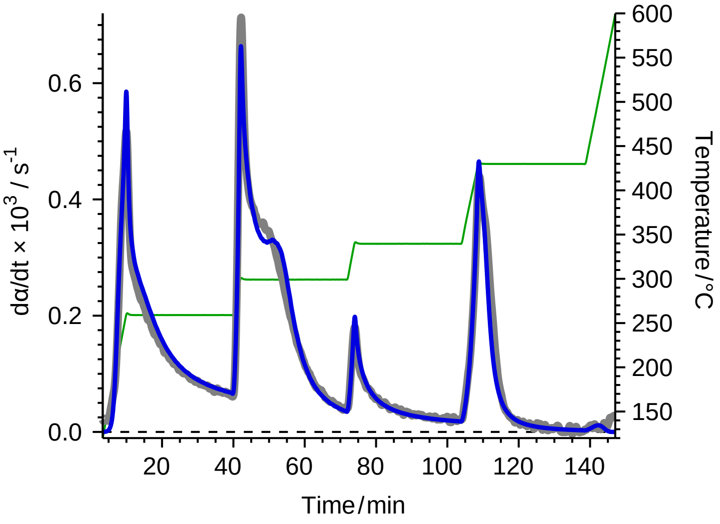
Willow G_0=1.4mg 4°C/min $[O_2]$=0.2 (20.3kPa)
Relative deviation: 2.54%, Deviation: 0.038 µg/s
rms rel. dev. of 5 experiments: 2.62%



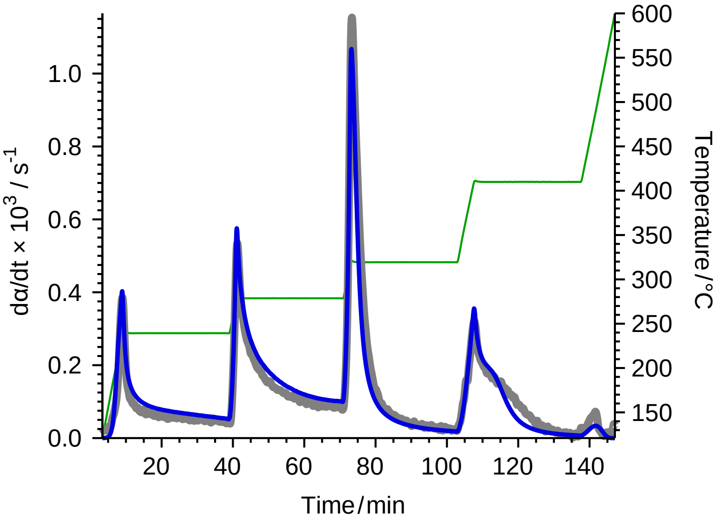
Willow G_0=0.3mg 20°C/min $[O_2]$=0.2 (20.3kPa)
Relative deviation: 2.54%, Deviation: 0.036 µg/s
rms rel. dev. of 5 experiments: 2.62%



Willow G_0=0.3mg 40°C/min $[O_2]$=0.2 (20.3kPa)
Relative deviation: 3.06%, Deviation: 0.061 µg/s
rms rel. dev. of 5 experiments: 2.62%



Willow G_0=1.5mg stepwise T(t) 1 $[O_2]$=0.2 (20.3kPa)
Relative deviation: 2.31%, Deviation: 0.025 µg/s
rms rel. dev. of 5 experiments: 2.62%



Willow G_0=1.5mg stepwise T(t) 2 $[O_2]$=0.2 (20.3kPa)
Relative deviation: 2.61%, Deviation: 0.045 µg/s
rms rel. dev. of 5 experiments: 2.62%