Supplementary Information for Article

Kinetics of the CO₂ gasification of woods, torrefied woods, and wood chars. Least squares evaluations by empirical models.

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Contents

1. Common *E* and common *f(X)* for the birch and spruce samples – Figures about the fit quality

All evaluated experiments on all samples were described by the same *E* and *f(X)* in evaluation *[1 f(X); 1 E]*, as outlined in Section 3.4 of the paper. Herewith the obtained fit quality is illustrated by figures. For a comparison, the corresponding curves from evaluations *[8 f(X); 2 E]* are also displayed.

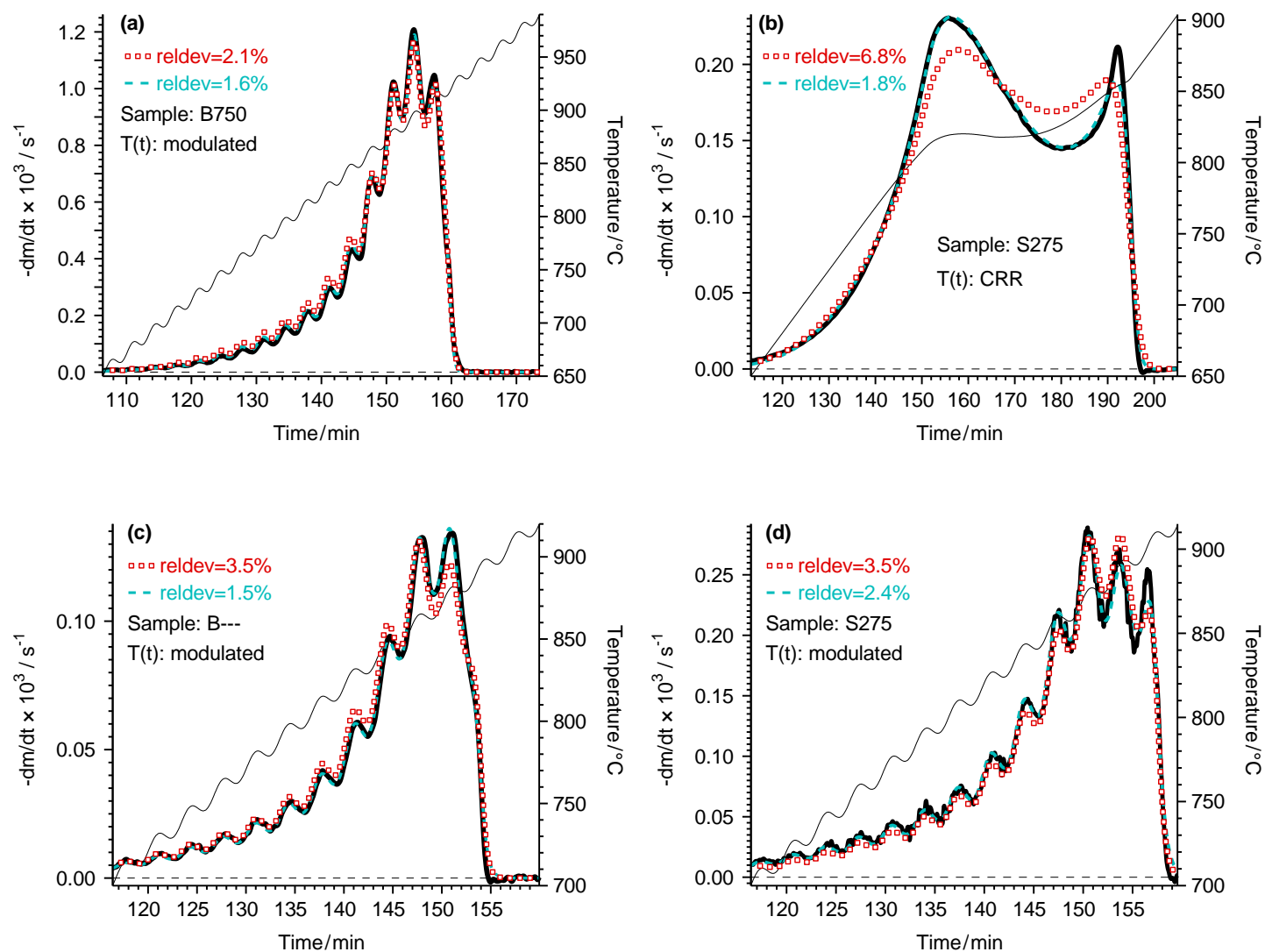**Figure S1.** The best, the worst and a typical fit quality are shown for evaluation *[1 f(X); 1 E]*. For a comparison, the corresponding results from the *[8 f(X); 2 E]* evaluations are also displayed. Notation: Thick solid lines: $(-dm/dt)^{obs}$; thin solid line, when present: $T(t)$; red squares and cyan colored dashed lines: $(-dm/dt)^{calc}$ curves for evaluations *[1 f(X); 1 E]* and *[8 f(X); 2 E]*, respectively.

2. Effects of the temperature programs of the TGA experiments on the reactivity of the chars

As outlined above, evaluation *[1 f(X); 1 E]* describes all experiments for all samples with a common E value and a common $f(X)$. Accordingly, the reactivity differences caused by the pretreatments and the TGA temperature programs are reflected only by the values of the preexponential factors in this approximation. Table S1 displays these preexponential factors. The first column indicates the pretreatment of the samples, where 225 and 275 °C are the temperatures of torrefaction while 750 °C is the temperature of the carbonization, as described in Section 2.1 of the paper. The second column refer to the $T(t)$ temperature programs that were employed in the TGA experiments. Those temperature programs are shown in Table S1 which were employed for all samples. Two further temperature programs are discussed in the next section.

It is worth to observe that the preexponential factors for the modulated and CRR experiments are smaller than those at 20 °C/min heating rate for both feedstocks at each pretreatment. The corresponding differences are denoted by $\Delta\log_{10}A$ in Table 2. The reason is the well-known thermal deactivation (annealing) of the chars that occurs at high temperatures [S1-S2]. At slower heating programs more time is available for the advance of this slow char transformation. Note that the base heating rate of the modulated experiments was 5 °C/min. The $T(t)$ functions of the CRR experiments are usually irregular; the mean dT/dt in the domain of gasification varied between 2.5 and 4.4 °C/min [S3].

Table S1. Preexponential Factors Determined in Evaluation *[1 f(X); 1 E]*

Pre-treatment	$T(t)$	Birch $\log_{10}A$	$\Delta\log_{10}A$	Spruce $\log_{10}A$	$\Delta\log_{10}A$	$\log_{10}A_{spruce} - \log_{10}A_{birch}$
none	20 °C/min	10.43		10.42		*-0.01*
	modulated	10.24	*-0.19*	10.30	*-0.12*	*0.06*
	CRR	10.24	*-0.19*	10.26	*-0.16*	*0.02*
225 °C	20 °C/min	10.29		10.38		*0.09*
	modulated	10.24	*-0.05*	10.23	*-0.15*	*-0.01*
	CRR	10.17	*-0.13*	10.21	*-0.17*	*0.04*
275 °C	20 °C/min	10.06		10.21		*0.14*
	modulated	10.01	*-0.05*	10.07	*-0.14*	*0.06*
	CRR	9.95	*-0.11*	10.09	*-0.11*	*0.14*
750 °C	20 °C/min	10.00		10.17		*0.18*
	modulated	9.93	*-0.07*	10.11	*-0.07*	*0.18*
	CRR	9.88	*-0.12*	10.12	*-0.05*	*0.25*

Three heating programs are shown here for each sample. The dimension of A is s⁻¹. $\Delta\log_{10}A$ is the difference of the values obtained for modulated or CRR heating and at 20°C/min for each sample. The last column displays the difference between the $\log_{10}A$ values belonging to the spruce and the birch feedstock.

3. Effect of the heating rate of the TGA experiments below 700 °C

As outlined in Section 2.1 of the paper, special TGA experiments were carried out to study the effect of the heating rate below 700 °C on the gasification of the formed chars in the work of Wang et al [S3]. These special experiments were evaluated together with the other experiments in the same least squares procedures. The corresponding $\log_{10} A$ values from evaluation *[1 f(X); 1 E]* are presented in Table 2, below. The values belonging to the regular 20 °C/min experiments are also displayed for comparison. As the data show, a heating rate of 2 °C/min instead of 20 °C/min below 700 °C has only negligible effect on the gasification reactivity. On the other hand, the high heating rate on the untreated woods considerably increased the reactivity. This is in accord with numerous previous works which proved that the chars forming at high heating rates from biomass are more reactive than the ones forming at slower heating [S4-S6]. However, the high heating rate did not affect the reactivity of samples B275 and S275 in our experiments: the corresponding $\Delta\log_{10} A$ differences are near to zero in Table 3. Note that the torrefaction procedure employed in our works consumes the hemicellulose content of the wood at 275 °C while leaves most of the cellulose intact [S7-S8].

Table S2. Effect of the heating rate below 700 °C on the reactivity at 20 °C/min above 700 °C

Pre-treatment	Heating rate below 700°C	Birch $\log_{10} A$	$\Delta\log_{10} A$	Spruce $\log_{10} A$	$\Delta\log_{10} A$	$\log_{10} A_{\text{spruce}} - \log_{10} A_{\text{birch}}$
none	20 °C/min	10.43		10.42		*-0.01*
	2 °C/min	10.43	*0.00*	10.41	*-0.01*	*-0.02*
	≈1400 °C/min	10.58	*0.15*	10.60	*0.19*	*0.03*
275 °C	20 °C/min	10.06		10.21		*0.14*
	2 °C/min	10.07	*0.01*	10.20	*-0.01*	*0.13*
	≈1400 °C/min	10.04	*-0.02*	10.21	*0.00*	*0.17*

See the footnote of Table 2 for explanations.

4. About the *f(X)* functions and their determination

4.1. Equations

The kinetic equation belonging to the models of this work was

$$dX/dt = \exp[p(X) - \frac{E}{RT}]\,(1\text{-}X) \tag{S1}$$

Here *p(X)* is a polynomial, and its coefficients are parameters to be determined:

$$p(X) = a_0 + a_1 X + a_2 X^2 + \; ... \; a_n X^7 \tag{S2}$$

The term (1-*X*) ensures that *dX/dt* is zero at *X*=1 for any polynomial coefficients.

If Eq. S1 is rearranged to the form

$$dX/dt = A\,f(X)\,\exp(-\frac{E}{RT}) \tag{S3}$$

we get

$$A\,f(X) = e^{p(X)}\,(1\text{-}X) \tag{S4}$$

*A f(X)*t can be factorized into an *A* value and an *f(X)* function by a normalization of *f(X)*. A simple and plausible normalization is to ensure that *f(X)* be 1 at *X*=0. The condition *f(0)*=1 is satisfied if

$$f(X) = e^{p(X) - p(0)}\,(1\text{-}X) \tag{S5}$$

hence

$$A = e^{p(0)} \tag{S6}$$

4.2. Improving the numerical properties of the model by simple transformations

Polynomials can be expressed in different ways [S9]. We selected such transformations that facilitate the determination of the polynomials without substantial changes in our decades-old least squares software. The procedure was described in Reference [S10]; herewith it is explained briefly as follows.

Seventh order polynomials were used in the present work. Their coefficients were determined by optimizing the fit between the experimental and measured data. *X* varies between 0 and 1. In this interval the higher powers of *X* are similar to each other, and their coefficients can highly compensate each other. For example, X^6 can be approximated well by a linear combination of X^5 and X^7. The situation is illustrated by Figure S2 which shows the powers of *X* as well as an approximation of X^6 by a linear combination of X^5 and X^7. The possibility of such compensations causes severe technical problems during the determination of the corresponding polynomial coefficients. The problem can easily be mitigated by expressing *p(X)* by Chebyshev polynomials of the second kind [S9]. Note that only the insertion of a few simple programming lines is needed for that purpose. The Chebyshev polynomials are very different from each other in interval [-1, 1] as Fig. S3 shows, hence their coefficients cannot compensate each other. Obviously variable *X* has to be mapped to the [-1,1] interval for the work with Chebyshev polynomials of the second kind. I.e., a variable *x* is introduced that varies from -1 to 1 as the reaction proceeds:

$$x = 2X - 1 \tag{S7}$$

p(x) is expressed as:

$$p(x) = b_0 + b_1 T_1(x) + b_2 T_2(x) + \; ... \; + b_7 T_7(x) \tag{S8}$$

Coefficients b_0, b_1 … b_7 are determined by the method of least squares together with the energy of activation. There is no need to transform back the obtained $p(x)$ to a polynomial expressed by the powers of X because the actual calculations by Eq. S8 are easy and fast.

Equations S5 and S6 have the following form when expressed as function of x:

$$f(x) = e^{p(x)-p(-1)}(1-x)/2 \tag{S9}$$

$$A = e^{p(-1)} \tag{S10}$$

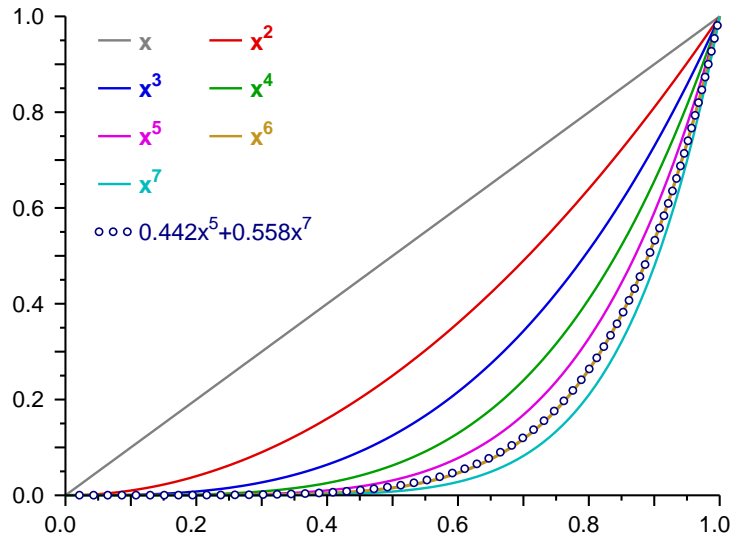**Fig. S2.** The solid lines denote X, X^2, … X^7. The circles represent an approximation of X^6 by a linear combination of X^5 and X^7.
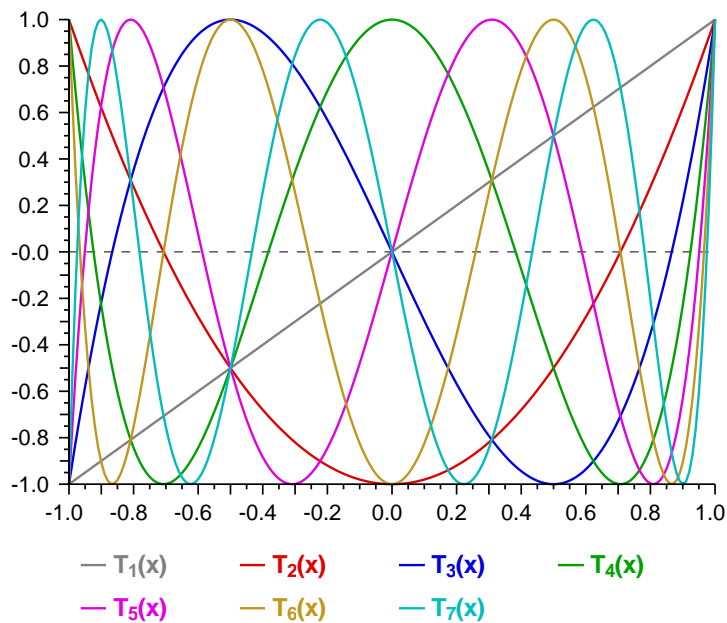

Fig. S3. Chebyshev polynomials of the first kind: $T_1(x)$, $T_2(x)$, … $T_7(x)$

As mentioned above, there is no need to know the actual forms of polynomials $T_1(x)$, $T_2(x)$, … $T_7(x)$ for the work with them because their values can be calculated easily by recurrence formulas: [S9]

$$T_0 = 1 \tag{S11}$$

$$T_1 = x \tag{S12}$$

4. About the f(X) functions and their determination

$$T_2 = 2xT_1 - T_0 \tag{S13}$$

…

$$T_n = 2xT_{n-1} - T_{n-2} \tag{S14}$$

4.3. Handling the compensation effects between the activation energy and the other parameters

The compensation effects between the parameters can hinder the convergence of the numerical minimization software in the least squares evaluations. For example: if a given parameter is changed a bit during the search for the optimum, other parameters can more or less compensate the effects of this change, as it was illustrated in Fig. S2 above. The problems caused by the kinetic compensation effect between E and $\ln A$ are well known for decades and can be mitigated by simple parameter transformations [S11]. However, other model parameters can also contribute to the compensation of a change in an E value, as outlined in the present paper. The numerical problems caused by the compensation effects between E and the other parameters can be avoided if the calculations are carried out on a grid of fixed E values. If E is a fixed value in a least-squares minimization, then, obviously, the compensation effects between E and the rest of the parameters cannot appear within that minimization. [S6]. Afterwards we select the E at which the fit quality is the best. One can refine the grid of fixed E values around the optimum found, if needed. However, the integer E values proved to be sufficiently precise for our work; a refinement to more significant digits caused only negligible changes in the fit quality. See Section 3.4 in Reference [S6] for further details and its Fig. 7 for a graphical illustration.

4.4. The mathematical formula for the f(X) function obtained by evaluation [1 f(X); 1 E]

According to Eq. S9, $f(x) = e^{p(x)-p(-1)}(1-x)/2$. Evaluation *[1 f(X); 1 E]* resulted in the following expression for the terms in the exponent:

$$p(x) - p(-1) = 0.0713 + 0.8582T_1(x) + 0.5785T_2(x) + 0.0445T_3(x) +$$
$$0.249T_4(x) + 0.0345T_5(x) + 0.0398T_6(x) + 0.0014T_7(x) \tag{S15}$$

Here the first term on the right-hand side, 0.0713, is not a parameter: it can be directly calculated from the coefficients of the $T_1(x)$, $T_2(x)$, ... $T_7(x)$ polynomials because Eq. S15 is zero at $x=-1$.

Equations S8 and S15 can easily be "economized" by omitting the terms with small coefficients [S9]. $T_7(x)$ varies between -1 and 1 (as shown in Figure S3), hence the error caused by the omission of the last term in Eq. S7 is only 0.0014. This is much smaller than the error of the truncation of the same polynomial expressed by the powers of X [S9]. This type of economizations has only negligible advantages in our work because the truncation of Eq. S15 would save only negligible computing time (a few arithmetic operations in Eq. 14). However, the small coefficient of $T_7(x)$ indicates that the coefficients of the higher order terms become negligible when they are not needed. This is in accordance with our earlier experience with this type of modelling [S12].

As described in the paper, a common *f(X)* function was determined for the evaluated experiments in each evaluation and the preexponential factors expressed the reactivity differences. During the evaluations it was achieved by assuming common b_1, b_2, … b_7 values in Eq. S8 for all evaluated experiments while coefficient b_0 was allowed to vary from experiment to experiment. At the end of the least squares evaluation the common $f(x)$ and the different A values were determined by Eqs. S9 and S10. Tables S1 and S2 lists the decimal logarithms of the A values obtained in the *[1 f(X); 1 E]* evaluation.

4.5. Calculations of the c coefficients in Eq. (5) of the paper

The *c* coefficients were defined in the paper as

$$(-dm/dt)^{\text{calc}} = c \, (dX/dt)^{\text{calc}} \tag{S16}$$

Eq. (S16) corresponds to a simple linear regression without the intercept term which can be solved by the following formula [S13]:

$$c = \frac{\sum_i^M (-dm/dt)_i (dX/dt)_i}{\sum_i^M (dX/dt)_i^2} \tag{S17}$$

where *M* is the number of points available in digital form for the given experiment.

4. About the f(X) functions and their determination

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