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Empirical Models with Constant and Variable Activation Energy for Biomass Pyrolysis

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S *Supporting Information*

ABSTRACT: The so-called "model-free" or isoconversional way of kinetic modeling was examined. In this field, the available evaluation methods do not aim at an optimal fit for the experimental data. In the present work, the functions of the corresponding kinetic equation were approximated by simple versatile formulas, the number of the unknown parameters was kept on reasonably low levels, and the evaluation aimed at the best fit for the experiments by the least-squares method. Considerations and methods were tested on 85 thermogravimetric (TGA) experiments, which had been published earlier with different types of kinetic modeling. The experiments belonged to 16 biomass samples including woody biomass, agricultural residues, and industrial wastes. The temperature programs comprised constant heating rates, stepwise heating, constant reaction rate heating, isothermal temperature programs, and a modulated temperature program. The evaluations were based on four to nine experiments for each sample. The best fit was searched for the mass loss rate curves because they reflect well the peculiarities of pyrolysis. An empirical model with variable activation energy provided good fit for all experimental data. It described the experiments of a biomass sample by 11 parameters. Another model with constant E values provided rougher but still usable approximations for the data. It allows fast numerical solutions that may be helpful in complex modeling tasks. Both models described the experiments at a variety of temperature programs by a given set of model parameters.

1. INTRODUCTION

The kinetics of biomass pyrolysis is usually based on models that are built of equations

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

where α is a reacted fraction (conversion), E is the apparent activation energy, A is the pre-exponential factor, and $f(\alpha)$ is an appropriate function. Obviously, more than one such equation is needed when the model reflects the complexity of biomass pyrolysis reactions. In such cases, α refers only to a part of the sample. If distributed activation energy models are employed, then an infinite number of reactions are assumed with an infinite number of α conversions.

An entirely different approach is when only one equation is assumed, with varying E and A

$$d\alpha/dt = A(\alpha)f(\alpha) \exp(-E(\alpha)/RT) \tag{2}$$

where $A(\alpha)$, $f(\alpha)$, and $E(\alpha)$ are empirical functions. Obviously, only the product of $A(\alpha)$ and $f(\alpha)$ can be determined from the experimental data. More precisely, an empirical $[A(\alpha)f(\alpha)]$ function can be factored to an $A(\alpha)$ and $f(\alpha)$ part in an infinite number of ways.

For historical reason, the kinetic evaluations by eq 2 are frequently called "model-free" methods. This term is misleading because eq 2 itself is a model.[1] It is more precise to call eq 2 "isoconversional", which means that the reaction rate $d\alpha/dt$ is a function of temperature only at any selected α value and does not depend on the temperature history that led to a given (α, T) point.[1] This definition and eq 2 itself can only be approximately true for biomass materials because they have complicated reactions, and the temperature history may affect

the importance of various partial reactions in the overall decomposition.

The literature of "model-free" or isoconversional evaluations is huge. About 4000 scientific papers contain the characteristic terms of these methods in the Web of Science database.[2] The present paper is restricted to the kinetic studies on biomass pyrolysis, where the isoconversional methods have been present for nearly 40 years.[3] According to Web of Science, more isoconversional evaluations are reported in the literature of biomass pyrolysis than all other methods combined. A recent review and case study deals with the isoconversional kinetics of lignocellulosic materials.[4] Its treatment includes a concise description of the most important evaluation techniques emphasizing their advantages and disadvantages and giving ample references from 1956 until the present.

Equation 2 is usually employed for thermogravimetric (TGA) and differential scanning calorimetric (DSC) experiments. Nevertheless, it may be employed for any experimental technique that provides the reacted fraction/conversion of either the whole sample or a given species, while the temperature of the sample is measured with an adequate precision. (Here, the term "adequate" depends obviously on the sensitivity of the model and the evaluation method to the experimental errors.)

Several factors led to the writing of the present work. One of them was that I see questions and problems with this type of research, as outlined below. Another factor was the high

number of the publications with isoconversional kinetics; I wished to contribute to the analysis of their reliability. Besides, the potential of eq 2 as a relatively simple empirical model is also interesting.[5−8]

One of the open questions with the isoconversional evaluations is the high number of the parameters, which are derived from a few rather similar TGA curves. Though there are evaluation methods that can be carried out at any $T(t)$ temperature programs,[1,4] practically all studies in the field are based on constant heating rate experiments only. The Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommends carrying out the evaluation at 9−19 fixed α values: "It is recommended to determine the E_α values in a wide range of $\alpha = 0.05−0.95$ with a step not larger than 0.05 and to report the resulting dependencies of E_α versus α."[1] (Here, E_α is a shorthand for $E(\alpha)$.) Keeping in mind that there is a $[A(\alpha)f(\alpha)]$ value for each E_α, the total number of the unknown parameters in a typical isoconversional evaluation is 9×2 to 19×2. However, a higher number of unknown parameters are also determined in the isoconversional studies. For example, Samuelsson et al. determined 23×2 parameters from 10 constant heating rates experiments,[5] while Carrier et al. presented $E − \alpha$ figures with 41 E_α values using four heating rates.[9] Naqvi et al. presented 39×2 parameters in a detailed table that were determined from three constant heating rate experiments.[10]

During my work in various teams for 30 years, we realized that the simultaneous evaluation of linear and nonlinear temperature programs increases the information of the series of TGA experiments,[11−17] and kinetic models with 12−13 adjustable parameters were sufficient for fitting such series of experiments by the least-squares method for pyrolysis of a wide variation of biomass samples.[13,14,16,17] (Models assuming pseudo-components and parallel reactions were employed in these works.) Moreover, the number of parameters could be decreased further by assuming partly common kinetic parameters for different biomass samples.[14−17] Here, questions arise: If 13 parameters are enough for a good fit, then why should anyone determine 19×2 or 39×2 parameters? Are the obtained parameters just redundant or do they serve to average out the experimental errors in their further processing? In the latter case, why is a true least-squares evaluation not chosen to average out the experimental errors via curve fitting?

Another question is the large variation of activation energies in the literature of isoconversional studies. In the case of biomass pyrolysis kinetics, E_α values as high as 1070 and 1327 kJ/mol were reported.[18,10] Unrealistically low E_α values also arose, for example, 10−12 kJ/mol.[10,19] (We shall turn back to the meaning of the term "unrealistic E" in the article.) Several causes may be assumed here, among others: (i) eq 2 is not suitable for the description of the given pyrolysis process with realistic E_α values; (ii) the evaluation method is too sensitive to the experimental errors; (iii) eq 2 itself is ill-conditioned, meaning that a small error in the initial data can result in much larger errors in the results, whatever evaluation method is employed. The present work aims at the clarification of the above questions.

The available "model-free" evaluation methods appear to be arbitrary and sensitive to the experimental errors. Here, the term "arbitrary" means that their elaboration aimed at relatively simple procedures instead of finding the best fit between the predicted values and observed data. I think that there is no need for such simplifications in the 21st century

due to the high development of computers and computing methods. In other areas of sciences, the usual way of the evaluation is to find the best fit between the predicted and observed data by the least-squares method. The use of this approach for isoconversional evaluations is the main goal in the present work.

2. SAMPLES AND METHODS

2.1. Samples and Experiments. The considerations of the present work were tested by evaluating TGA experiments that had been evaluated earlier by other models and appeared in six publications in *Energy & Fuels*.[12−17] Eighty-five TGA experiments were re-evaluated in the present paper. They belonged to 16 biomass samples, which comprised woody biomasses,[12,16,17] agricultural residues,[14,15] and industrial wastes.[13] The temperature programs included constant heating rates, stepwise heating, constant reaction rate heating (CRR), isothermal temperature programs, and a modulated temperature program. There were four to nine experiments for each biomass sample. The list of the samples and TGA experiments belonging to them is given in Section 4.3. Figure 1
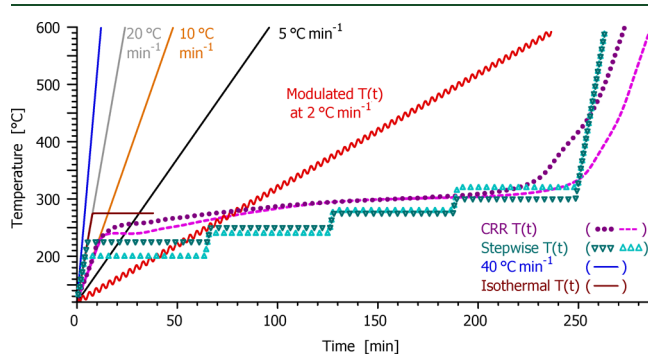
Figure 1. Temperature programs used in the TGA experiments of Tapasvi et al.[16]

displays the temperature programs employed in the work of Tapasvi et al.[16] The corresponding figures for the other samples are given in the Supporting Information. Four different TGA apparatuses were involved in the studies. Emphasis was given to ensure a true kinetic regime by employing small sample masses and considering that very small sample masses are needed at higher heating rates (because the peak height of mass loss rate curves is roughly proportional to the heating rate).[12−17]

2.2. Evaluation by Least-Squares Method and Characterization of Fit Quality. Such values were searched for the unknown model parameters that minimize the difference between the experimental (X^{obs}) and the predicted (X^{calc}) data

$$of = \sum_{j=1}^{N_{exper}} \sum_{i=1}^{N_j} w_j [X_j^{obs}(t_i) - X_j^{calc}(t_i)]^2 \tag{3}$$

where of is the objective function to be minimized, N_{exper} is the number of experiments evaluated together, N_j is the number of t_i time values in experiment j, and w_j is the weight factor expressing the different uncertainties of different experimental curves. In the case of TGA experiments, eq 3 may aim at an optimal fit either on the normalized sample mass $m^{obs}(t)$ or on its derivative. The latter is more characteristic for biomass pyrolysis; we fitted the $-dm^{obs}/dt$ curves in nearly all of our works since 1989.[20] In this case, the objective function is

$$of = \sum_{j=1}^{N_{exper}} \sum_{i=1}^{N_j} \frac{\left[\left(\frac{dm}{dt}\right)_j^{obs}(t_i) - \left(\frac{dm}{dt}\right)_j^{calc}(t_i)\right]^2}{N_j h_j^2} \tag{4}$$

where m is the sample mass normalized by the initial dry sample mass. The division by h_j^2 serves to counterbalance the high magnitude differences. Traditionally, h_j is the highest observed value of the given experiment

$$h_j = \max\left(\frac{dm}{dt}\right)_j^{obs} \qquad (5)$$

The normalization by the highest observed values in the least-squares sum assumes implicitly that the relative precision is roughly the same for different experiments. This assumption has proved to be useful in numerous works on nonisothermal kinetics since 1993.[21]

The obtained fit quality can be characterized separately for each of the experiments evaluated together. For this purpose, the relative deviation (reldev, %) will be used. The root-mean-square (rms) difference between the observed and calculated values is expressed as percent of peak maximum. For experiment j, we get

$$\text{reldev (\%)} = 100 \left\{ \sum_{i=1}^{N_j} \frac{\left[\left(\frac{dm}{dt}\right)_j^{obs}(t_i) - \left(\frac{dm}{dt}\right)_j^{calc}(t_i)\right]^2}{N_j h_j^2} \right\}^{0.5} \qquad (6)$$

The fit quality for a given group of experiments is characterized by the root mean square of the corresponding relative deviations. For example, the root-mean-square reldev on all 85 experiments of this study is denoted by reldev_{85}.

Section 5 deals with the least-squares curve fitting for other experimental quantities.

2.3. Computational Methods. Simple but safe numerical methods were selected similarly to our previous works.[11−17,20−22] The experimental temperature values were connected by linear interpolation, and the kinetic differential equation (eq 2) was solved by an adaptive stepwise Runge−Kutta method[23] for each experiment in each $[t_{i-1}, t_i]$ interval. (The forms of the $E(\alpha)$ and $A(\alpha)f(\alpha)$ functions considered in this work are shown in Sections 3.1 and 3.2.)

The minimization of the objective function was carried out by a variant of the Hook−Jeeves method. The Hook−Jeeves method is a slow but simple and dependable direct search algorithm.[24] The original algorithm was supplemented by a parabolic interpolation to find the optimal step sizes. The safety and speed of the convergence were enhanced by simple parameter transformations, which are outlined after the setup of the model in Section 3.2. The scaling of the parameters to similar magnitudes may also be helpful in the direct search method. The Supporting Information contains 32 sets of model parameters that an interested reader may use in his/her own calculations as initial values. It is also possible to start the optimization from the results of a plain first-order kinetic evaluation.

The experimental $-dm/dt$ values were obtained by approximating the measured $m(t)$ values by smoothing splines.[25] The root-mean-square difference between the original $m(t)$ and smoothing spline was typically around 0.1 μg. Such a small difference does not introduce considerable systematic errors into the least-squares kinetic evaluations.[22]

Fortran 2003 and C++ programs were used for numerical calculations and graphics handling, respectively.

2.4. Automation. The present work was based on around 1000 least-squares evaluations of which 556 proved to be useful for the tables and figures of this article and its Supporting Information. Sixteen experimental series were evaluated in 34 ways, as described in Section 4, and a few additional evaluations were needed in Section 5. Obviously, some automation was needed for so many evaluations. The calculations were organized by batch files. The user dialogues of the evaluation programs were recorded in text files, which were read together with the experimental data by the programs at each evaluation. The evaluation programs generated several thousands of graphical and textual output files that were collected and arranged by small script programs so that they could be surveyed within reasonable amounts of time.

3. EMPIRICAL FUNCTIONS FOR MODELING

3.1. Formulation. As outlined in Introduction, the $E(\alpha)$ and $A(\alpha)f(\alpha)$ functions are approximated by simple formulas so that the resulting empirical model would contain only a limited number of parameters and the evaluation could be carried out by the least-squares method. This is the topic of the present section.

$E(\alpha)$ and $A(\alpha)f(\alpha)$ can be arbitrary functions with positive values in the domain $0 \leq \alpha < 1$ in eq 2. $A(\alpha)f(\alpha)$ must be zero at $\alpha = 1$ because only a zero value ensures mathematically the termination of the process. To make the fulfillment of this requirement easier, we shall introduce a $(1 - \alpha)$ factor into $A(\alpha)f(\alpha)$ and write eq 2 as follows

$$d\alpha/dt = \tilde{A}(\alpha)(1 - \alpha)\exp(-E(\alpha)/RT) \qquad (7)$$

where $\tilde{A}(\alpha)$ is $A(\alpha)f(\alpha)/(1 - \alpha)$ when $\alpha < 1$. The division by $(1 - \alpha)$ is not possible at the $\alpha = 1$ point, but $\tilde{A}(\alpha)$ can have any finite value there. Note that the appearance of $(1 - \alpha)$ in eq 7 does not mean the assumption of a first-order kinetics; it serves only for a convenient treatment.

Taking the logarithm of $\tilde{A}(\alpha)$ and rearranging eq 7, we get

$$d\alpha/dt = (1 - \alpha)\exp(\ln \tilde{A}(\alpha) - E(\alpha)/RT) \qquad (8)$$

When taking a logarithm, one must assume that the argument does not take zero values. However, this is not a strong assumption because $\tilde{A}(\alpha)$ may have arbitrarily small positive values. For example, the lowest $\tilde{A}(\alpha)$ value in the test evaluations of this work was around 10^{-72} at $\alpha = 1$.

The next step of the work is to introduce straightforward approximations for $\ln \tilde{A}(\alpha)$ and $E(\alpha)$. A general and widespread way for function approximations is the use of polynomials because they have a simple form, their handling is easy, and they can approximate a wide range of functions. Accordingly, polynomials up to fifth order will be used in this work.

3.2. Simple Parameter Transformations for Safer Optimization. Elementary mathematical operations will be given here, which enhance the safety and speed of the convergence during the minimization of the least-squares sum. They aim at decreasing the interrelations (compensation effects) between the parameters in the evaluation process. The first step is to map the domain of the polynomials from $[0,1]$ to $[-1,1]$. For this, variable x is introduced

$$x = 2\alpha - 1 \qquad (9)$$

The polynomials describing E and $\ln \tilde{A}$ will be written as functions of x

$$E(\alpha) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4 + a_5 x^5 \qquad (10)$$

$$\ln \tilde{A}(\alpha) = b_0 + b_1 x + b_2 x^2 + b_3 x^3 + b_4 x^4 + b_5 x^5 \qquad (11)$$

An example for the usefulness of this mapping is as follows: The α^4 and α^5 values are close to each other in domain $[0,1]$; hence, their coefficients can compensate each other a bit during minimization. On the other hand, x^4 and x^5 differ very much at negative x values; hence, their coefficients cannot compensate each other. A further optional step in this direction is the use of Chebyshev polynomials of the first kind due to their favorable properties.[23] An identical rearrangement of eqs 10 and 11 yields

Table 1. Evaluations with Different Degrees of Polynomials^{a,b}

order of polynomials		separate c_j for each experiment				common c value for a sample			
$E(\alpha)$	$\ln \tilde{A}(\alpha)$	reldev$_{85}$	mean E	lowest E	highest E	reldev$_{85}$	mean E	lowest E	highest E
0	5	3.60	188	163	210	3.75	185	168	207
1	5	3.44	190	127	266	3.63	190	130	268
2	5	3.08	179	75	276	3.34	182	91	278
3	5	2.72	184	67	408	2.97	185	63	469
4	5	2.61	172	−600	429	2.84	173	−666	529
5	5	2.55	178	−347	395	2.76	180	−76	408
3	3	4.70	152	−430	235	4.73	152	−430	235
4	4	3.06	158	−736	364	3.08	157	−733	360

^{a}The experiments for 16 biomass samples were evaluated in different ways. reldev$_{85}$ is the root-mean-square relative deviation, which was calculated for the 85 available experimental $-\mathrm{d}m/\mathrm{d}t$ curves at each type of evaluations. ^{b}The dimensions of E and reldev$_{85}$ are kJ/mol and %, respectively.

$$E(\alpha) = \bar{a}_0 + \bar{a}_1 T_1(x) + \bar{a}_2 T_2(T) + \bar{a}_3 T_3(x) + \bar{a}_4 T_4(x)$$
$$+ \bar{a}_5 T_5(x) \tag{12}$$

$$\ln \tilde{A}(\alpha) = \bar{b}_0 + \bar{b}_1 T_1(x) + \bar{b}_2 T_2(x) + \bar{b}_3 T_3(x) + \bar{b}_4 T_4(x)$$
$$+ \bar{b}_5 T_5(x) \tag{13}$$

where T_1 ... T_5 are the Chebyshev polynomials of the first kind,[23] and $\bar{a}$ and $\bar{b}$ are the coefficients to be determined during minimization of the objective function. Note that the calculations with the Chebyshev polynomials of the first kind are fast and easy through their well-known recurrence relations.[23] (The evaluation of the T_1 ... T_5 polynomials at any x can be carried out through a few simple program lines.) The results can be transformed back to the form of eqs 10 and 11 for reports and publications. The models given in the Supporting Information are presented in both formats.

Another elementary parameter transformation serves to decrease the interrelation between the pre-exponential factor and activation energy during minimization.[26] At constants A and E, it can be carried out by minimizing a transformed variable Z instead of A

$$Z = \ln A - E/RT_\mathrm{m} \tag{14}$$

where T_m is the arbitrarily chosen fixed temperature somewhere in the middle of the temperature interval.[26] This method can also be employed for $\tilde{A}(\alpha)$ and $E(\alpha)$ by substituting eqs 12 and 13 (or eqs 10 and 11) into the place of E and $\ln A$ in eq 14. Then, the coefficients of the resulting Z polynomial are determined together with the coefficients of the E polynomial.

3.3. Scale Factors. The solution of eq 2 yields the calculated α and $\mathrm{d}\alpha/\mathrm{d}t$ values. It would be straightforward to compare them to the experimental α or $\mathrm{d}\alpha/\mathrm{d}t$ points by the least-squares method. This topic will be treated in Section 5. The correct determination of the experimental $\alpha(t)$ values is problematic because the thermal decomposition of biomass materials continues at very high temperatures by the slow carbonization of chars.[27] A part of the pyrolysis reactions overlap more or less with the charring of the residues, especially when the sample contains a considerable amount of lignin. Accordingly, α^{exp} can only be determined approximately. We shall turn back to this point in Section 5.

Herewith, a simpler approach is employed: $\mathrm{d}m^{\mathrm{calc}}/\mathrm{d}t$ is obtained from $\mathrm{d}\alpha^{\mathrm{calc}}/\mathrm{d}t$ by multiplication

$$\mathrm{d}m^{\mathrm{calc}}/\mathrm{d}t = c \, \mathrm{d}\alpha^{\mathrm{calc}}/\mathrm{d}t \tag{15}$$

where c is a scale factor to be determined during the evaluation. c is equal to the amount of volatiles forming from a unit mass of the sample by the model. Hence, $1 - c$ is the char yield predicted by the model.

Three options will be considered for the determination of c:

(1) A separate c_j value is assumed for each experiment, and the c_j values are determined together with other model parameters in the least-squares evaluation. (Disadvantage: this approach highly increases the number of parameters in the model.)

(2) A common c value is assumed for all experiments. c is determined together with other model parameters in the least-squares evaluation. (Disadvantage: this is only an approximation because the char yield $1 - c$ may depend on the temperature programs.[27] However, this dependence is usually smaller than the baseline uncertainties of the apparatuses.)

(3) A separate c_j value is assumed for each experiment, and the c_j values are approximated by the experimental mass loss values in the domain of experiments. (Disadvantages: (i) it is only an approximation, and (ii) it cannot be employed if the temperature programs are terminated without heating to higher temperatures (like the isothermal experiments in Figure 1).)

In the present work, each of the above approaches was tested. The numbers of least-squares evaluations were 224, 224, and 96 for methods (1), (2), and (3), respectively, as outlined in the next section. The results were roughly the same at each approach. The author's preference is method (2). The figures of the next section and the models and figures in the Supporting Information were determined in that way, assuming a common c for all experiments with a given sample.

4. RESULTS AND DISCUSSION

4.1. Effects of Polynomial Order on Results. Experiments belonging to the 16 biomass samples have been evaluated in different ways. When fifth-order polynomial approximation was employed for both E and $\ln \tilde{A}$, the model proved to be ill-conditioned. Four of the 16 samples yielded $E(\alpha)$ curves with negative values around $\alpha = 1$ in that case, and two other samples produced E values of 15−17 kJ/mol. To get rid of such meaningless E values, the calculations were also carried out with polynomials of lower order. The results are shown in Table 1. The first two columns show the orders of the polynomials tested. In each case, all available experiments were evaluated by the least-squares method (eq 4) for the 16 biomass samples. Both methods (1) and (2) of the previous
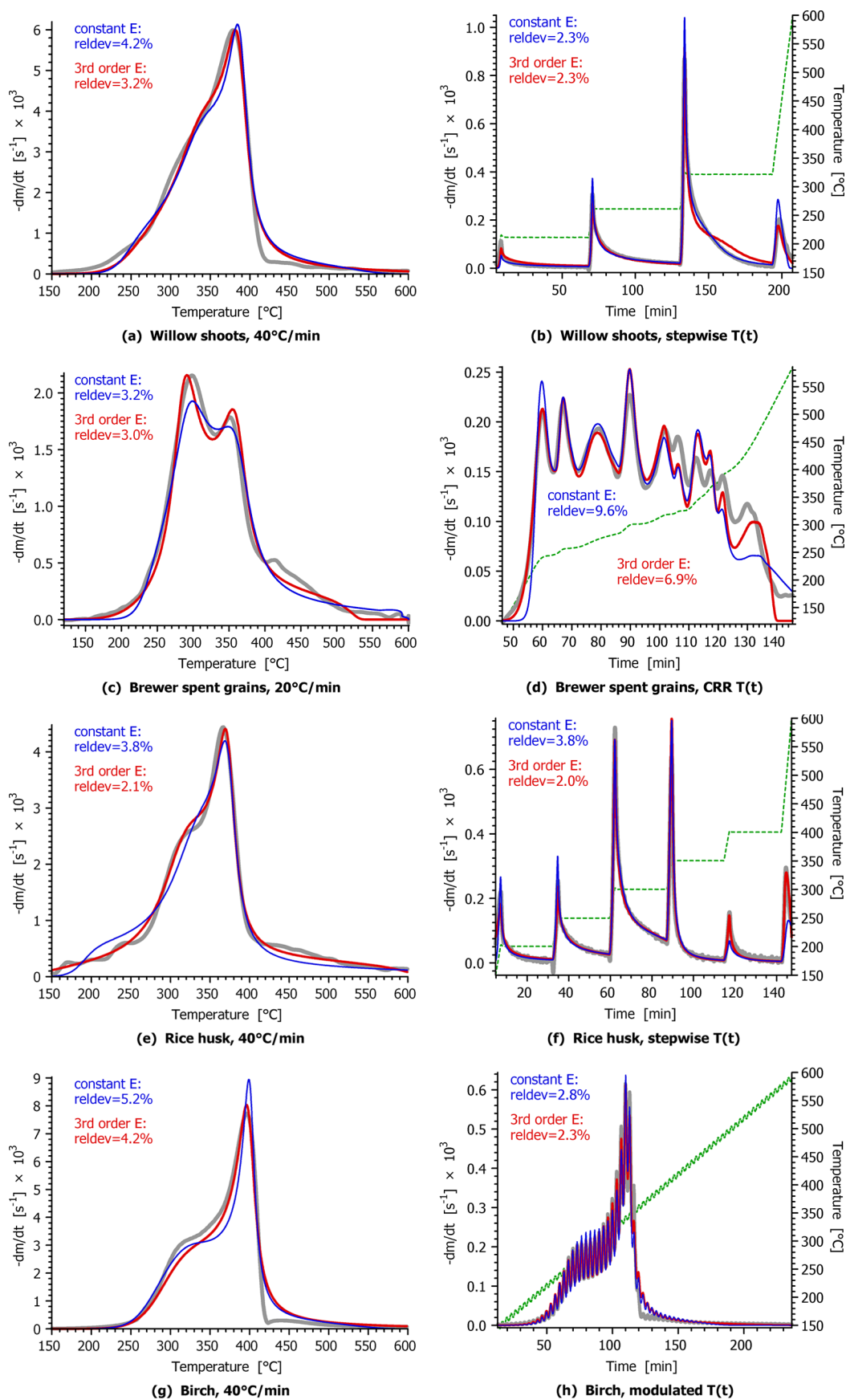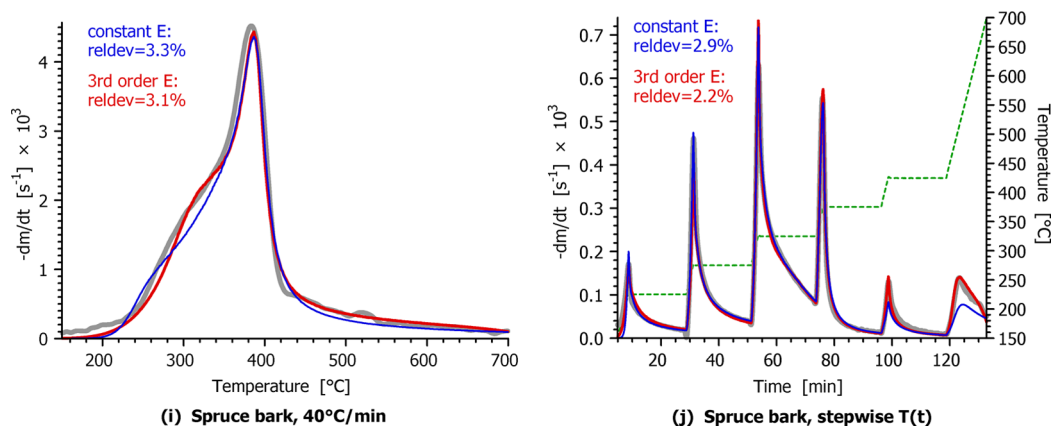
(a) Willow shoots, 40°C/min

(b) Willow shoots, stepwise T(t)

(c) Brewer spent grains, 20°C/min

(d) Brewer spent grains, CRR T(t)

(e) Rice husk, 40°C/min

(f) Rice husk, stepwise T(t)

(g) Birch, 40°C/min

(h) Birch, modulated T(t)

Figure 2. continued

(i) Spruce bark, 40°C/min   **(j) Spruce bark, stepwise T(t)**

Figure 2. Illustration of the fit quality when E is constant (blue color), and E is a third-order polynomial of α (red color). $\tilde{A}(\alpha)$ was approximated by fifth-order polynomials. The thick gray lines represent the experimental curves. The temperature programs, when present, are shown by thin, dashed green lines. Note that the same experimental curves were presented with other type of modeling in the works of (a, b) Mészáros et al.,[12] (c, d) Becidan et al.,[13] (e, f) Várhegyi et al.,[14] (g, h) Tapasvi et al.,[16] and (i, j) Barta-Rajnai et al.[17]
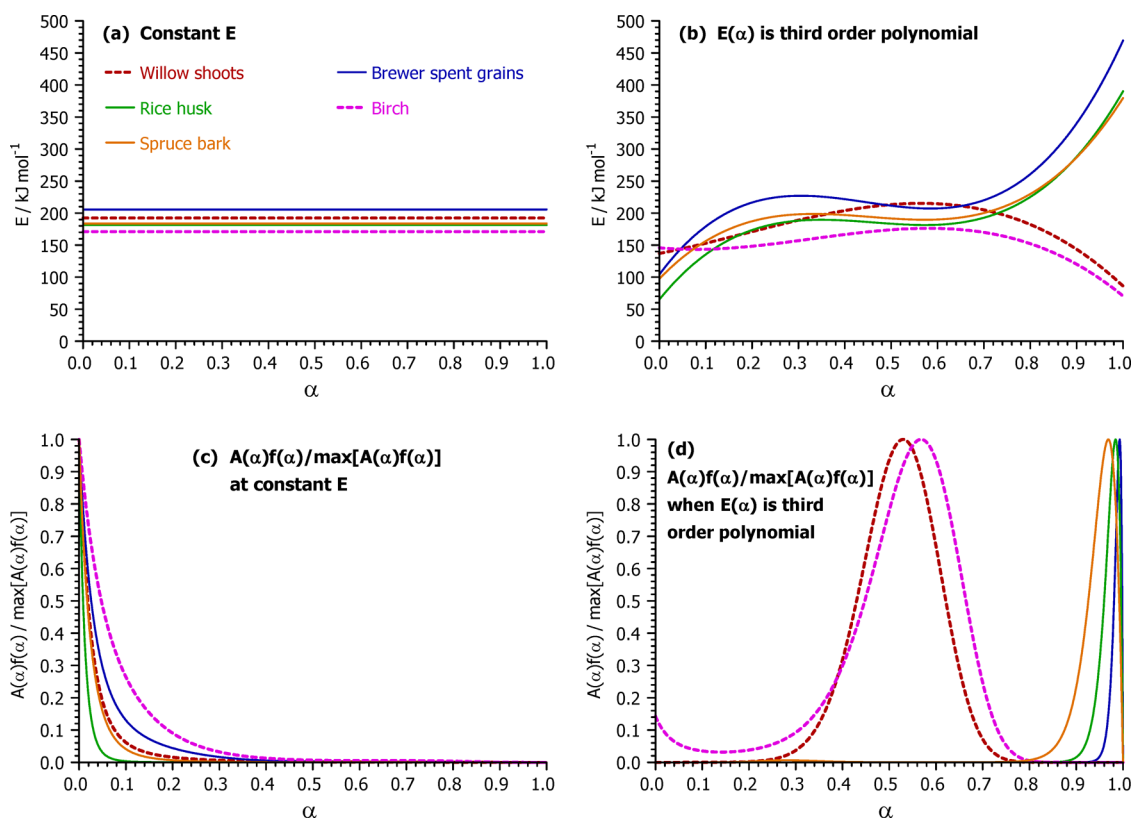
Figure 3. $E(\alpha)$ and $A(\alpha)f(\alpha)$ functions for five biomasses presented in Figure 2 at (a, c) constant E and at (b, d) $E(\alpha)$ functions approximated by third-order polynomials. (The color codes and line types are presented in (a); their listing follows the order in Figure 2.)

section were tested in these evaluations. Accordingly, the eight rows in Table 1 contain data that were obtained from $8 \times 16 \times 2$ least-squares evaluations on 85 TGA experiments. The results were characterized by calculating the root mean square of the relative deviations for the 85 experiments. The average, lowest, and highest E values are also displayed in each group.

The activation energies varied in reasonable ranges when $E(\alpha)$ was approximated by polynomials of zero to third order and $\ln \tilde{A}(\alpha)$ was described by fifth-order polynomials. When the order of polynomials for $\ln \tilde{A}(\alpha)$ was decreased, unacceptable results were obtained, as shown in the last two rows in Table 1.

Obviously, the fit qualities were the best when fifth-order polynomials were employed for both $E(\alpha)$ and $\ln \tilde{A}(\alpha)$: reldev$_{85}$ values of 2.55 and 2.66% were obtained then. It is possible to force the values of $E(\alpha)$ into preset limits by constraints during minimization to avoid the meaningless activation energies. However, the use of third-order polynomials for $E(\alpha)$ is much simpler than the use of constraints, and the increase of the reldev$_{85}$ values was not substantial in this way, as shown in the data in Table 1. For third-order $E(\alpha)$ polynomials, the number of parameters is 11 if common c values are used for the experiments of a biomass sample: four coefficients for E, and six coefficients for $\tilde{A}$, and a c scale factor.

Table 2. Evaluations of 16 Biomass Samples by Two Selected Model Variants[a,b]

source of the experiments	temperature programs	biomass	E is constant		E is third-order polynomial of α		
			reldev$_N$	E	reldev$_N$	E_{mean}	$E_{\alpha=1}$
Mészáros et al.[12]	10, 20, and 40 °C/min; stepwise $T(t)$	black locust shoots	3.11	201	2.65	178	71
		poplar shoots	3.78	207	3.13	187	68
		willow shoots	3.42	192	2.74	179	86
Becidan et al.[13]	5, 10, and 20 °C/min; CRR $T(t)$; stepwise $T(t)$	brewer spent grains	5.28	206	3.94	237	469
		coffee waste	3.76	206	2.65	223	343
		medium-density fiberboard	3.56	179	3.08	167	99
Várhegyi et al.[14]	4 and 40 °C/min; two stepwise $T(t)$ programs	corn stalk	2.99	188	1.83	189	300
		rice husk	3.54	181	2.17	198	390
		sorghum	2.49	188	2.23	165	63
		wheat straw	1.76	188	1.60	188	229
Trninić et al.[15]	5, 10, and 20 °C/min; stepwise $T(t)$	corncob (Hawaii)	3.09	185	2.44	183	248
		corncob (Serbia)	2.21	187	2.17	194	252
Tapasvi et al.[16]	5, 10, 20, and 40 °C/min; CRR $T(t)$; modulated $T(t)$; stepwise $T(t)$; two isothermal $T(t)$ programs	birch	5.17	171	3.43	152	71
		spruce	3.51	168	3.30	161	139
Barta-Rajnai et al.[17]	2.5, 10, and 40 °C/min; 2 stepwise and 3 isothermal $T(t)$	bark of spruce	3.33	184	2.18	207	380
		spruce	4.43	174	4.26	186	260

[a]reldev$_N$ is the root-mean-square relative deviation of the experimental $-\mathrm{d}m/\mathrm{d}t$ curves of a given sample. [b]The dimensions of E and reldev$_N$ are kJ/mol and %, respectively.

The fit quality and curves calculated from this model variant are shown in Figure 2 and in the figures of the Supporting Information.

4.2. Approximations with Constant Activation Energies. The first line of data in Table 1 shows evaluations when E did not depend on α. They provided reasonable descriptions for the 85 experiments treated in this work. The fit quality is illustrated in Figure 2 and in further figures in the Supporting Information. The blue-colored curves belong to this approximation. If the c scale factors are determined by the second method in Section 3.3, then the number of model parameters is 8: one E, six coefficients for $\tilde{A}$, and a c scale factor. Four to nine experiments were available for each biomass sample; hence, the number of unknowns for an experiment varied between 0.9 and 2 in this type of evaluations. Therefore, the model parameters were based on an ample amount of experimental information.

This approximation can be recommended for complex modeling tasks because it can be solved numerically by high-speed algorithms with relatively easy computer programming. For this purpose, the obtained $A(\alpha)f(\alpha)$ function can be factored into a constant A and an $f(\alpha)$ part. The uniqueness of the factorization can be ensured by normalization so that the maximum of $f(\alpha)$ would be 1. (This sort of normalization has also been employed for other empirical $f(\alpha)$ functions.[11]) In this way, the kinetic equation has the form of eq 1 and can be solved numerically by separating the variables

$$\int_0^\alpha \frac{\mathrm{d}\alpha}{f(\alpha)} = A \int_0^t \exp\left(-\frac{E}{RT}\right)\mathrm{d}t \tag{16}$$

The left-hand side is usually denoted by $g(\alpha)$. No analytical approximations are available for the present $g(\alpha)$ or for its inverse function. However, one can calculate numerically a few thousand values for this integral and store them together with the corresponding α and $f(\alpha)$ values in arrays for the modeling work. (The search in a sorted array is very fast. At each right-hand-side value arising in the work, the software can search for the nearest $g(\alpha)$ in the array and α and $f(\alpha)$ values stored with it.) The right-hand side contains the well-known exponential integral at constant heating rates or at $T(t)$ programs consisting of linear sections. In such cases, one of the widely used approximate formulas can be employed. Otherwise, quadrature formulas can be recommended.

Compared to the one-step kinetic models of the literature, the present empirical model variant has an advantage: it can describe pyrolysis at a wide range of $T(t)$ functions with a given set of model parameters. Among others, it could reasonably approximate the TGA experiments from the work of Tapasvi et al.[16] at the $T(t)$ programs shown in Figure 1. (The Supporting Information contains 10 figures on the fit quality for these samples.)

4.3. Shape of Employed Empirical Functions and Fit Quality for 16 Biomass Samples. E versus α dependences and the shape of the $A(\alpha)f(\alpha)$ functions are shown in Figure 3 for the five biomasses presented in Figure 2. Figure 3a,b visualizes the spread of the E values. The constant E values scatter in a narrow interval, while the employment of third-order polynomials results in a much wider range of E values. It may be interesting to observe that the $E(\alpha)$ of the two woody biomasses, denoted by dashed lines in Figure 3, tend to low E values at high α values, whereas the other three biomasses had high E values around $\alpha = 1$. We have no reason to assume a physical reality behind this behavior; it may be simply two different ways to describe formally the flat tailing sections of the $-\mathrm{d}m^{\mathrm{exp}}/\mathrm{d}t$ curves of the biomass materials. The corresponding $A(\alpha)f(\alpha)$ functions also show different behaviors for the dashed and solid lines in Figure 3d; this may be connected to the well-known compensation effect between A and E: an increase in E induces a rise in A.

Table 2 displays more details on the evaluation of the biomasses. The results with the third-order $E(\alpha)$ polynomials were characterized by the mean E values and by the E values at the end of the domain, $E_{\alpha=1}$. $E_{\alpha=1} < 100$ kJ/mol values appeared mainly at the wood samples. The exceptions are

spruce and its bark in the last two rows. On the other hand, the sorghum sample also exhibited low $E_{\alpha=1}$. These observations support the view that the isoconversional kinetics provides only formal approximations for biomass pyrolysis.

The lowest fit quality was obtained for the brewer spent grains and birch samples at constant E: $\text{reldev}_5 = 5.28\%$ and $\text{reldev}_9 = 5.17\%$. Both samples are shown in Figure 2. The Supporting Information contains further figures on the fit quality of these samples. As shown in these plots, the fit quality is also reasonable for these samples.

4.4. Restricting the Evaluations to Constant Heating Rate Experiments. As mentioned in Introduction, almost all isoconversional kinetic studies were based only on constant heating rate experiments. Herewith, we examine this approach from the aspects of the present work. In Tables 1 and 2, there was at least one experiment with nonlinear $T(t)$ for each sample. Table 3 shows the evaluations that were carried out

Table 3. Evaluations of the Constant Heating Rate Experiments Only[a,b]

order of polynomials for E		0	1	2	3
separate c_i for each experiment	fit (reldev₄₆)	2.70	2.56	2.43	2.23
	predictions (reldev₃₉)	5.95	6.12	5.61	5.71
	mean E	203	207	190	191
	lowest E	172	126	−56	−492
	highest E	261	410	478	645
common c for the experiments of a sample	reldev₄₆	2.77	2.61	2.48	2.27
	predictions (reldev₃₉)	6.29	6.42	6.19	6.13
	mean E	203	207	191	192
	lowest E	172	139	24	−478
	highest E	261	408	478	648
c_i were approximated by mass loss values	reldev₄₆	2.85	2.74	2.56	2.33
	predictions (reldev₃₉)	6.01	6.16	5.99	5.93
	mean E	203	207	191	193
	lowest E	172	144	82	19
	highest E	262	383	411	669

[a]The constant heating rate experiments were evaluated in different ways for the 16 biomass samples. reldev₄₆ is the root-mean-square relative deviation calculated for all constant heating rate $-dm^{obs}/dt$ curves. reldev₃₉ characterizes how the obtained models can predict the 39 experiments with nonlinear $T(t)$. [b]The dimensions of E, reldev₄₆, and reldev₃₉ are kJ/mol and %, respectively.

only on the constant heating rate experiments. Here, three ways were used for the determination of c factors (as shown in Section 3.3), while the order of polynomials for $E(\alpha)$ varied from 0 to 3. The evaluations were based on 46 constant heating rate experiments that were available for the 16 biomass samples; hence, Table 3 was based on $3 \times 4 \times 16$ evaluations.

It turned out that model variants with constant E gave better fit qualities (lower reldev₄₆ values) for the subset of the constant heating rate experiments than the third-order polynomials for all available experiments (reldev₈₅) in Table 2. Accordingly, we do not need variable $E(\alpha)$ functions if the aim of the modeling is to describe only constant heating rate experiments.

The parameters obtained from the constant heating rate experiments can provide some rough predictions for the remaining 39 experiments with nonlinear $T(t)$, as shown in the corresponding reldev₃₉ values in the table. In this respect, the

prediction power of the constant E model is close to those of the $E(\alpha)$ model variants.

4.5. Realistic and Unrealistic E Values. As shown in Table 3, the evaluation of the constant heating rate experiments resulted in highly negative $E_{\alpha=1}$ values when third-order polynomials were used for $E(\alpha)$, and the c scale factors were determined by the first and second methods in Section 3.3. There were no negative E values when the c factors were approximated by the third method in Section 3.3, and the model contained only 10 parameters (four coefficients for $E(\alpha)$ and six coefficients for $\ln \tilde{A}(\alpha)$). However, unrealistic E values also appeared in this case. Positive but unrealistically low E values were then obtained at 4 of the 16 biomass samples. The highest E value in this group, 669 kJ/mol, also appears to be unrealistic. At this point, we should clarify the term "unrealistic". One can start from the IUPAC definition of activation energy: "an empirical parameter characterizing the exponential temperature dependence of the rate coefficient".[28] Therefore, we may expect that even an empirical model should give realistic temperature dependences for the reaction rate at any α value. The activation energy values 19 and 669 kJ/mol in Table 2 would correspond to rather unusual temperature dependences at 600 °C: an increase from 600 to 915 °C doubles only the reaction rate at $E = 19$ kJ/mol, whereas a step from 600 to 650 °C increases the reaction rate by a factor of 150 at $E = 699$ kJ/mol. Such temperature dependences do not occur in the thermal analysis of biomass samples in the kinetic regime. Accordingly, one should choose a model variant with less than 10 parameters if the evaluation is based only on constant heating rate experiments.

The above observations indicate a particularly strong compensation effect between $E(\alpha)$ and $A(\alpha)f(\alpha)$ in eq 2. As mentioned above, $E(\alpha)$ and $A(\alpha)f(\alpha)$ can be arbitrary functions, which may have any positive values in the domain $0 \le \alpha < 1$. The test calculations of this work indicated that an arbitrary $A(\alpha)f(\alpha)$ can compensate even the negative E values without worsening of the fit quality.

5. LEAST-SQUARES CURVE FITTING FOR α^{obs} AND $d\alpha^{obs}/dt$

5.1. Evaluation of α^{obs} Values. The literature of the "model-free" evaluations is based on parameter determinations either from α^{obs} values or from α^{obs} and $d\alpha^{obs}/dt$ values.[1,3,4] The present section deals with the least-squares evaluation of these experimental quantities. As mentioned above, the experimental reacted fraction can only be determined approximately for biomass samples because a part of the pyrolysis reactions overlap with the carbonization of the formed char. An alternative would be the modeling of the whole thermal decomposition, pyrolysis and char carbonization together, but the latter process lasts until very high temperatures.[27]

The biomass samples from the work of Mészáros et al.[12] were selected for test evaluations in this section. The reacted fraction was approximated as

$$\alpha^{obs}(t) \cong \frac{m_{150°C}^{obs} - m^{obs}(t)}{m_{150°C}^{obs} - m_{600°C}^{obs}} \tag{17}$$

Here, the starting point was selected to be 150 °C, which is after the drying of the sample and before the start of the thermal decomposition. The selected final point, 600 °C, is a compromise: the reaction rate is already low there, while the

long, flat, featureless tailing is not overemphasized in the domain of evaluation (see Figure 2a,b and the figures on these samples in the Supporting Information). When α^{obs} is evaluated, the objective function, eq 3, and the formula for the relative deviation, eq 6, are written for α^{obs} and α^{calc}.

The results are summarized in Table 4. The evaluation of the α^{exp} values by constant E and third-order polynomials for

Table 4. Least-Squares Evaluation of α^{exp} and $d\alpha^{exp}/dt^{a,b}$

| sample		B	P	W
constant E; evaluation of α^{exp}	E	192	213	197
	reldev$_4$	1.05	1.48	1.08
E is third-order polynomial; evaluation of α^{exp}	mean E	189	211	196
	lowest E	161	155	182
	highest E	202	227	204
	reldev$_4$	0.97	1.45	1.05
constant E; evaluation of $d\alpha^{exp}/dt$	E	197	207	193
	reldev$_4$	3.26	3.79	3.39
E is third-order polynomial; evaluation of $d\alpha^{exp}/dt$	mean E	179	189	181
	lowest E	70	78	89
	highest E	216	229	215
	reldev$_4$	2.62	3.15	2.74

^{a}The experiments on young shoots of black locust (B), poplar (P), and willow (W) were evaluated. ^{b}The dimensions of E and reldev$_4$ are kJ/mol and %, respectively.

$E(\alpha)$ gave nearly identical fit qualities. The differences in reldev$_4$ are 0.08 for the black locust and only 0.03 for the other two samples. These data suggest that there is no need for a variable E when the investigators are only interested in the modeling of α^{obs}. The parameters derived from the α^{obs} values also provide some rough approximations for the $d\alpha^{obs}/dt$ curves, as shown in Figure 4. There are no substantial differences between the constant E and third-order $E(\alpha)$ models from this aspect. Figure 4 illustrates the fit qualities obtained by the constant E model.

5.2. Evaluation of $d\alpha^{obs}/dt$ Curves. The differentiation of eq 17 with respect to time yields eq 15 with the c constants by method (3) in Section 3.3. Accordingly, the results of this evaluation are similar to the results presented in Section 4. Figure 4a illustrates that the parameters obtained from the $d\alpha^{obs}/dt$ curves are also suitable for an approximate description of the α^{obs} data.

6. CONCLUSIONS

(1) The $E(\alpha)$ and $A(\alpha)f(\alpha)$ functions of the isoconversional ("model-free") evaluation were approximated by simple, versatile formulas. The corresponding parameters were determined by the least-squares method by finding the best fit for the experimental data $-dm^{obs}/dt$ or $\alpha^{obs}(t)$.

(2) To provide a sound basis for the work, the evaluations with various model variants were carried out on 85 thermogravimetric experiments, which had been published earlier with different types of kinetic modeling. The experiments belonged to 16 biomass samples, including woody biomass, agricultural residues, and industrial wastes, and were performed at a variety of linear and nonlinear temperature programs.

(3) Ten kinetic parameters and one or more scale factors provided good fit with reasonable E values for the experimental $-dm/dt$ data. In this model variant, $E(\alpha)$ was approximated by third-order polynomials, and the prefactor part of the kinetic equation, $A(\alpha)f(\alpha)$, was approximated by an empirical formula with six adjustable parameters. When the model contained more parameters, the evaluation proved to be ill-conditioned. Quite different kinetic parameters could provide similar fit qualities in such cases, while the $E(\alpha)$ functions exhibited meaningless E values in the vicinity of $\alpha = 1$.

(4) A model with constant E values provided acceptable fit qualities in all tested cases. Here again, $A(\alpha)f(\alpha)$ was described by an empirical formula with six parameters. This empirical model allows fast numerical solutions that may be helpful in complex multidimensional modeling tasks. Compared to one-step kinetic models of the literature, the presented empirical model with constant E has an advantage: it can describe pyrolysis at a wide range of $T(t)$ functions with a given set of model parameters. Among others, it could reasonably approximate the TGA experiments performed with the $T(t)$ programs in Figure 1.

(5) When the evaluation was restricted to the constant heating rate experiments, model variants with constant E or with first- and second-order $E(\alpha)$ polynomials provided good fit qualities. This subset of experiments could not provide enough experimental information for a meaningful evaluation by third-order $E(\alpha)$ polynomials.
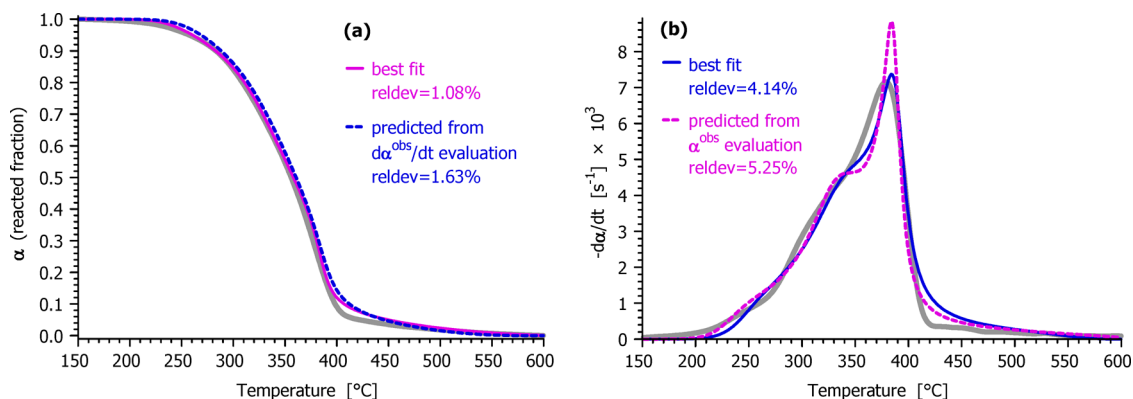
Figure 4. Fit qualities for the 40 °C/min experiment on the willow shoot sample. The constant E model was employed for the least-squares evaluation of (a) α^{obs} and (b) $d\alpha^{obs}/dt$. The experimental data are shown by a thick gray line. The best fitting and predicted curves are denoted by solid and dashed lines, respectively. The magenta and blue colors correspond to the evaluation of α^{obs} and $d\alpha^{obs}/dt$ data.

(6) When the α^{obs} data were evaluated instead of the $-dm^{obs}/dt$ curves, model variants with constant E and third-order $E(\alpha)$ polynomials provided nearly the same fit qualities. One should note here that the $-dm^{obs}/dt$ curves are known to be more characteristic to the peculiarities of biomass pyrolysis than the integral curves (m^{obs} or α^{obs}). If investigations are restricted to the integral curves, then the model variant with constant E is adequate.

(7) The results suggest that the kinetic equations with variable E and A are ill-conditioned due to the compensation effect between $E(\alpha)$ and $A(\alpha)f(\alpha)$. The compensation effects between constant E and A values are well-known, and the problems are more serious when E and A are arbitrary functions of α.

(8) Transparent ways are needed to choose reasonable approximations from the infinite number of solutions that can give good fit for the experiments. In the present work, the order of the polynomials for $E(\alpha)$ was decreased to third order or below, while corresponding changes in the fit quality were carefully checked.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.energy-fuels.9b00040.

Obtained parameters presented together with figures on $E(\alpha)$, $A(\alpha)f(\alpha)$, and the fit quality for 16 biomass samples at two model variants (PDF)

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NOMENCLATURE

α = reacted fraction (dimensionless)
A = pre-exponential factor (s^{-1})
$\tilde{A}(\alpha) = A(\alpha)f(\alpha)/(1-\alpha)$ at $\alpha < 1$ (s^{-1})
$a, \bar{a}, b, \bar{b}$ = coefficients in the polynomial approximations of $E(\alpha)$ and $\ln \tilde{A}(\alpha)$ (kJ/mol, ln s^{-1})
E = activation energy (kJ/mol)
$f(\alpha)$ = empirical function expressing the change of the reactivity as the reactions proceed (dimensionless)
$g(\alpha)$ = the integral of $1/f(\alpha)$ in eq [16] (dimensionless)

h_j = height of an experimental $-dm/dt$ curve (s^{-1})
m = the mass of the sample normalized by the initial dry sample mass (dimensionless)
of = objective function minimized in the least-squares evaluation (dimensionless)
N_{exper} = number of the experiments evaluated together by the least-squares method
N_j = number of the evaluated data on the jth experimental curve
R = gas constant (8.3143×10^{-3} kJ mol^{-1} K^{-1})
reldev = the deviation between the observed and calculated data expressed as percent of the corresponding peak height (%)
$reldev_{85}$ = root mean square of the reldev values of 85 experiments (%)
t = time (s)
T = temperature (°C, K)
$T_1(x) \dots T_5(x)$ = Chebyshev polynomials of the first kind
$x = 2\alpha - 1$ (dimensionless)
i = digitized point on an experimental curve
j = experiment

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