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## Kinetic modeling of biomass pyrolysis. 10 years of a US-Hungarian cooperation

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### ABSTRACT

The thermal decomposition of lignocellulosic biomass materials and their major components is discussed. Thermogravimetric and DSC curves at different T(t) heating programs were evaluated by the method of least squares. Pseudo-first order models, parallel, successive and competitive reaction schemes and complex reaction networks were employed in the modeling. The following topics are treated: thermal decomposition of cellulose at low (2°/min) and high (50 - 80°C/min) heating rates; low temperature phenomena; the validity of the Broido – Shafizadeh model; effects of mineral catalysts; cellulose pyrolysis in closed sample holders; thermal decomposition kinetics of xylan, lignin and lignocellulosic plant samples.

*Keywords:* Biomass, Cellulose, Hemicellulose, Lignin, Reaction kinetics, Thermogravimetry, DSC

## 1. Introduction

Due to an increase of interest in renewable energy sources and utilization of various wastes and by-products in the eighties, a cooperation on biomass research was established between the Research Laboratory for Inorganic Chemistry of the Hungarian Academy of Sciences and the Hawaii Natural Energy Institute of the University of Hawaii. The aim of the work was to get a deeper insight into the kinetics and mechanism of the thermal decomposition and, in this way, to aid the development of biomass utilization processes. The thermal behavior of the main biomass components and various plant samples were studied. The work included investigations on catalyzed and uncatalyzed reactions, open and closed sample holders, low and medium temperature pyrolysis, simple global kinetics and complex reaction networks. Recently the research was extended to the gasification properties of biomass chars.

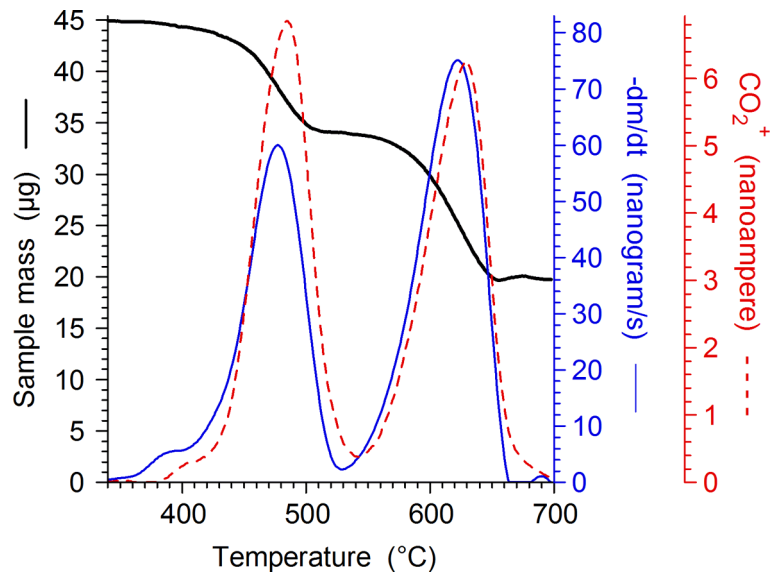
In the present paper we deal with the kinetic modeling of biomass pyrolysis. We wish to give a concise overview on a decade of our diverse research activities in this field. No general literature survey is presented since detailed reviews are available in the field [1-4]. The state of knowledge of hemicellulose decomposition kinetics is thoroughly discussed in a recent work of Di Blasi and Lanzetta [5]. A new mathematical model describing the complexity of lignin decomposition was presented recently by Caballero et al. [6].

## 2. Experimental

### 2.1. Equipment and procedure

The thermogravimetric signal of a computerized thermobalance – mass spectrometer (TG–MS) system was used [7]. The 0.1  $\mu\text{g}$  sensitivity of the thermobalance (Perkin Elmer TGS–2), a stable gas flow control and a high precision digital to analogue converter allowed the use of small sample sizes (0.3 – 3 mg) which were needed to ensure the kinetic regime of the decomposition. The heating rate varied between 2 and 80°C/min. Part of the T(t) programs included isothermal sections of 1 – 17 hours. An argon flow of 140 ml/min was employed. A few experiments were carried out in helium to check the effect of the transport processes. The DTG curves were calculated by spline smoothing.

The reliability of the procedure employed is illustrated by Figure 1 which shows the TG, DTG and a mass spectrometric ion intensity curve during the thermal decomposition of 0.05 mg calcium oxalate. The mass loss in the first reaction step is due to the evolution of 10  $\mu\text{g}$  CO which quickly reacts with the O<sub>2</sub> traces of the ambient to CO<sub>2</sub>. The second step produces 15  $\mu\text{g}$  CO<sub>2</sub>. The accord between the DTG curve and the simultaneously measured CO<sub>2</sub><sup>+</sup> intensity in the second step proves the reliability of the DTG signals.



**Figure 1.** Sensitivity check of the TG-MS system: Thermal decomposition of 0.05 mg  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  at  $dT/dt = 20^\circ\text{C}/\text{min}$ . In the domain shown, the sample mass (—) decreased from  $45\mu\text{g}$  to  $20\mu\text{g}$  while equal molar amounts of CO and  $\text{CO}_2$  were produced in two well separated reactions. The CO, forming in the first step, was oxidized to  $\text{CO}_2$ . The DTG curve (—) is compared to the  $\text{CO}_2^+$  intensity (---).

During biomass decomposition high amounts of heavy volatiles (“tars”) are released which deposit in the various parts of the equipment. Due to this problem, the mass spectrometric signals are more biased by experimental errors than the TG and DTG curves. Hence our kinetic models are based on the least squares evaluation of TG or DTG curves. The reaction kinetic interpretation of the mass spectrometric signals is part of our future plans.

The high pressure experiments were carried out in a computerized Setaram DSC 111 differential scanning calorimeter using sealed high pressure sample holders [8].

## 2.2. Samples

The decomposition kinetics of 9 different celluloses, several lignin (MWL) and xylan samples and 10 lignocellulosic plant samples were studied. The examples shown in details in the paper belong to (i) Avicel PH-105 microcrystalline cellulose; (ii) (4-O-methyl-D-glucurono)-D-xylan provided by Dr. I. Simkovic [9]; (iii) and an IEA-NIST standard sugar cane bagasse sample.

## 3. Kinetic evaluation methods

The method of least squares was employed. Denoting the experimental data (sample mass, DTG or DSC signal) by  $X^{\text{obs}}$  and the corresponding points of the calculated functions by  $X^{\text{calc}}$ , we search for those values of the unknown parameters at which the sum

$$S = \sum_{j=1}^M \sum_{i=1}^{N_j} w_{ij} [X_{ij}^{\text{calc}} - X_{ij}^{\text{obs}}]^2 / N_j M \quad (1)$$

is minimal. Here  $w_{ij}$  are weight factors,  $M$  is the number of experimental curves used in the evaluations and  $N_j$  is the number of points on the  $j$ th experimental curve. The resulting fit can be expressed for each evaluated curve as

$$\text{fit (\%)} = 100 \left( \sum_{i=1}^{N_j} [X_{ij}^{\text{calc}} - X_{ij}^{\text{obs}}]^2 / N_j \right)^{1/2} / X_{\text{highest}} \quad (2)$$

Here the division by the highest observed value,  $X_{\text{highest}}$  serves for normalization when DTG or DSC curves are evaluated.

We observed in several studies [10-12] that different thermoanalytical experiments cannot be described by *exactly* the same parameters. Modern experimental and data acquisition techniques filter out the random components of the errors. The remaining uncertainties of points  $X^{\text{obs}}(i,j)$  are neither random nor independent. Consequently, the method of least squares does not work so perfectly as it is suggested by the textbooks of mathematical statistics. Among others, we have to face the following uncertainties:

- (i) The models can only approximate the real complexity of the decomposition processes.
- (ii) Only biased values of the sample temperature are available and the bias varies with the experimental conditions.
- (iii) Samples of 0.3 – 3 mg may vary in composition or contamination level from experiment to experiment.

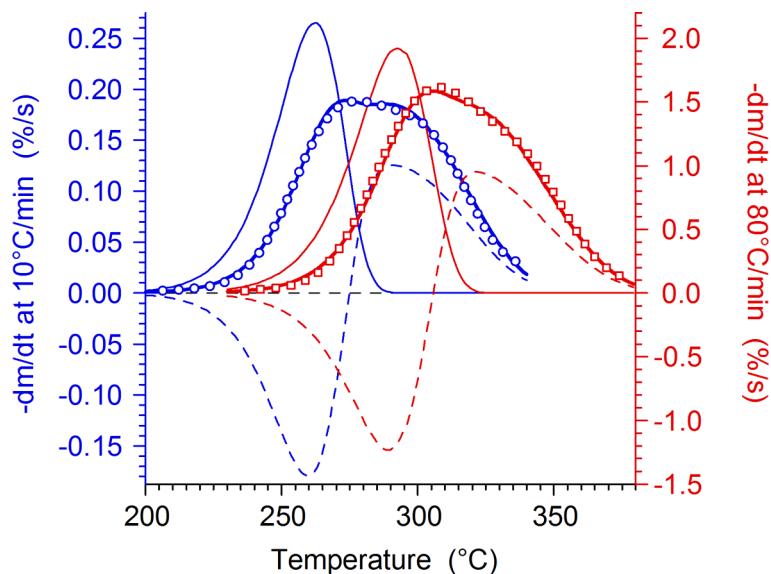
Though the magnitude of the above listed errors is usually small, their combined effect should be taken into account during the evaluation. According to our experience, the simplest way to cope with this problem is not to describe all experiments by exactly the same parameters. Complex, multiparameter models do require the simultaneous least squares evaluation of more than one experiment, but a slight variance of the model parameters should be allowed to formally describe errors (i) - (iii). The magnitude of the scattering of the parameters can be kept within reasonable limits by simple mathematical techniques [10-12].

## 4. Results and discussion

### 4.1. Hemicellulose

(4-O-methyl-D-glucurono)-D-xylan, prepared from beech sawdust, was investigated by TG–MS. The interpretation of the mass spectrometric curves led to the assumption of successive reactions [9]. The reaction kinetic analysis of the DTG curves also supported this conclusion [13]. We tried to describe the double peaks observed by models based on competitive, successive and independent parallel reactions. The model of competitive reactions was unable to describe the DTG curves. The assumption of successive reactions led to a good fit to the experimental data and a good agreement between the A, E and c values obtained from 10 and 80°C/min experiments. When the independent parallel reaction model was used, the fit was worse (about 3%) and the difference between the parameters associated with the 10 and 80°C/min

experiments was higher. Recently, we reevaluated the same experiments using the simultaneous least squares curve fitting technique described in Section 3 and obtained  $E$  and  $\log A$  values close to the earlier ones. The yields of solid products, however, differed due to misprints in our earlier publication. The new, revised results are shown in Figure 2 and Table 1.



**Figure 2.** Simultaneous least squares evaluation of DTG curves of (4-O-methyl-D-glucurono)-D-xylan assuming two successive first order reactions. Notation:  $-\text{dm}^{\text{obs}}/\text{dt}$  at  $10^\circ\text{C}/\text{min}$  ( $\circ \circ \circ$ );  $-\text{dm}^{\text{obs}}/\text{dt}$  at  $80^\circ\text{C}/\text{min}$  ( $\square \square \square$ );  $-\text{dm}^{\text{calc}}/\text{dt}$  ( $—$ ,  $—$ ); calculated mass loss rate of the unreacted part of the sample ( $—$ ,  $—$ ); calculated mass loss rate of the intermediate solid products ( $- - -$ ,  $- - -$ ).

**Table 1.** Simultaneous least squares evaluation of DTG curves of (4-O-methyl-D-glucurono)-D-xylan assuming two successive first order reactions.

Heating rate $^\circ\text{C}/\text{min}$	$E_1$ kJ/mol	$\log A_1$ $\log \text{s}^{-1}$	Yield of solid residue 1	$E_2$ kJ/mol	$\log A_2$ $\log \text{s}^{-1}$	Yield of solid residue 2	fit %
10	193	17.0	0.85	84	5.50	0.27	1.6
80	194	16.9	0.84	81	5.78	0.25	1.7

#### 4.2. Uncatalyzed cellulose pyrolysis at linear heating programs

A pure microcrystalline sample, Avicel PH-105 was investigated at heating rates 2, 5, 10, 20, 50 and  $80^\circ\text{C}/\text{min}$ . 21 experiments were evaluated assuming first order reaction kinetics [11]. Each experiment was analyzed separately from the others. The kinetic parameters evidenced a random scattering of ca. 5%. The activation energy,  $E_v = 238 \pm 10$  kJ/mol, is in good agreement with the value Broido [14] reported for linear  $T(t)$  thermogravimetric experiments ( $230 \pm 8$  kJ/mol).

Similar results [15] have been obtained from the evaluation of other celluloses, too:

- (i) Whatman filter paper #1 and #42 ( $10^\circ\text{C}/\text{min}$ ).

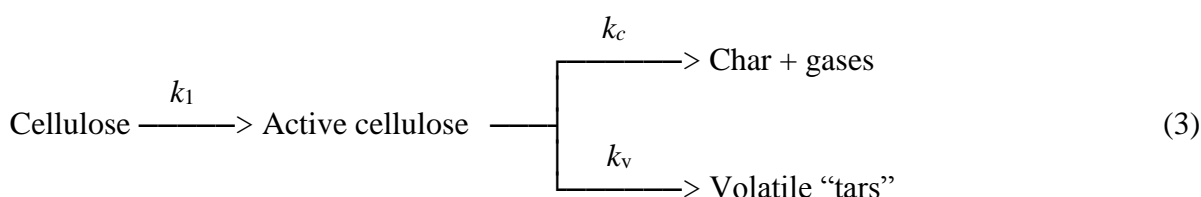
(ii) Sugar cane bagasse samples subjected to 1 hour hydrolysis by dilute acid (5 mM/l H<sub>2</sub>SO<sub>4</sub>) at 150°C and 175°C, respectively (10°C/min).

(iii) Sugar cane bagasse and sweet gum samples subjected to 2-minute hydrolysis by water at 230°C (10°C/min).

The most plausible interpretation for the first order global kinetics is to assume that there is a high activation energy rate determining step in a complex mechanism scheme.

#### 4.3. About the Broido – Shafizadeh Model for cellulose pyrolysis

Broido and his coworkers showed that cellulose decomposes by a multistep mechanism at low temperatures [16]. Later Bradbury, Sakai and Shafizadeh [17] simplified Broido's reaction network:



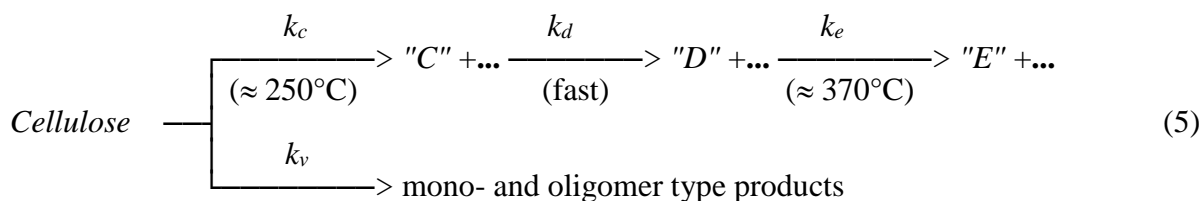
This simplified reaction scheme, called the "*Broido-Shafizadeh model*", is generally accepted nowadays and the kinetic parameters presented by Bradbury et al. [17] are frequently quoted and used in simulations. Nevertheless, a scheme of this type can be criticized as an over-simplification of extremely complex chemical and physical phenomena. One rationale for the modeling of complicated organic reactions by simplified reaction schemes is that a partial reaction in the scheme may correspond in reality to a group of reactions. For example, a partial reaction may be the average of several parallel reactions or the slowest step in a sequence of consecutive reactions.

Around 250°C, when the overall reaction rate is very low, the two branches of the scheme are equally important. As the temperature increases, the lower branch of reaction scheme (3) becomes dominant and the overall reaction can be described by a single first order reaction. To investigate the whole reaction scheme we carried out experiments with temperature programs containing isothermal sections of 30 – 999 minutes connected by temperature ramps of 40°C/min. Two typical experiments of this type are shown in Figure 3. In the time of the earlier workers of the field [16-17] only a single isothermal section of a thermoanalytical curve could be used in the evaluation. However, the high level computing facilities of our age permit the simultaneous evaluation of a group of experiments by solving the system of kinetic differential equations along the given temperature vs. time functions. When we carried out a simultaneous least squares evaluation of five experiments with different temperature programs, the fit was better when the

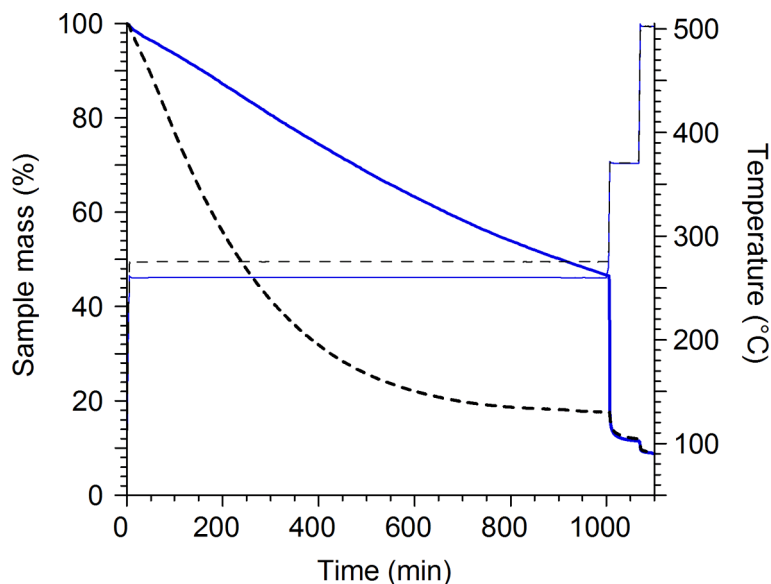


reaction was omitted from reaction scheme (3). Note that reaction (4) does not result in mass loss hence there has not been any direct proof of its existence in the temperature domain of the thermal decomposition.

Our results indicate that reaction (4) either completes *before* the start of the mass loss or does not take place at all. Extending the study to 370°C, we obtained the following reaction scheme:



where "C", "D" and "E" are solid intermediate products and the ellipses (...) indicate volatile formation.

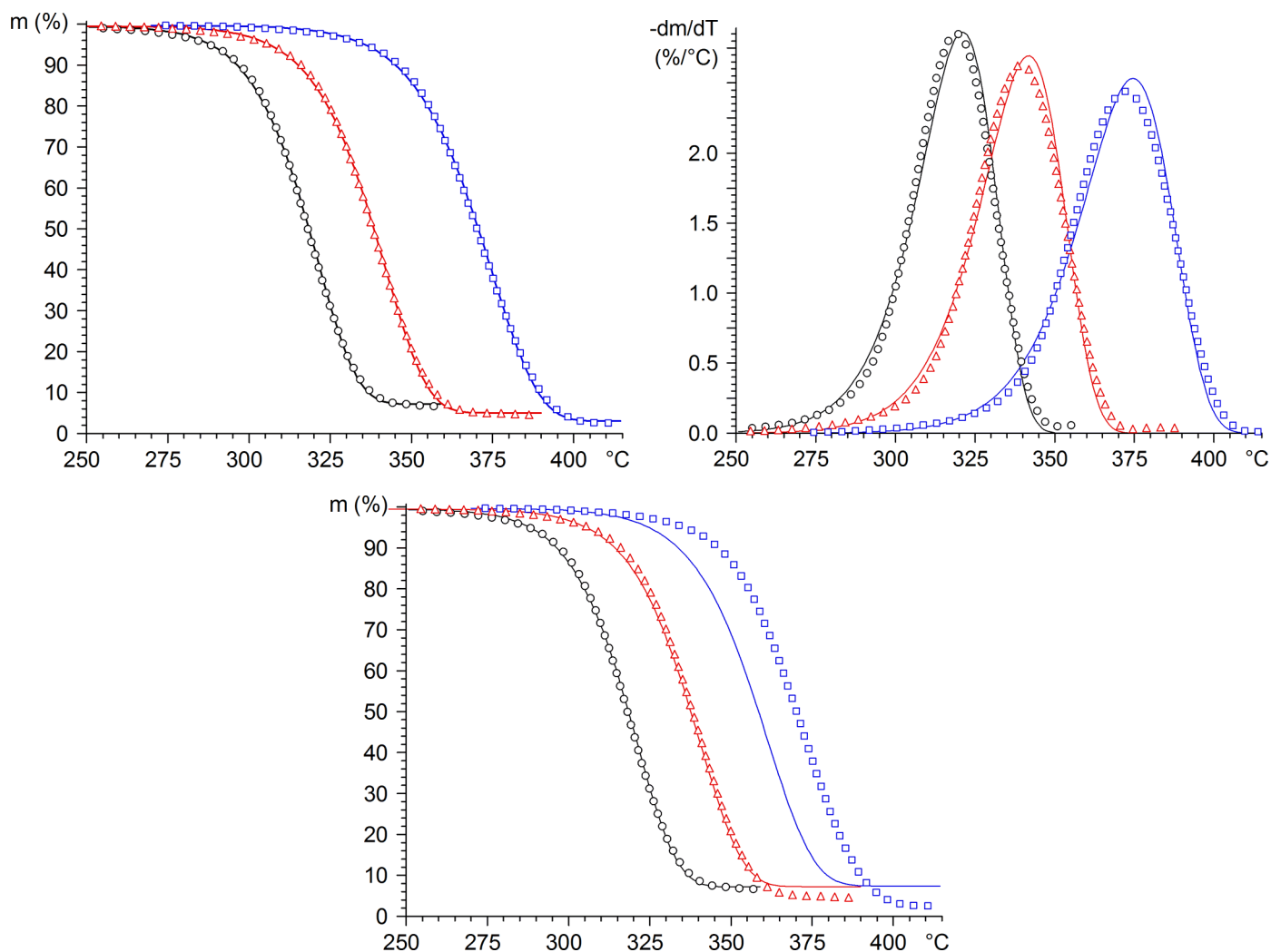


**Figure 3.** Two TG experiments (— and - - -) for the study of the low and high temperature phenomena during cellulose pyrolysis. The bold and thin lines represent the sample mass and temperature curves, respectively. The temperature of the first, long isothermal section is 260°C (—) and 275°C (- - -).

#### 4.4. Thermal decomposition of cellulose at low and high heating rates

Several authors reported relatively low activation energies in the literature of the cellulose decomposition. Recently Milosavljevic and Suuberg observed low (140-155 kJ/mol) activation energies at higher heating rates [18]. In our opinion, the phenomenon reported is closely related to heat transfer problems. We shall discuss this question in details in a separate publication. Nevertheless, we should like to emphasize here, too, that one can reduce the heat transfer problems by using low sample masses, 0.3 - 0.5 mg, at heating rates of 50-80°C/min. In this way the thermal lags, inherent in thermogravimetric investigations, affects only slightly the shape of the DTG curves. As an illustration, we show the kinetic evaluation of three cellulose experiments with heating rates 2, 10 and 50°C/min in helium ambient gas. Due to the similarity of the shape of the curves, it is possible to describe these experiments with identical activation energies. Earlier we evaluated these experiments as parts of a series of 21 TG curves, as described in Section 4.2. In the present paper a more detailed analysis will be shown. The three TG curves were evaluated simultaneously. A common E value was searched for, while log A was allowed to vary for a formal description of the experimental thermal lag errors. (See Section 3.) The corresponding fit is

displayed in panel (a) of Figure 4. The parameters giving the best fit for the TG curves also result in a good fit of the DTG peaks, as shown in panel (b). The least squares procedure resulted in  $E=240$  kJ/mol and  $\log A/s = 18.5, 18.5$  and  $18.1$ . The identical preexponential factors for the 2 and  $10^\circ\text{C}/\text{min}$  experiments can be due to the good heat conductivity of the helium ambient. The lower value at  $50^\circ\text{C}/\text{min}$  can be explained by assuming a thermal lag. One way to illustrate the significance of the decrease of  $\log A$  is to simulate TG curves at higher heating rates from the parameters of the lowest heating rate experiment, as it is shown in panel (c) of Figure 4. The temperature difference observed at  $50^\circ/\text{min}$  is about  $10^\circ/\text{min}$ . However, the temperature errors effect only slightly the shape of the DTG peaks, as shown in panel (b) of Figure 4.



**Figure 4.** Thermal decomposition of cellulose in helium atmosphere at  $2^\circ\text{C}/\text{min}$  ( $\circ$ ),  $10^\circ\text{C}/\text{min}$  ( $\Delta$ ), and  $50^\circ\text{C}/\text{min}$  ( $\square$ ). (a) Least squares curve fitting of the TG curves assuming identical  $E$  and variable  $\log A$  and  $m_\infty$  values. (b) The differential quotients of the best fitting TG curves approximate well the experimental DTG curves. (c) The difference between the experimental data and the  $m(t)$  curves calculated from the kinetic parameters of the  $2^\circ\text{C}/\text{min}$  experiment indicates the magnitude of the thermal lag at  $dT/dt = 10$  and  $50^\circ\text{C}/\text{min}$ .

Figure 4 also shows a decrease in the char yield of the reaction, which can be due to the competition of a high and a low char yield reaction path, as discussed in the previous section. At low heating rates the sample spends a considerable time below  $300^\circ\text{C}$ , where the two branches of reaction scheme (5) have comparable reaction rates. As a result, more char yield is expected. In our opinion, the char yield of the



reaction cannot be read from the TG charts with a sufficient precision, since the amount of solid residue is continuously decreased by a subsequent, slow carbonization process. In our calculations we regarded the char yield,  $m_{\text{final}}$  as an unknown parameter defined by equations

$$\alpha = (m - m_{\text{final}}) / (m_0 - m_{\text{final}})$$

$$d\alpha/dt = A \exp(-E/RT) (1 - \alpha) \quad (6)$$

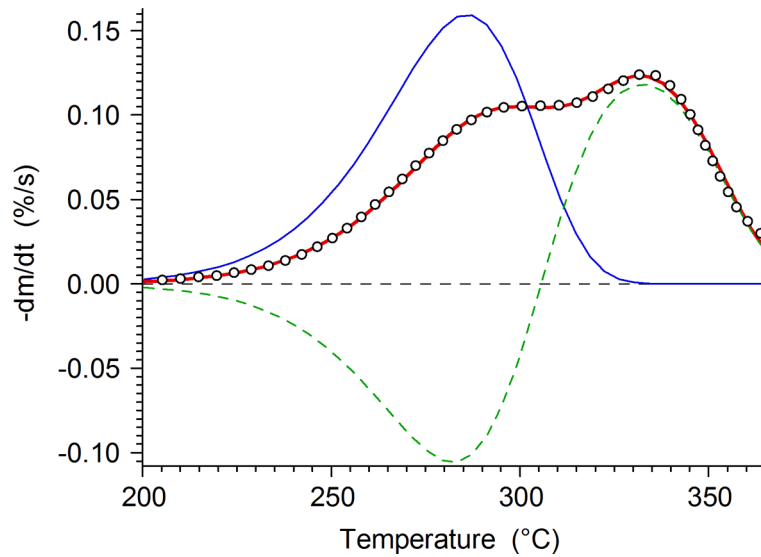
where  $\alpha$  is the conversion (reacted fraction) at time  $t$ . The values of  $m_{\text{final}}$  were determined together with  $E$  and  $\log A$  by the method of the least squares. For the experiments shown in Figure 4 we obtained  $m_{\text{final}} = 8, 6$  and  $3\%$  (dry basis) at  $dT/dt = 2, 10$  and  $50$  °C/min, respectively.

#### 4.5. Effects of mineral catalysts on the thermal decomposition of cellulose

It is well known that minute amounts of mineral matter naturally present in whole biomass samples strongly catalyze the decomposition of the cellulose component. We carried out a series of experiments with inorganic catalysts ( $\text{NaCl}$ ,  $\text{FeSO}_4$  and  $\text{ZnCl}_2$ ) added from dilute solution to cellulose and bagasse samples [7,19]. The concentrations were chosen so that one cation was added per 100 monomer units of polymer in the cellulose experiments. Three simplified kinetic models were used for the evaluation of these experiments [13]:

- (i) Independent parallel reactions. The primary use of this model is the (approximate) description of the thermal decomposition of mixtures. However, this model may describe the catalytic decomposition of a one-component sample, too, if we assume that the catalyst has direct contact only with a portion of the sample or only with selected parts of the molecules composing the sample.
- (ii) Competitive reactions, supposing that the catalyst opens new pathways in the reaction schemes.
- (iii) Successive reactions. Here we assume that an initial step (e.g. dehydration) leads to an intermediate product which decomposes further in a second reaction step.

Figure 5 shows an example for an evaluation by hypothesis (iii).

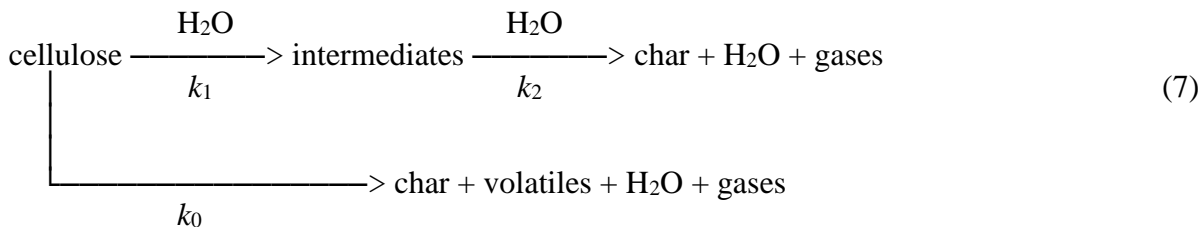


**Figure 5.** Kinetic evaluation of the DTG curves of cellulose with 0.8%  $\text{ZnCl}_2$  catalyst at  $10^\circ\text{C}/\text{min}$  [13]:  $-\text{dm}^{\text{obs}}/\text{dt}$  (ooo);  $-\text{dm}^{\text{calc}}/\text{dt}$  (—); calculated mass loss rate of the unreacted part of the sample (—); calculated mass loss rate of the intermediate solid products (---).

#### 4.6. Cellulose pyrolysis in closed sample holders. Catalytic effect of water vapors

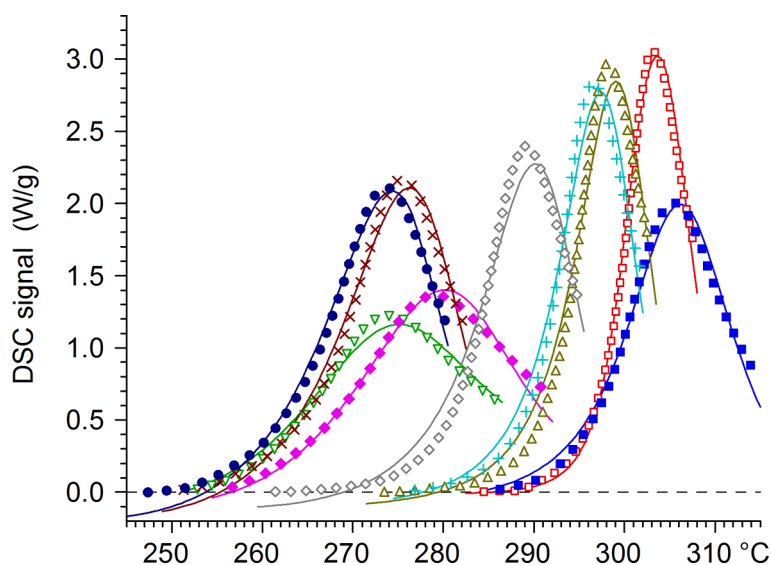
When pure, untreated cellulose samples were heated in closed crucibles with a pinhole on the top, the char yield increased to 20% from the usual low level of 3 – 6% and the reaction temperature revealed a slight decrease [7]. These experiments were carried out by thermogravimetry at 10 and  $80^\circ\text{C}/\text{min}$ .

Later we studied cellulose pyrolysis in completely sealed sample holders by a differential scanning calorimeter [8]. To ensure a chemical kinetic control, the heat transfer problems were reduced by applying low heating rate ( $5^\circ\text{C}/\text{min}$ ). Some of the experiments were carried out with the addition of 0.6 to 1.8 mg water to the cellulose. The pressure during the decomposition was estimated in separate experiments and was found to be between 3 and 14 MPa. A very high char yield, 36 – 40% was observed in all of our sealed sample holder experiments due to the secondary cracking of the formed volatiles. We proved the validity of the following reaction kinetic scheme under the given experimental conditions [10]:



Here  $k_0$ ,  $k_1$  and  $k_2$  are rate constants for reactions 0, 1, and 2, respectively. Reaction 0 is the non-catalyzed decomposition observed in open pan TG experiments. Reaction 1 is the hydrolysis of cellulose in the presence of water. Reaction 2 is the secondary reaction of the intermediates in the sealed sample holder. The rates of reactions 1 and 2 depend on the amount of water vapors in the system. Note that water arises from three sources: (i) initial moisture content of the samples; (ii) extra water added optionally before the start of the experiments; (iii) water formed as a major decomposition product.

The corresponding mathematical model contained eight unknown parameters. The determination of the unknown parameters required the simultaneous evaluation of nine experiments (see Figure 6). The experiments shown in Figure 6 differed in the water vapor concentration of the gas phase due to the different sample mass and/or to the addition of extra water before the start of the reactions. When a higher amount of cellulose was enclosed in the sample holder, more water produced and the acceleration of the reaction occurred at lower temperature. A similar effect was observed when extra amounts of water were added to the samples.



**Figure 6.** Thermal decomposition of cellulose in sealed sample holders at 5°C/min [10]. The different symbols represent nine high pressure DSC experiments differing in the initial amounts of cellulose and H<sub>2</sub>O in the 0.15 ml volume of the sealed sample holders. The leftmost (●) and the rightmost (■) curves belong to 9.59 mg cellulose (dry basis) + 2.63 mg H<sub>2</sub>O and 4.89 mg cellulose + 0.35 mg H<sub>2</sub>O, respectively. The solid lines stand for simulated curves obtained by a simultaneous least squares evaluation assuming reaction scheme (7).

#### 4.7. Lignin

It is well known that the thermal decomposition of lignins occurs in a broad temperature range resulting in 30-50 % char and a significant amount of low molecular mass volatiles, in addition to the monomeric and oligomeric products. The low molecular mass products are formed by the cleavage of functional groups. Since lignins contain various oxygen functionalities having different thermal stability, the scission of the functional groups takes place at different temperatures. At higher temperatures, complex char forming reactions occur involving the complete rearrangement of the carbon skeleton and the release of gas products. The presence of cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>) has a significant effect on the course of decomposition, sodium enhances the formation of char and gaseous products. Jakab et al. [20-22] carried out TG-MS studies to clarify the details of these reactions. However, the corresponding mechanisms were too complex for a mathematical modeling.

In comparison to the sharper DTG peaks of cellulose and hemicelluloses, lignins result in wide, flat DTG peaks. When we examined a series of milled wood lignins, a formal approximation by a pseudo first

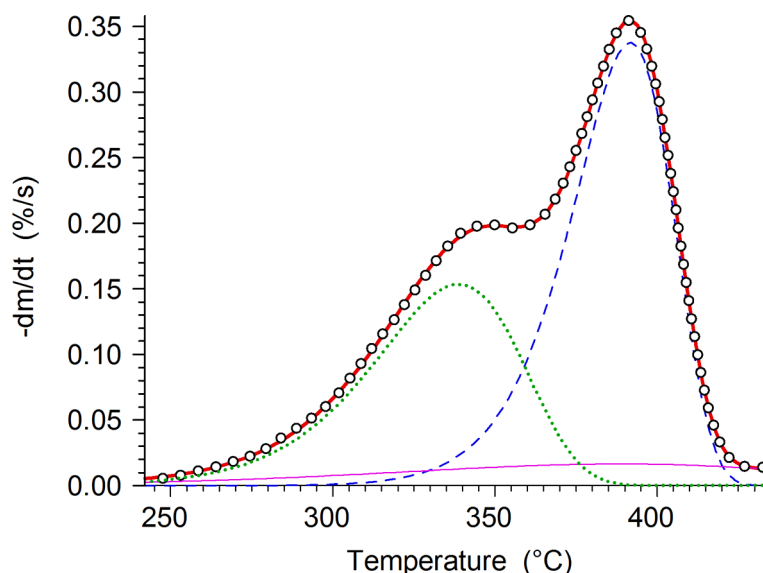
order reaction gave extremely low “activation energies” in the range of 34 – 65 kJ/mol. The corresponding preexponential factors were also very low ( $10^{0.3} - 10^3$ ). During the thermal decomposition of lignocellulosic biomass plant samples, the DTG peaks of cellulose and hemicelluloses appear to be superposed on the flat, base-line type lignin peaks. Since the lignin decomposition is concealed by the more prominent cellulose and hemicellulose peaks, the determination of its kinetics is an ill defined problem. When we evaluated lignocellulosic biomass samples, we added quadratic ‘penalty’ terms to the objective function of the evaluation to keep the formal kinetic parameters of the lignin components in the range observed for MWL samples.

Recently Caballero et al. proposed a continuous distribution type model for the lignin decomposition [6], but it appears to be too complex for our kinetic calculations.

#### 4.8. Thermal decomposition of biomass plant samples

From a chemical point of view, most biomass plant samples can be regarded as mixtures of cellulose, hemicelluloses, lignin and several minor components. In 1979, Várhegyi published a non-linear least squares algorithm for the non-isothermal thermal analysis of decomposing mixtures [23] and applied it for metallic alloy analysis [24]. 10 years later the same algorithm was used in the evaluation of sugar cane bagasse experiments assuming three independent parallel reactions [13]. The calculations resulted in  $E_{\text{cellulose}} = 195 - 213$  and  $E_{\text{hemicellulose}} = 105 - 111$  kJ/mol. Similar least squares evaluation was presented by Font et al. in 1991 for the analysis of almond shells [25]. They obtained  $E_{\text{cellulose}} = 200 - 240$  and  $E_{\text{hemicellulose}} = 100 - 112$  kJ/mol, in good agreement with our bagasse results.

Later we introduced a rough, formal approximation to describe the decomposition of the lignin component, as discussed in the previous section [15, 26-27]. Figure 7 shows the kinetic evaluation of a sugar cane bagasse assuming one reaction for each component [15]. In several cases we observed double hemicellulose peaks on the DTG curves of lignocellulosic materials. This problem was handled in two different ways. One can assume more than one hemicellulose components and one can consider that hemicelluloses decompose in two consecutive reaction steps [5, 13, 28]. From a practical point of view, however, the two approaches are equivalent, since the DTG peaks of the successive reactions can be formally approximated by the model of independent parallel reactions [13].



**Figure 7.** Kinetic evaluation of the DTG curve of a hot water washed sugar cane bagasse sample at 20°C/min [15]:  $-dm^{obs}/dt$  (○○○);  $-dm^{calc}/dt$  (—); calculated mass loss rates of components cellulose (---), hemicellulose (····) and lignin (—).

Many biomass samples are highly contaminated by inorganic salts. This is especially true for agricultural wastes: the ash content of corn stalks and straws may be in the order of 10%. Since inorganic salts shifts cellulose decomposition to lower temperatures, the DTG peaks of the cellulose and hemicellulose highly overlap each other. To simplify the reaction kinetic studies, the amount of mineral matter has to be diminished by acid washing or hot water washing procedures. Thus a much better resolution of the peaks were obtained for many herbaceous plant materials [29, 15, 26-27]. We found that a simple leaching in 80°C water is as effective as an acid washing procedure [26]. After a proper washing procedure the cellulose component of the samples shows approximately the same behavior as the pure cellulose samples.

Similar kinetic evaluation techniques can be employed to resolve the overlapping DTG peaks of industrial cellulose samples contaminated by hemicellulose. We compared the kinetic parameters of the cellulose decomposition in the following samples:

- (i) Cellulose and hydrolyzed lignocellulosic samples listed in Section 4.2;
- (ii) Technical celluloses prepared from an energy cane and wheat straw, respectively, by the ASAM pulping process (10°C/min).
- (iii) Sugar cane bagasse after consuming the majority of its hemicellulose content by a preheating of 2 hours at 260°C (10°C/min).
- (iv) Sugar cane bagasse samples (10 and 20°C/min).
- (v) Corn stalk samples (2, 5, 10°C/min).
- (vi) Herbaceous energy crop samples (20°C/min).
- (vii) IEA-NIST standard bagasse and wheat straw samples (5 and 20°C/min).

Altogether, the results of fifty experiments were compared giving an average activation energy of 221 kJ/mol with a standard deviation of 16 kJ/mol for the cellulose decomposition step [15].

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