REACTION KINETICS OF THE THERMAL DECOMPOSITION OF CELLULOSE AND HEMICELLULOSE IN BIOMASS MATERIALS

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ABSTRACT

Sugar cane bagasse, wheat straw, pine and cotton wood pyrolysis was studied by TGA in argon at heating rates of 5 and 20°C/min. The DTG ($-dm/dt$) peaks associated with the components of an untreated plant material are relatively wide and strongly overlap each other. A reduction in the amount of inorganic ions in the samples by simple water or dilute acid washing procedures resulted in sharper peaks with a better separation. The thermal decomposition of the major biomass components was described, more or less formally, by first order reactions and the DTG curves of the biomass samples were approximated by a linear combination of first order reactions. Good fits between the calculated and the experimental data and good reproducibility of the model parameters were achieved. The kinetic model applied here may serve as a starting point to build more complex models capable of describing the thermal behavior of plant materials during a thermal or thermochemical processing or burning. Theoretically, there is also a possibility to utilise this sort of calculation in the quantitative analysis of the cellulose and hemicellulose content of the lignocellulosic materials.

INTRODUCTION

Thermal analysis of lignocellulosic biomass materials usually gives complex curves composed of more or less overlapping partial curves. Any quantitative characterization or interpretation of the results requires some sort of a mathematical modelling of the data. A proper mathematical description of the thermoanalytical experiments may serve as a starting point to build more complex models capable of describing the thermal behavior of plant materials during a thermal or thermochemical processing or burning.

A straightforward and relatively simple approach is to assume the components of a biomass material decompose approximately independently of each other. In this way the overall reaction rate of the sample will be the sum of the reaction rates of the independent components. In the case of thermogravimetric curves

$$\mathrm{d}m/\mathrm{d}t = \sum c_j \, \mathrm{d}\alpha_j/\mathrm{d}t \qquad (1)$$

where m is the mass loss of the sample divided by the initial sample mass and α_j is the fraction of volatiles which escaped from component j until time t. Coefficients c_j express the contribution of the partial processes to m. Here c_j is proportional to the concentration (m/m) of the jth component in the sample.:

$$c_j = (concentration)_j * (yield\ of\ volatiles)_j \qquad (2)$$

where the term *(yield of volatiles)$_j$* denotes the amount of volatiles formed from a unit mass of component j. Hence this type of modeling may give an estimate of the amount of the individual components of the biomass materials. In actual calculations the following constraints have to be applied to avoid convergence to meaningless combinations of the partial curves:

$$c_j \geq 0 \qquad (j=1,\ 2,\ ..\ ) \qquad (3)$$

The aim of this communication is to survey some of the problems which may arise in connection with this type of mathematical modeling. The choice of equations describing the partial processes, the conditions of their applicability, the reproducibility of the obtained parameters, and the effects of the various pretreatments will be discussed.

MATERIALS AND METHODS

Materials

Four biomass samples obtained from the U.S. National Institute of Standards and Technology were used:

1. Wheat straw (*Triticum aestivum*, NIST #8494)

2. Sugar cane bagasse (*Saccharum spp. hybrid*, NIST #8491)

3. Monterey pine (*Pinus radiata*, NIST #8493)

4. Eastern cottonwood (*Populus deltoides*, NIST #8492)

Experiments published in earlier work [1,2,3] provide a background knowledge of the thermal decomposition of the chemical components of biomass. Thermogravimetric measurements of Avicel ph 105 cellulose, birchwood xylan purchased from Sigma Co., 4-methyl-D-glucorono-D-xylan prepared in the Institute for Carbohydrate Chemistry of the Slovakian Academy of Sciences [2] and milled wood lignin samples prepared from spruce, beech, bamboo and cane by the Federal Institute of Wood Chemistry, Hamburg [3] were used.

Pretreatment of the samples

For reasons outlined later, the effects of three different pretreatments were studied:

1. Acid washing at room temperature by 0.1 mol/l HCl as proposed by DeGroot and Shafizadeh [4]: a 1 g sample was placed in 20 ml of 0.1 mol/l HCl and stirred for 4 h at room temperature. The suspension was filtered and washed with distiled water until neutrality.

2. The same procedure with 1 mol/l acetic acid instead of HCl

3. A similar washing by pure, twice distiled, 80°C water for two hours. (In this later case 120 ml water was used for 1 g sample.)

Thermal Analysis

The experiments were carried out using a Perkin - Elmer TGS-2 thermobalance with a 140 ml/min flow of Ar. To avoid heat and mass transfer problems, low sample masses (ca. 2 mg) were employed with heating rates of 5 and 20°C/min.

Numerical calculations

The data acquisition was computerized and the DTG was determined by differentiation of smoothing splines. The reliability of the DTG curves were carefully checked by comparing them in test experiments to simultaneously measured mass spectrometric intensities [1]. Since their error was found negligible and the differentiation of a TG curve quasi magnifies the features characteristic of the partial peaks, the DTG curves were evaluated by the method of the least squares. Denoting the points of a DTG curve and the corresponding dm/dt values calculated from the kinetic model by $(dm/dt)_i^{exper}$ and $(dm/dt)_i^{calc}$, respectively, the sum of squares to be minimized has the following form:

$$S = \sum [(dm/dt)_i^{exper} - (dm/dt)_i^{calc}]^2 \qquad (4)$$

The calculations were carried out on an AT-386 compatible computer. The non-isothermal kinetic differential equations were

integrated by a high precision analytical approximation (a continued fraction) due to Legendre [5]. The minimization was carried out by a direct search algorithm applying a parameter transformation and a computational scheme published earlier [6]. The program was written in Fortran. Double precision arithmetic was used. The initial parameter sets of the iteration were determined from a rough estimate of the position and width of the partial curves. The choice of reasonable initial parameters proved to be essential to eliminate the convergence to false minima.

RESULTS AND DISCUSSIONS

Thermal decomposition of the pure components

Under the experimental conditions outlined above, pure cellulose produces sharp DTG peaks which can be described by first order reaction kinetics. This fact does not imply a simple unimolecular reaction scheme; it can be interpreted in such a way that one partial reaction, probably the depolymerization, is rate determining [7]. The DTG of the hemicellulose samples used in this study could be well described by two first order independent parallel reactions. Contrary to the avicel experiments, we do not give a physical interpretation to the mathematical approximation of the DTG curve of the hemicellulose by parallel first order reactions; we use here this type of modelling only as a formal approximation. Since the shoulder indicating the two partial peaks on the DTG curve is not distinct, a single first order peak can also be used for the formal decomposition of a given hemicellulose component. Very little is known about the thermal decomposition of the lignin component in the plant materials. Every separation method results in some sort of change to its physical and chemical structure. Milled wood lignins (MWL) are believed to be closest to the original lignins. The four MWL samples evidenced low, very wide DTG peaks which, in a rough approximation, could formally be described by first order reactions of extremely low activation energies and preexponential factors. In two cases smaller double peaks were found on the top of the low base peak. In whole biomass samples these smaller peaks merge with the higher hemicellulose or cellulose peaks and in this way cannot be described by separate curves.

The considerations outlined in this paragraph suggests that, more or less formally, first order reaction kinetics can be used to the description of the partial processes:

$$\mathrm{d}\alpha_j/\mathrm{d}t = A_j \exp(-E_j/RT)\ (1-\alpha_j) \qquad (5)$$

Necessity of a pretreatment

There is a serious problem with the application of equations (1) - (5) to biomass materials. The various inorganic cations and anions present in a natural plant material strongly influence the thermal decomposition. The mineral matter has an especially important effect

on the DTG peak of cellulose. Due to the catalytic effects, the temperature of the cellulose peak may be reduced into the range of the hemicellulose peak. (See the bold line in Figure 1.) Furthermore, cellulose and hemicellulose evidence different thermal behavior in different parts of the plants [8], which may be due to the uneven distribution of the mineral matter in the different plant tissues. A really correct model would probably require the simultaneous application of catalytic reaction kinetic models and a mathematical description of the distribution of the catalysts in the biomass. At present, however, this sort of modelling seems to be hopelessly complicated. Hence we are forced to restrict the treatment to biomass samples of which a major part of the inorganic ions have been washed out by an appropriate procedure.

In an earlier work [8] we observed that a room temperature washing by dilute hydrochloric acid, as proposed by DeGroot and Shafizadeh [4], enhances the separation of the cellulose and hemicellulose peaks. However, acid washing has a potential danger: it may dissolve part of the hemicellulose. For this reason, an alternative acid washing procedure was defined with 1 mol/l room temperature acetic acid. At these conditions only ca. 1% of the acetic acid is dissociated, hence its hydrolysing ability is hoped to be 10 times smaller than that of the 0.1 mol/l HCl. The third method we employed was a washing of the samples by a large quantity of hot water.

Effects of the pretreatments

Previous studies have shown that the highest temperature DTG peak is due to cellulose decomposition. In the case of wheat straw, pine, and cotton wood samples, all of the pretreatments resulted in a better separation of the cellulose peak.
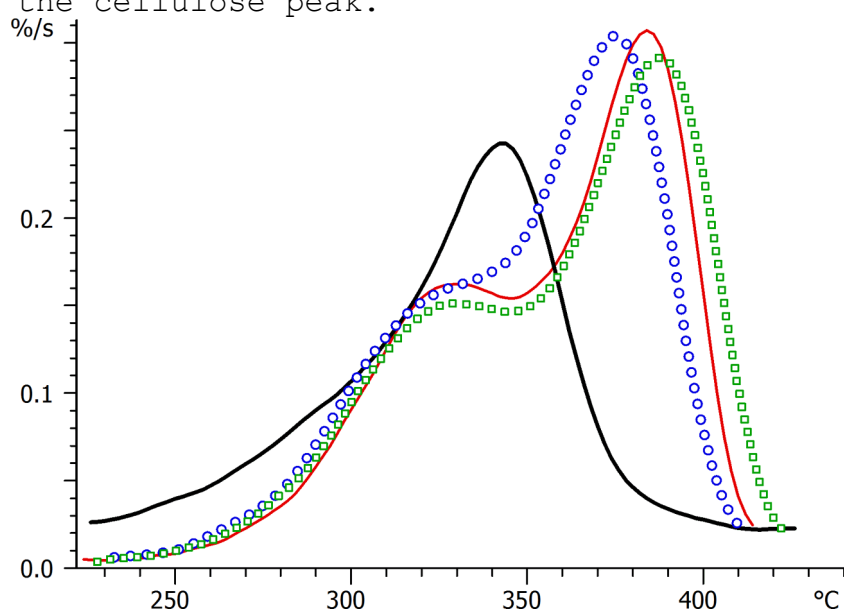

Figure 1: Effects of pretreatments on the DTG curves of wheat straw. (Bold solid line (black): no pretreatment; thin solid line (red): 80°C H_2O; blue circles: 0.1 mol/l HCl, green squares: 1 mol/l acetic acid.)

It is interesting to note in Figure 1 that the DTG peak of the untreated wheat straw is a featureless, single-peak curve, while the pretreatments resulted in well separated double peaks. As already mentioned, the removal of the catalytic ions increases the peak temperature of the cellulose decomposition. Another cause for the better resolution is the enhanced sharpness of the partial peaks.

The behavior of bagasse, however, differed from the other samples studied. Bagasse, resulting from an industrial hot water juice extraction, shows well separated peaks without any additional pretreatment.

Kinetic evaluations

Kinetic evaluations are illustrated in Figures 2 and 3. The thin lines correspond to the partial curves ($c_j d\alpha_j/dt$), of which the simulated mass loss rate curve (dm/dt, denoted by bold line) is formed. The experimental dm/dt curves are represented by gray cirlces. The hemicellulose decomposition is described by one or two partial curves. The highest peak belongs to cellulose. The low, very flat peak which forms something like a sloping, curved base-line is intended to simulate the thermal behavior of the lignin. Unfortunately, one can construct an endless variety of low, wide peaks resulting in almost the same fit between $(dm/dt)^{calc}$ and $(dm/dt)^{exper}$. To avoid this problem, constraints were applied to force the lignin peak into position and width intervals observed for the milled wood lignin samples.
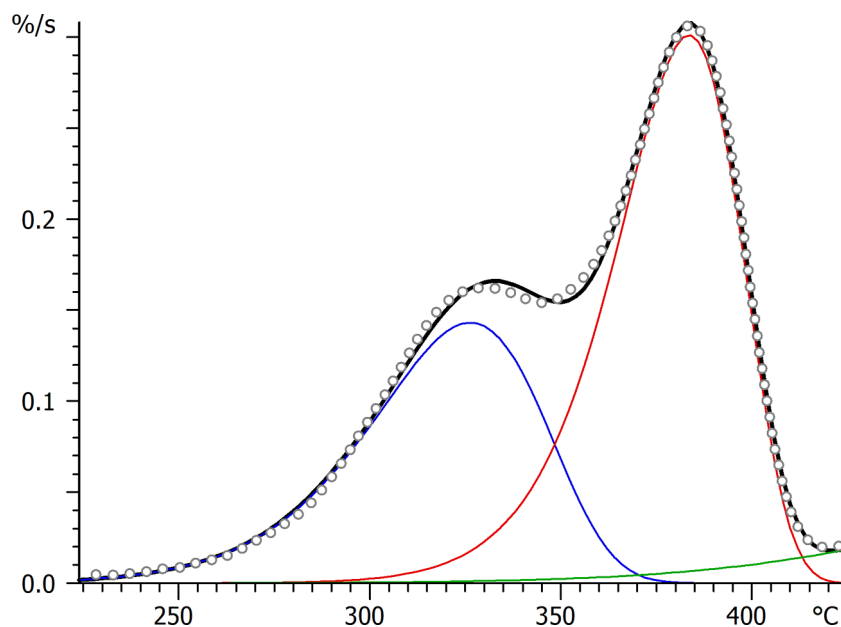

Figure 2: Kinetic evaluation of the DTG curve of hot water washed wheat straw. (See the text.)
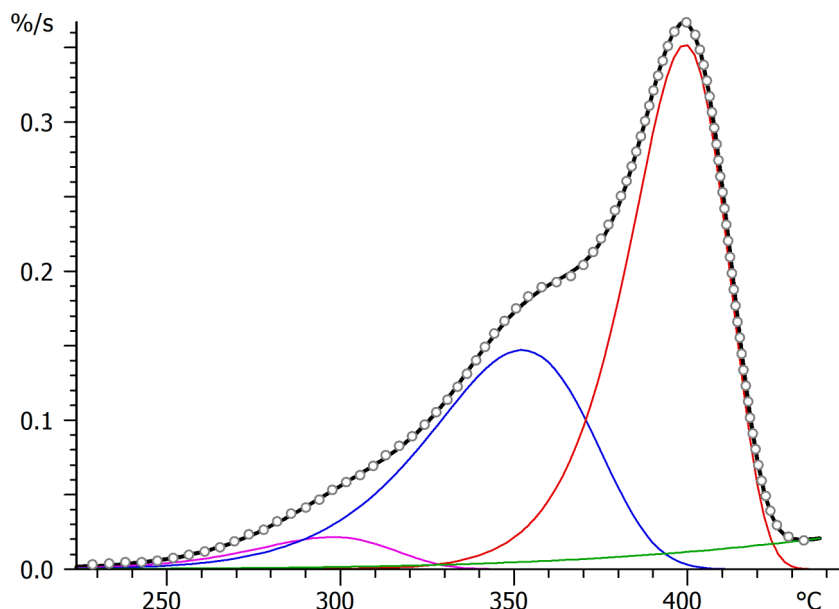
Figure 3: Kinetic evaluation of the DTG curve of a hot water washed pine sample. (See the text.)

Reproducibility and related questions.

A good fit (i.e. $|(dm/dt)_i^{exper} - (dm/dt)_i^{calc}| \leq 1\%$) was achieved in all of the calculations. Unfortunately, we cannot apply the usual methods of mathematical statistics to check the significance of the obtained fit. The problem is that the laws of the mathematical statistics cannot be applied to TG data for which random errors (noise) were filtered out by the analog filter of the instrument and by numerical averaging applied during the computerized data acquisition. A plausible way to get a picture of the reliability of the kinetic parameters is a study of their reproducibility. A series of 12 experiments, carried out on hot water washed bagasse, straw, pine and cottonwood and HCl treated bagasse, indicated a standard deviation for the E_j parameters of about 4 kJ/mol. The standard deviation of the log A_j and c_j parameters were about 0.3 and 0.01, respectively.

The effect of the heating rate was examined on H_2O and HCl treated samples. In the case of the hot water washed samples the differences between the parameters associated with the 5 and 20°C/min experiments were approximately equal to differences in the parameters of the 20°C/min experiments, indicating that there were no heat or mass transfer problems present. In the case of the HCl-washed samples, however, roughly 10 % lower E_j and log A_j values were obtained at 20°C/min than at 5°C/min. The reasons for this irregularity are not known.

The activation energy of cellulose decomposition

In the case of the two grass samples (bagasse and wheat straw) the activation energy and preexponential factor for cellulose decomposition were in the range observed formerly for pure cellulose samples [7] (200 - 230 kJ and 10^{15} - 10^{17} s^{-1}, respectively.). Similar values were found in earlier studies of sunflower stem, corn stalk,

and another bagasse sample [7,8]. In the case of the two wood samples, however, higher values were obtained, around 250 - 270 kJ/mol and 10^{18} - 10^{20} s^{-1}. We do not have enough information to provide an unambiguous explanation for this observation. The reliability of the higher E values obtained for the wood samples was checked in the following way. An isothermal section of 20 minutes at 300°C was inserted into the non-isothermal heating program of 20°C/min heating rate. In the isothermal section the majority of the hemicellulose decomposed, hence the non-isothermal DTG curve above 300°C was dominated by cellulose decomposition. The resulting activation energy values for cellulose, however, remained close to the values calculated using the standard non-isothermal heating programs.

The activation energies obtained for the hemicellulose peaks varied between 120 and 170 kJ/mol with preexponential factors in the order of 10^9 - 10^{12} s^{-1}.

The c_j coefficients

The c_j coefficients are related to the concentrations of the components through equation (2). In the future, we will make a careful comparison of the c_j values obtained using different samples and pretreatments with the actual concentrations of the hemicellulose and cellulose components. Unfortunately, there is no hope of establishing a quantitative relationship between the c_j value and the concentration of the lignin component since the mass loss of the lignin is concealed by the more protuberant DTG peaks associated with the cellulose and hemicellulose decomposition at lower temperatures. At higher temperatures the slow charring of the residue of the cellulose and hemicellulose hinder the observation of the lignin decomposition.

At present we can only compare the c_j values of the same sample with different pretreatments. In this way we found that the hemicellulose / cellulose ratio is 20 - 40 % higher in the hot water washed samples than in the acid washed samples. This observation may be due to hydrolysis of the hemicellulose during the room temperature dilute HCl wash. In the case of acetic acid washing the above differences varied between 0 and 20 %.

CONCLUSIONS

Kinetic modelling of the thermal behavior of whole biomass materials is a difficult problem. Considerable simplification can be achieved if the inorganic ions, which catalyse the decomposition, are washed out of the sample by 80°C water. The exchange of cations with H$^+$ by dilute acid wash, proposed by other authors, may considerably diminish the hemicellulose content. Reproducibility of the parameters which result from the kinetic evaluation was very good. The differences between the calculated and the experimental DTG data were less than 1% of the corresponding peak maxima. An isothermal section at 300°C, where the

majority of the hemicellulose decomposed, did not cause significant changes in the kinetic parameters of the cellulose decomposition. These results encourage further efforts to find the practical applications of the procedures.

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