Kinetics of Biomass Thermal Decomposition*

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As a representative of biomass, in particular the sewage sludge, the raw bacterial cellulose was chosen. The thermogravimetric analysis (TGA) was employed in the investigation of thermal processing of the biomass. The experiments were carried out in the temperature range 30—1000 °C. Different values of heating rate from 2.5 to 20 K min^{-1} were applied. In order to determine kinetics of thermal decomposition of the biomass derivative of TG curve (DTG) was deconvoluted, using Gauss profile, into few fractions (lumps), each of which was represented by a single first-order reaction. The first-order kinetic parameters such as activation energy E_i and pre-exponential factor A_i were estimated. The high values of activation energy indicated the chemical reaction regime of thermal processing of the biomass.

Biomass has been used by mankind for a very long time in order to satisfy its energetic needs. After energy crisis and nowadays because of increasing environmental problems caused by various organic wastes, biomass is considered as the most important source of renewable energy. Apart from combustion which is a direct transformation of biomass into energy there are several possible routes of biomass thermal processing like pyrolysis and gasification. Slow pyrolysis is in use for the production of solids (charcoal) whereas fast pyrolysis is carried out for production of gas or liquids (bio-oils). Gasification processes are intended for the preparation of syngas – mixture of H_2 and CO for chemical synthesis or heat and energy generation. The study of pyrolysis and gasification is gaining increasing importance in the biomass upgrading to produce chemicals or energy. The thermochemical conversion of biomass by pyrolysis, gasification or combustion is one of the most promising non-nuclear forms of future energy [1].

The kinetics of biomass pyrolysis is of great importance in the context of energy recovery. Modelling the processes of pyrolysis and gasification of biomass requires kinetics of mass loss and gas evolving. During the past decades the mass loss kinetics has been found to be able to describe the thermal decomposition behaviour of the complex polymer such as biomass [1—5]. The thermal decomposition of biomass involves a high number of different reactions due to the chemical complexity. Thermogravimetry provides a rapid method for determining the temperature-decomposition profile of a material and the kinetics of its thermal decomposition [6]. This test method covers determination of the kinetic parameters such as Arrhenius activation energy and pre-exponential factor, based on the assumption that the decomposition obeys the first-order kinetics. Only knowledge of reaction-process mechanism enables proper approach to intrinsic kinetics. However, in most practical situations, in particular in the case of solid wastes like sewage sludge, which are not precisely defined, the decomposition mechanism is not available.

In order to approximate the thermal decomposition of such a complex biomass as sewage sludge a raw bacterial cellulose was chosen as one of possible representatives. The raw bacterial cellulose contains bacterial biomass and the components of fermentation broth: culture medium and the main products such as hemicellulose and cellulose. These products are the main components of all ligno-cellulosic materials. Sewage sludge of which thermal decomposition was investigated by us earlier [7] has revealed even 7 lumps of products. The positions of the most important lumps in microbial cellulose have indicated that they are of hemicellulose and cellulose origin. Therefore, the raw bacterial cellulose seemed to us to be the most appropriate mimic material for investigation of thermal decomposition of so complex biomass such as sewage sludge.

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THEORETICAL

Typical approach to the kinetics of thermal decomposition of a complex solid waste is dividing the volatile evolution into a few fractions – lumps, each of which is represented by a single first-order reaction. These lumps are assumed to be noninteracting and evolved by independent parallel reactions

$$\text{substrate} \rightarrow \text{volatile}_i \qquad i = 1, 2, \ldots n$$

If pyrolysis is performed at a constant heating rate β, the first-order rate can be expressed in the following form

$$\frac{\mathrm{d}V_i}{\mathrm{d}T} = \frac{k_i}{\beta}\,(V_i^* - V_i) \qquad (1)$$

where V_i^* is the ultimate yield of the i-th volatile ($\tau \rightarrow \infty$), V_i is the accumulated amount of evolved volatiles from lump i up to time τ, k_i is the rate constant, which depends on temperature according to the Arrhenius equation

$$k_i = A_i \exp(-E_i/(RT)) \qquad (2)$$

At the peak temperature at which volatile evolution reaches a maximum ($T_{\max}$), the time derivative of the reaction rate should be equal to zero. The values of $T_{\max}$ of the volatile lumps at different heating rates were determined from peak-resolution curves (DTG). After some simple rearrangements the final form of equation which allows to determine kinetic parameters is as follows

$$\ln\left\{\frac{\beta}{T_{\max}^2}\right\} = \ln\left\{\frac{RA_i}{E_i}\right\} - \frac{E_i}{RT_{\max}} \qquad (3)$$

The parameters E_i and A_i can be determined from the slope and intercept of a linear plot of $\ln\{\beta/T_{\max}^2\}$ *vs.* $1/T_{\max}$ at various heating rates β. This method standardized in USA [8, 9] has been already verified by us successfully to determine the values of the kinetic parameters for pyrolysis of municipal solid wastes [10] and by *Teng et al.* [11] for rice hulls.

EXPERIMENTAL

The object of our investigations was raw bacterial cellulose biosynthesized by acetic bacteria *Acetobacter xylinum*. The semisynthetic culture medium contained glucose, yeast extract, peptone, Na_2HPO_4, citric acid, $MgSO_4$, ethanol. The cultivation was carried out batchwise for 7 days at the temperature of 30 °C. The main product of surface fermentation was a raw bacterial cellulose in the form of microfibrils forming a ribbon of crystalline cellulose [12]. After drying at 70 °C the biomass was powdered in the lab mill and subjected to pyrolysis in argon atmosphere.

The experiments have been carried out by means of thermobalance, Mettler—Toledo type TGA/SDTA851 LF, in the temperature range 30—1000 °C. Five different values of heating rate have been applied, $\beta/(\mathrm{K\ min^{-1}}) = 2$, 5, 10, 15, and 20. The samples of dried bacterial cellulose were inserted in 150 $\mathrm{mm^3}$ crucible made of Al_2O_3. During the thermal decomposition of the biomass the inert gas (Ar) was flowing around the sample with the rate of 100 $\mathrm{cm^3\ min^{-1}}$. Then the pyrolysis product – charcoal was burnt in the air, *in situ* at 1000 °C or held at argon atmosphere (isothermal segment) during 30 min.

RESULTS AND DISCUSSION

The typical time courses of sample mass (TG curves) are presented in Fig. 1. Additionally, a derivative of TG curve (DTG) was shown as well. Two distinct peaks with extremes at 206 °C and 315 °C that can be seen in the DTG curve correspond to hemicellulose and cellulose. The other peak at higher temperature overlaps with the peak of cellulose. Additional peak at the higher temperature of about 960 °C can be recognized.

As it was mentioned, the kinetic investigation procedure required to carry out thermogravimetric decomposition at various heating rates. Fig. 2 shows DTG curves for bacterial cellulose at various heating rates. One can observe that increasing heating rate shifts the position of the peak extreme ($T_{\max}$) to a higher temperature region.

In order to determine precisely the position of the peaks the DTG curve was deconvoluted by means of Gaussian profile. Fig. 3 presents the deconvolution of DTG curve for raw bacterial cellulose at the heating rate of 5 °C $\mathrm{min^{-1}}$. It should be stated that the three first peaks representing the product lumps overlap each other. The small fourth peak at the temperature about 960 °C corresponding to charcoal is prob-

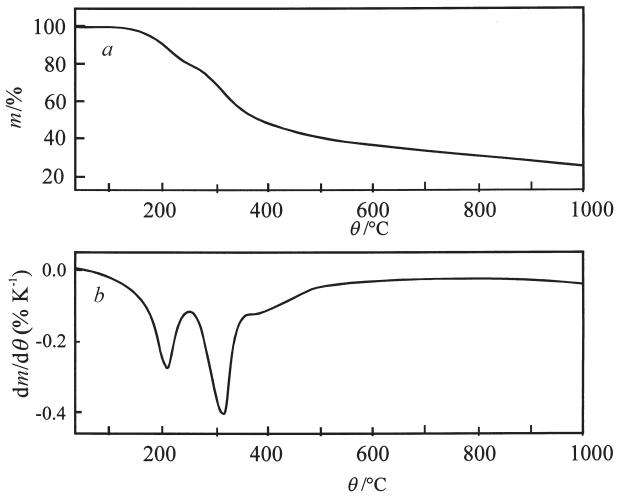

Fig. 1. TG (*a*) and DTG (*b*) curves of raw bacterial cellulose.

Table 1. Kinetic Parameters of Thermal Decomposition of Raw Bacterial Cellulose

Kinetic parameter	Lump 1	Lump 2	Lump 3	Lump 4
Activation energy E_i/(kJ mol^{-1})	92.7	154.8	167.8	471.0
Pre-exponential factor A_i/s^{-1}	1.05×10^8	6.52×10^{11}	1.27×10^{11}	4.15×10^{17}

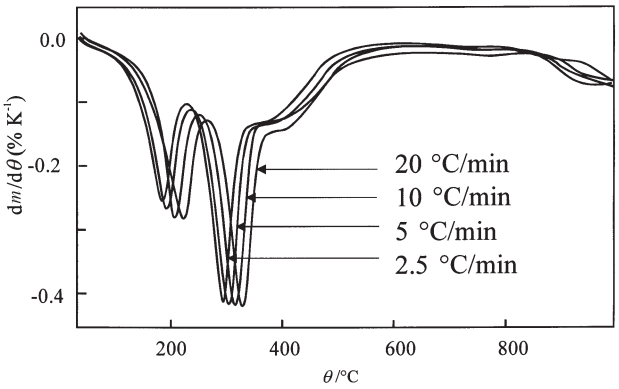

Fig. 2. DTG curves for various heating rates.

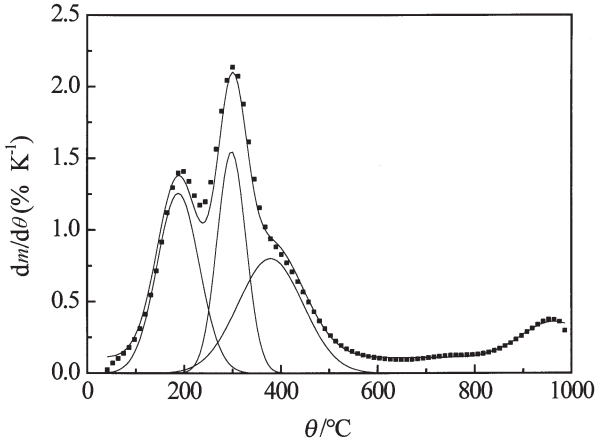

Fig. 3. Deconvolution of DTG curve (Gauss profile).

ably due to polymerization reaction of solid intermediate products of biomass pyrolysis.

Plotting the values of the left-hand side of eqn (3) *vs.* reciprocal of temperature $\ln\{\beta/T^2_{\max}\} = f(1/T_{\max})$ enables to calculate the kinetic parameters. The kinetic parameters E_i and A_i were determined from the slope and intercept of a linear plot.

Fig. 4 shows an example of the application of the method of parameters determination (for the 2nd lump corresponding to the 2nd peak of the deconvoluted DTG curve). The estimated kinetic parameters for the pyrolysis of the raw bacterial cellulose are presented in Table 1. The high values of activation energy indicate the chemical reaction regime of thermal processing of the biomass. The highest value of activation energy for the 4th lump denotes the high temperature sensitivity of the charcoal formation reaction.

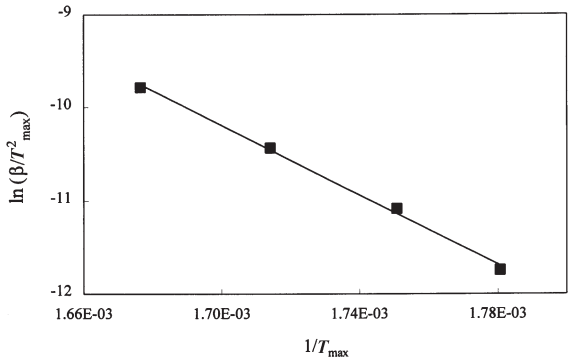

Fig. 4. Diagram for determination of kinetic parameters for the 2nd lump of decomposition product.

Table 2. Mass Loss Fractions of Various Lumps of Bacterial Cellulose Pyrolysis

Lump	w_i/%
1	19.48
2	24.35
3	21.13
4	9.07
Total in argon atmosphere	74.03

The volatile yields corresponding to identified lumps can be read out from the area under single peak in Fig. 3. Table 2 shows the values of mass loss. It is interesting that the 2nd lump corresponding to cellulose decomposition represents the highest fraction of the biomass, which has been expected as the cellulose was the main product of biosynthesis. During formation of charcoal additional mass fraction loss of 9.1 % was observed. The charcoal being the final solid product of biomass pyrolysis represents about one quarter of the whole biomass and can be almost completely burnt in the air.

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