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Pyrolysis of Rapidly Growing Grass Biomass under Isothermal Conditions

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Abstract—The pyrolysis of rapidly growing grass biomass in an inert atmosphere was studied by thermogravimetric analysis using sorghum as an example. Pyrolysis was performed under isothermal conditions at temperatures from 250 to 400°C. To describe the reaction kinetics, a single-component model including six first-order reactions was proposed. A special feature of this model is the occurrence of a step of the formation of an intermediate carbonaceous substance from the volatile products of biomass decomposition.

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INTRODUCTION

Currently, new methods for fuel production have been intensively developed because of the prospect of the exhaustion of petroleum resources and the increase in the prices of petroleum products [1]. The pyrolysis of biomass to produce liquid (bio-oil), gaseous, and solid fuels is a method of this kind. More than a hundred of different forms of biomass were tested as raw materials for the manufacture of biofuels [2]. The effects of the following various factors on the final products of pyrolysis were investigated: the type and granule size of raw materials, temperature conditions, and reactor design. The kinetics of pyrolysis of some types of biomass and wastes was also studied [3–27].

The kinetics of pyrolysis has been studied experimentally in both isothermal experiments [3, 4, 6, 8, 11, 18, 19, 22] and experiences with dynamic temperature conditions [3, 5–7, 9–18, 20–27], mainly, under conditions of a linear increase in the temperature. The dynamics of sample weight changes in the course of an experiment was investigated using thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG), and the composition of the gas phase was determined in more detailed studies [18, 25, 28]. Comparing experimental data with the results of calculations according to the kinetic models proposed, the kinetic parameters of these models were determined.

The true mechanism of the pyrolysis of biomass cannot be currently described in detail because this is a complex process due to a great number and a wide variety of substances that participate in different parallel and consecutive reactions. For this reason, attempts at the development of simplified formal kinetic models of pyrolysis have been made without ceasing. The advantages of a formal approach are its simplicity and the possibility of conducting applied calculations on its basis, and the main disadvantage is that, as a rule, it is applicable only in the range of parameters in which the experimental data were obtained. The composition of raw materials and the temperature conditions are key parameters for describing pyrolysis. It is likely that the variety of raw materials and temperature conditions leads to the appearance of a set of formal kinetic models for the test process.

The models proposed in the literature can be classified according to several signs: the number of components (single-component or multicomponent), the number of stages (single-stage or multistage), and the orders of reactions (first-order and other).

In the single-component single-stage models, the process is simulated by one reaction with complex kinetics. In this case, the task of a kinetic study is the selection of three values, which compose a so-called kinetic triplet: a preexponential factor, an activation energy, and a function that describes the dependence of the rate of reaction on conversion [11, 15, 22].

In a number of publications, a multicomponent single-stage model was used, in which it was assumed that the main component of biomass (hemicellulose, cellulose, and lignin) decomposed independently of each other in first-order reactions. The model of three independent parallel first-order reactions was successfully used for describing the kinetics of pyrolysis of various types of biomass and wastes [5, 7, 9, 10, 12–14, 16, 18, 25].

In more complex models, it is assumed that more than three components participate in the process and non-first-order reactions are considered. Thus, Gronli et al. [14] used five first-order reactions for describing the process of pyrolysis. The pyrolysis of

hemicellulose and cellulose was simulated by first-order reactions, and the pyrolysis of lignin, by a third-order reaction [17, 20]. Gomez et al. [23, 29] included four parallel reactions into their model, whereas Meszaros et al. [21] used a model of six first-order reactions and also a model of four reactions, three of which were of second order. In a number of multistage models, secondary reactions of the decomposition of pyrolysis products were considered [4, 6, 8, 19, 26, 27]. Currently available kinetic schemes and models were surveyed in more detail in reviews [30, 31].

A universal model suitable for different types of biomass to describe the process of pyrolysis over a wide range of temperatures, including both isothermal and dynamic conditions, is currently unavailable, although a great number of kinetic models were published.

Rapidly growing grassy plants, such as sorghum, miscanthus, reed, and switchgrass, belong to the promising sources of biomass. The pyrolysis of some of them has been studied [8, 28, 29, 32, 33]. Sorghum can be a promising crop from an energy point of view for Russia, Ukraine, Moldavia, and Uzbekistan because it is widely cultivated in these countries. The pyrolysis of sorghum biomass was examined by Piskorz et al. [32], who studied the dependence of the yield of pyrolytic liquid on temperature and reaction time. However, the kinetic studies of the pyrolysis of sorghum were not carried out.

The aim of this work was to study the kinetics of pyrolysis of sorghum biomass in an inert atmosphere under isothermal conditions and to develop a kinetic model for satisfactorily describing experimental data. The results obtained can be used for a further development of the process of pyrolysis of rapidly growing grassy plants as an energy source.

EXPERIMENTAL

The samples of sorghum biomass as granules 6 mm in diameter and from 1 cm to several centimeters in length were provided by the EUBIA Association (Belgium). The granules were ground using a mill and separated on sieves into several fractions. A fraction of 100–125 μm was used in the experiments. The elemental composition of the sorghum biomass was determined using an EA-3000 CHNS analyzer at the Vorozhtsov Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk. The moisture content of the biomass was determined based on a sample weight change after drying at a temperature of 105°C for 1.5 h, and the ash content was found by sample calcination in a muffle furnace at 580°C for 3.5 h. The test samples had the following characteristics: moisture content, 4.6%; ash content, 4.4%. Elemental composition: C, 46.2%; H, 6.2%; N, 1.4%; and O, 46.2% (the oxygen content was calculated by difference).

The pyrolysis of the samples was performed in a quartz reactor in an atmosphere of argon. The flow rate of argon was 20 l/h. The reactor was equipped with a McBain balance for measuring the sample weight in the course of the experiment. A quartz basket suspended with the aid of a thread to a calibrated quartz spring was placed inside the reactor. The spring modulus of elongation was 0.146 mm/mg. The expansion of the spring was measured with a cathetometer to within 0.03 mm. The accuracy of sample weight measurements was 0.2 mg.

The pyrolysis of biomass samples was studied under isothermal conditions at 250, 340, 360, 380, and 400°C. A 50-mg sample was rapidly placed in a preheated reactor; thereafter, changes in the sample weight in the course of the experiment were determined at regular intervals from 1 to 5 min. The sample weight was referred to the initial sample weight and the dependence of the relative weight was plotted as a function of pyrolysis time. Henceforth, the relative weight is referred to as the sample weight.

The correctness of isothermal experiments can be doubted because of the presence of a nonisothermal section in TGA curves, in which the sample was heated from room temperature to the reactor temperature. The heating time of a sample particle can be estimated using the thermal conductivity equation

$$\tau = \frac{l^2 \rho c}{\lambda}, \quad (1)$$

where τ is the characteristic time of particle heating, l is the characteristic particle size, ρ is density, c is the specific heat capacity, and λ is the thermal conductivity of the particle. At the particle size $l = 1.1 \times 10^{-4}$ m and the physical parameters characteristic of the materials of plant origin [34], namely, $\rho = 0.5 \times 10^3$ kg/m^3, $c = 1.5 \times 10^3$ K kg^{-1} K^{-1}, and $\lambda = 0.1$ W m^{-1} K^{-1}, the characteristic time of particle heating is about 0.1 s. The maximum rate of sample weight change in the rapid section was reached at a temperature of 400°C; according to the experimental data (Fig. 1), it was about 10^{-2} s^{-1}. Correspondingly, the sample weight changed by 10^{-3} (or 0.1%) in time $\tau = 0.1$ s. Thus, the change in the sample weight in the initial section of particle heating can be ignored and the experimental conditions can be considered isothermal.

RESULTS

Figure 1 shows changes in the sample weights in the course of experiments performed at different temperatures. At each temperature, the TGA curve exhibited two characteristic sections with different weight change rates, rapid and slow. Initially, the sample weight rapidly decreased to a certain level for several minutes; thereafter, it continued to slowly decrease at an almost constant rate. In this case, the duration of the rapid section and the sample weight at the end of this section decreased with temperature. These qualitative characteristics of the isothermal process of the pyrolysis of sorghum biomass, namely, a decrease in

the yield of solid carbon residue and an acceleration of lignocellulose destruction with temperature, are consistent with published data obtained upon the pyrolysis of other substances [3, 4, 6, 8, 35].

KINETIC SIMULATION

The aim of the kinetic simulation was to find a kinetic model for satisfactorily describing the experimental data.

Taking into account the high temperature of the sample, we can assume that moisture present in the biomass was evaporates in the rapid section of pyrolysis. In view of the low moisture content of the sample (about 4%) and the short duration of a rapid section, we assumed that moisture was absent from the sample already at the second measurement point. Correspondingly, the weight of the dry sample at the point in time of the onset of measurements was $m_0 = 0.96$.

The formal mathematical analysis of the TGA curves showed that they were adequately described (with an absolute error of 0.01) by a function that includes the sum of a constant and two exponents (rapidly and slowly decreasing exponents). Thus, the process of pyrolysis can be described by a mechanism that consists of first-order reactions.

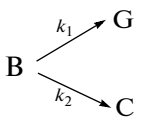
The search for the best model was performed by going from simple to more complicated models. The kinetic parameters were determined by the least squares technique, comparing experimental data with the results of calculations according to the model. In this case, the following function was minimized:

$$F = \sum_n (m_n^{\exp} - m_n^{\text{calc}})^2, \qquad (2)$$

where n is the experimental point number, and $m_n^{\exp}$ and m_n^{calc} are the experimental and calculated sample weights at the nth experimental point, respectively. The minimization was performed both for each individual experiment and over all of the experiments simultaneously, excluding points corresponding to the initial moment of time. The calculations were carried out with the use of the Mathcad program.

Kinetic Scheme 1

The simplest kinetic scheme, which considers the temperature dependence of the yield of carbonaceous substance at an infinite time of pyrolysis is given below:



Scheme 1. Single-component single-stage kinetic scheme including two parallel reactions.

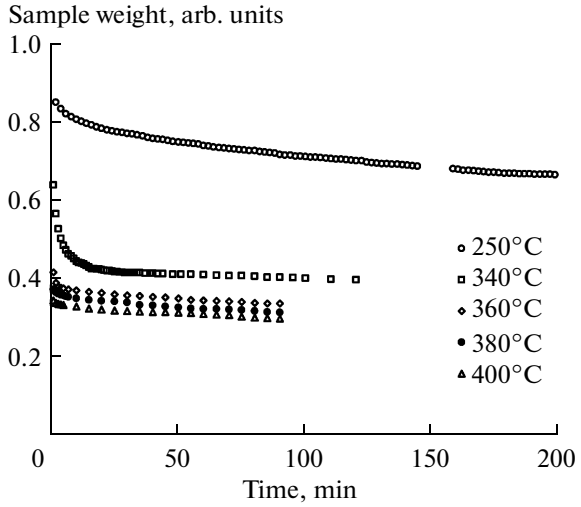


Fig. 1. Dependence of sample weight on reaction time at various temperatures.

According to Scheme 1, biomass B decomposes in two parallel first-order reactions into volatile products G and carbon substance C with the reaction rate constants k_1 and k_2, respectively [30].

Scheme 1 corresponds to the following equations and initial conditions:

$$\frac{dm_B}{dt} = -(k_1 + k_2)m_B, \qquad m_B(0) = m_0, \qquad (3)$$

$$\frac{dm_C}{dt} = k_2 m_B, \qquad m_C(0) = 0, \qquad (4)$$

where m_B and m_C are the weights of the biomass and the carbon substance, respectively, and t is the reaction time.

The solution of the set has the form

$$m_B = m_0 e^{-(k_1+k_2)t}, \qquad (5)$$

$$m_C = m_0 \frac{k_2}{k_1 + k_2}\left(1 - e^{-(k_1+k_2)t}\right). \qquad (6)$$

The sample weight m is the sum of the weights of the biomass and the carbon substance:

$$m = m_B + m_C = m_0 \frac{k_2 + k_1 e^{-(k_1+k_2)t}}{k_1 + k_2}. \qquad (7)$$

The yield of carbon substance m_∞ at an infinite time of pyrolysis is

$$m_\infty = m_0 \frac{k_2}{k_1 + k_2}. \qquad (8)$$

The temperature dependence of the yield of carbon substance follows from the fact that the reaction rate constants depend on temperature in accordance with the Arrhenius equation

$$k_i = A_i \exp\left(-\frac{E_i}{RT}\right), \qquad (9)$$

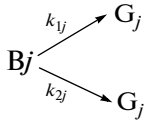
where i is the reaction rate constant number; A_i and E_i are the preexponential factor and the activation energy of the i reaction, respectively; R is the gas constant; and T is temperature.

A disadvantage of Scheme 1 is the presence of only one exponent in Eq. (7), which can describe only one section of pyrolysis, either rapid or slow, but it is impossible to satisfactorily describe the process as a whole. To adequately describe the entire process, the time dependence of sample weight should include no less than two exponents. Two versions are the simplest. According to the first version, biomass consists of several components, and some of them are rapidly pyrolyzed, whereas the others are slowly pyrolyzed. According to the second version, the pyrolysis of biomass occurs in two stages: at the first stage, the biomass is rapidly pyrolyzed with the formation of primary carbon substance and volatile products, whereas the primary carbon substance is decomposed into secondary carbon substance and volatile products at the second slow stage. More complicated combined versions are also possible.

Subsequently, we tested three mechanisms (Kinetic Schemes 2–4), which contained Scheme 1 as a constituent, for describing the process of pyrolysis.

Kinetic Scheme 2

Biomass is considered as the sum of three components: hemicellulose, cellulose, and lignin. The pyrolysis of each particular component occurs according to Scheme 2, where j is the component number.



Scheme 2. Three-component single-step kinetic scheme including two parallel reactions for each component.

Scheme 2 is a single-step three-component kinetic scheme. The decomposition of hemicellulose and cellulose corresponds to a rapid section in the TGA curve, whereas the decomposition of lignin corresponds to a slow section. In this case, the time dependence of sample weight has the form

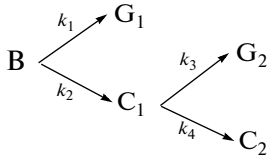
$$m = \sum_j m_{0j} \frac{k_{2j} + k_{1j} e^{-(k_{1j}+k_{2j})t}}{k_{1j} + k_{2j}}, \qquad (10)$$

where m_{0j} is the weight of the jth component at the initial point in time, and k_{1j} and k_{2j} are the reaction rate constants of formation of volatile products and carbon substance, respectively, in the pyrolysis of the jth component.

We managed to choose model parameters (m_{0j}, k_{1j}, and k_{2j}) at each particular temperature so that the process was described with an absolute accuracy of 0.003; however, we failed to adequately describe simultaneously all of the experiments with the use of a set of parameters (m_{0j}, A_{1j}, A_{2j}, E_{1j}, and E_{2j}).

Kinetic Scheme 3

The next scheme tested is shown below:



Scheme 3. Single-component two-stage kinetic scheme including four reactions.

Scheme 3, which was used by Di Blasi and Lanzetta [4, 8], is a single-component two-stage kinetic scheme. Reactions 1 and 2 correspond to a rapid section of the pyrolysis curve, whereas reactions 3 and 4 correspond to a slow section. The sample weight is the sum of the weights of biomass B, carbon substance C_1 (m_{C1}), and carbon substance C_2 (m_{C2}):

$$m = m_B + m_{C1} + m_{C2}. \qquad (11)$$

Scheme 3 corresponds to the following equations and initial conditions:

$$\frac{dm_B}{dt} = -(k_1 + k_2) m_B, \qquad m_B(0) = m_0, \qquad (12)$$

$$\frac{dm_{C1}}{dt} = k_2 m_B - (k_3 + k_4) m_{C1}, \qquad m_{C1}(0) = 0, \qquad (13)$$

$$\frac{dm_{C2}}{dt} = k_4 m_{C1}, \qquad m_{C2}(0) = 0. \qquad (14)$$

A solution to the set of Eqs. (12)–(14) has the form

$$m_B = m_0 e^{-(k_1+k_2)t}, \qquad (15)$$

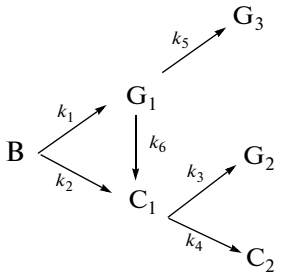
$$\frac{m_{C1}}{m_0} = \frac{k_2}{k_1 + k_2 - k_3 - k_4}\left(e^{-(k_3+k_4)t} - e^{-(k_1+k_2)t}\right), \qquad (16)$$

$$\frac{m_{C2}}{m_0} = \frac{k_2 k_4}{k_1 + k_2 - k_3 - k_4}\left(\frac{1 - e^{-(k_3+k_4)t}}{k_3 + k_4} - \frac{1 - e^{-(k_1+k_2)t}}{k_1 + k_2}\right). \qquad (17)$$

With the use of Scheme 3, as well as Scheme 2, model parameters (k_i) were chosen for description with an absolute accuracy of 0.003; however, we also failed to find a set of parameters (A_i and E_i) for simultaneously describing the results of all of the experiments. Deviations were observed in the rapid segment of a TGA curve. For correcting these deviations, one additional reaction related to the formation of carbon substance from volatile products, which was observed in the pyrolysis of biopetroleum [31], was added to Scheme 3.

Kinetic Scheme 4

The following refined reaction scheme of pyrolysis was proposed:



Scheme 4. Single-component kinetic scheme including six reactions.

Scheme 4 corresponds to the following equations and initial conditions:

$$\frac{dm_B}{dt} = -(k_1 + k_2)m_B, \quad m_B(0) = m_0, \tag{18}$$

$$\frac{dm_{Gl}}{dt} = k_1 m_B - (k_5 + k_6)m_{Gl}, \quad m_{Gl}(0) = 0, \tag{19}$$

$$\frac{dm_{Cl}}{dt} = k_2 m_B + k_6 m_{Gl} - (k_3 + k_4)m_{Cl}, \quad m_{Cl}(0) = 0, \tag{20}$$

$$\frac{dm_{C2}}{dt} = k_4 m_{Cl}, \quad m_{C2}(0) = 0, \tag{21}$$

where m_{G1} is the weight of volatile products G_1.

As in Scheme 3, the sample weight is determined by Eq. (11). A solution to the set of Eqs. (18)–(21) allows us to find the dependence of the weights of biomass and carbon substances C_1 and C_2 on reaction time:

$$\frac{m_B}{m_0} = e^{-k_{12}t}, \tag{22}$$

$$\frac{m_{Cl}}{m_0} = \left(k_2 - \frac{k_1 k_6}{k_{12} - k_{56}}\right)\frac{e^{-k_{34}t} - e^{-k_{12}t}}{k_{12} - k_{34}} + \frac{k_1 k_6}{k_{12} - k_{56}}\frac{e^{-k_{34}t} - e^{-k_{56}t}}{k_{56} - k_{34}} \tag{23}$$

$$\frac{m_{C2}}{m_0} = \left(k_2 - \frac{k_1 k_6}{k_{12} - k_{56}}\right)\frac{k_4}{k_{12} - k_{34}}\left(\frac{1 - e^{-k_{34}t}}{k_{34}} - \frac{1 - e^{-k_{12}t}}{k_{12}}\right) + \frac{k_1 k_6}{k_{12} - k_{56}}\frac{k_4}{k_{56} - k_{34}}\left(\frac{1 - e^{-k_{34}t}}{k_{34}} - \frac{1 - e^{-k_{56}t}}{k_{56}}\right). \tag{24}$$

For brevity, the following designations are used in Eqs. (22)–(24): $k_{12} = k_1 + k_2$, $k_{34} = k_3 + k_4$, and $k_{56} = k_5 + k_6$.

The calculation according to Scheme 4 gave the best description, as compared with those based on Schemes 2 and 3. Table 1 summarizes the numerical values of the obtained kinetic parameters, and Fig. 2 compares the calculated and experimental data. The accuracy of the determination of kinetic parameters was calculated by introducing disturbances into the experimental data with the aid of a random-number generator with an absolute error of 0.004. The standard deviations were calculated using 30 points.

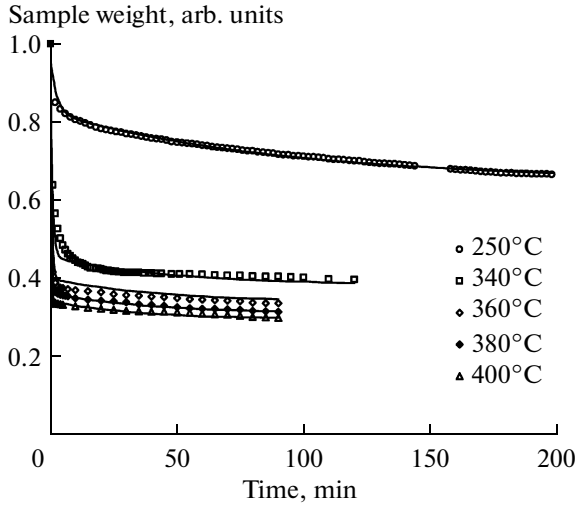


Fig. 2. Comparison between the calculated (points) and experimental (lines) dependences of sample weight on the reaction time at various temperatures.

Table 1. Numerical values of the parameters of a kinetic model for the pyrolysis of sorghum in accordance with Scheme 4

Constant no. (i)	$\ln A_i$ [min^{-1}]	E_i, kJ/mol
1	13.5 ± 0.20	70.9 ± 1.0
2	0.283 ± 0.079	6.12 ± 0.39
3	−3.65 ± 0.10	10.6 ± 0.49
4	−0.050 ± 0.002	20.4 ± 0.26
5	0.573 ± 0.056	0.864 ± 0.022
6	4.04 ± 1.3	26.9 ± 7.6

Table 2. Deviations of calculated curves from the experimental curves, as calculated in accordance with Eq. (25)

Temperature, °C	δ, %
250	0.7
340	3.9
360	5.0
380	1.3
400	1.4

Table 3. Characteristics of wheat straw and cornstalk biomasses [8]

Characteristic	Wheat straw	Corns talks
Ash content, %	10.7	5
Concentration, %:		
hemicellulose	32	35
cellulose	41	42
lignin	18	20

Table 4. Numerical values of kinetic model parameters for the pyrolysis of wheat straw and corn stalks in accordance with Scheme 3 [8]

Constant no. (i)	Wheat straw		Corn stalks	
	$\ln A_i$, [min^{-1}]	E_i, kJ/mol	$\ln A_i$ [min^{-1}]	E_i, kJ/mol
1	15.7	75.15	21.5	102.7
2	11.2	53.6	15.9	76.95
3	11.2	66.6	15.3	84.6
4	5.13	27.6	5.58	38.1

Quantitatively, the deviation of calculated curves from experimental ones (in the percentages) at each temperature was evaluated by the quantity

$$\delta = 100\sqrt{\frac{\sum_n \left(m_n^{\exp} - m_n^{\text{calc}}\right)^2}{\sum_n \left(m_n^{\exp}\right)^2}}. \quad (25)$$

The calculated deviations given in Table 2 confirm the satisfactory description of experimental data.

DISCUSSION

The preexponential factors and activation energies found for formal models can be correctly compared with published data only on condition that raw material compositions, temperature conditions, and kinetic model structures are similar because these characteristics considerably affect the kinetic parameters. Special features of the composition of grassy biomass, as compared with wood biomass, are a decreased lignin content and an increased ash content. The compounds of K, Na, Fe, and Ca are the constituents of ashes; these compounds serve as catalysts for the pyrolysis of lignocellulose raw materials and influence the quantitative characteristics of the process. There are a few publications on the kinetics of the isothermal pyrolysis of biomasses. As applied to grassy biomass, a publication by Lanzetta and Di Blasi [8], who studied the isothermal pyrolysis of wheat straw and corn stalks and processed experimental data according to Scheme 3, can be noted. Tables 3 and 4 summarize data on the composition of biomasses and the numerical values of kinetic parameters in dimensionalities accepted in this work. Table 3 indicates that wheat and corn biomasses had almost the same lignocellulose composition, but they differ in ash contents by a factor of about 2. In this case, the kinetic parameters of the pyrolysis of these crops were noticeably different (Table 4). It seems obvious that the main reason for this difference consists in different concentrations of alkali and alkaline earth metal compounds, which are catalysts for the pyrolysis of lignocellulose, as already mentioned above. As applied to the pyrolysis of sorghum, the kinetic parameters of the model proposed, with the exception of the first coefficient, which corresponds to the main change in sample weight, are also strongly different from the parameters found by Lanzetta and Di Blasi [8]. This is likely due to the fact that the compositions of sorghum biomass on the one hand and wheat and corn biomasses on the other are considerably different, as well as the structures of kinetic models. Qualitatively, the TGA curves obtained in the study of the pyrolysis of wheat, corn, and sorghum biomasses are similar, whereas they are quantitatively different to a considerable extent. Di Blasi [31] also noted the wide scatter of kinetic model parameters; this is likely characteristic of a formal approach.

Thus, based on an example of sorghum, we investigated the pyrolysis of the rapidly growing grassy biomass under isothermal conditions. The pyrolysis of ground samples of size 100–125 μm was carried out in an inert atmosphere at temperatures of 250, 340, 360, 380, and 400°C with the use of TGA. The TGA curves at each particular temperature consisted of two sections (rapid and slow) with different rates of changes in the sample weight. The duration of the rapid section and the sample weight at the end of this section decreased with temperature. For describing the experimental curves, we used the well-known kinetic schemes of the pyrolysis of biomass and a new scheme, which is characterized by the presence of a stage of the formation of intermediate carbon substance from the volatile products of biomass decomposition. The best quantitative description was achieved with the use of the last model. Note that the proposed model, which includes the decomposition of volatile pyrolysis products into lighter compounds and carbon material, more correctly describes real chemical processes that occur on the thermal decomposition of lignocellulose than Schemes 2 and 3.

Thus, a single-component kinetic model including six first-order reactions can be used for describing the pyrolysis of grassy biomass under isothermal conditions. This model can be applied to grassy biomass whose ash residue is close to sorghum in elemental composition.

The experimental results can be used to develop processes for the manufacture of second-generation biofuels from plant biomass.

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REFERENCES

1. *Biomass Conversion Processes for Energy and Fuels*, Sofer, S.S. and Zaborsky, O.R., Eds., New York: Plenum, 1981, p. 420.
2. Yaman, S., *Energy Convers. Manage.*, 2004, vol. 45, p. 651.
3. Koufopanos, C.A., Maschio, G., and Lucchesi, A., *Can. J. Chem. Eng.*, 1989, vol. 67, p. 75.
4. Di Blasi, C. and Lanzetta, M., *J. Anal. Appl. Pyrolysis*, 1997, vols. 40–41, p. 287.
5. Caballero, J.A., Conesa, J.A., Font, R., and Marcilla, A., *J. Anal. Appl. Pyrolysis*, 1997, vol. 42, p. 159.
6. Miller, R.S. and Bellan, J., *Combust. Sci. Technol.*, 1997, vol. 126, p. 97.
7. Teng, H. and Wei, Y.C., *Ind. Eng. Chem. Res.*, 1998, vol. 37, p. 3806.
8. Lanzetta, M. and Di Blasi, C., *J. Anal. Appl. Pyrolysis*, 1998, vol. 44, p. 181.
9. Orfao, J.J.M., Antunes, F.J.A., and Figueiredo, J.L., *Fuel,* 1999, vol. 78, p. 349.
10. Helsen, L. and Bulck, E., *J. Anal. Appl. Pyrolysis*, 2000, vol. 53, p. 51.
11. Guo, J. and Lua, A.C., *J. Therm. Anal. Calorim.*, 2000, vol. 59, p. 763.
12. Sorum, L., Gronli, M.G., and Hustad, J.E., *Fuel*, 2001, vol. 80, p. 1217.
13. Garsia-Perez, M., Chaala, A., Yang, J., and Roy, C., *Fuel*, 2001, vol. 80, p. 1245.
14. Gronli, M.G., Varhegyi, G., and Di Blasi, C., *Ind. Eng. Chem. Res.*, 2002, vol. 41, p. 4201.
15. Vlaev, L.T., Markovska, I.G., and Lyubchev, L.A., *Thermochim. Acta*, 2003, vol. 406, p. 1.
16. Vamvuka, D., Karakas, E., Kastanaki, E., and Grammelis, P., *Fuel*, 2003, vol. 82, p. 1949.
17. Manya, J.J., Velo, E., and Puigjaner, L., *Ind. Eng. Chem. Res.*, 2003, vol. 42, p. 434.
18. Gonzalez, J.F., Encinar, J.M., Canito, J.L., Sabio, E., and Chacon, M., *J. Anal. Appl. Pyrolysis*, 2003, vol. 67, p. 165.
19. Branca, C. and Di Blasi, C., *J. Anal. Appl. Pyrolysis*, 2003, vol. 67, p. 207.
20. Gomez, C.J., Manya, J.J., Velo, E., and Puigjaner, L., *Ind. Eng. Chem. Res.*, 2004, vol. 43, p. 901.
21. Meszaros, E., Varhegyi, G., Jakab, E., and Marosvolgyi, B., *Energy Fuels*, 2004, vol. 18, p. 497.
22. Capart, R., Khesami, L., and Burnham, A.K., *Thermochim. Acta*, 2004, vol. 417, p. 79.
23. Gomez, C.J., Varhegyi, G., and Puigjaner, L., *Ind. Eng. Chem. Res.*, 2005, vol. 44, p. 6650.
24. Ayllón, M., Gea, G., Murillo, M.B., Sánchez, J.L., and Arauzo, J., *J. Anal. Appl. Pyrolysis*, 2005, vol. 74, p. 445.
25. Radmanesh, R., Courbariaux, Y., Chaouki, J., and Guy, C., *Fuel*, 2006, vol. 85, p. 1211.
26. Molto, J., Font, R., Conesa, J.A., and Martin-Gullon, I., *J. Anal. Appl. Pyrolysis*, 2006, vol. 76, p. 124.
27. Miranda, R., Blanco, C.S., Bustos-Martinez, D., and Vasile, C., *J. Anal. Appl. Pyrolysis*, 2007, vol. 80, p. 489.
28. De Jong, W., Pirone, A., and Wojtowicz, M.A., *Fuel*, 2003, vol. 82, p. 1139.
29. Gomez, C.J., Varhegyi, G., and Puigjaner, L., *Ind. Eng. Chem. Res.*, 2005, vol. 44, p. 6650.
30. Conesa, J.A., Marcilla, A., Caballero, J.A., and Font, R., *J. Anal. Appl. Pyrolysis*, 2001, vols. 58–59, p. 617.
31. Di Blasi, C., *Prog. Energy Combust. Sci.*, 2008, vol. 34, p. 47.
32. Piskorz, J., Majerski, P., Radlein, D., Scott, D.S., and Bridgwater, A.V., *J. Anal. Appl. Pyrolysis*, 1998, vol. 46, p. 15.
33. Bridgeman, T.G., Darvell, L.I., Jones, J.M., Williams, P.T., Fahmi, R., Bridgwater, A.V., Barraclough, T., Shield, I., Yates, N., Thain, S.C., and Donnison, I.S., *Fuel*, 2007, vol. 86, p. 60.
34. *Tablitsy fizicheskikh velichin: Spravochnik* (Physical Quantities in Tables: A Handbook), Kikoin, I.K., Ed., Moscow: Atomizdat, 1976.
35. Bridgewater, A.V., *Appl. Catal., A*, 1994, vol. 116, p. 5.