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## Investigation of the Oxidation of Powdered Biofuel with Different Lignin Content: A Rough Assessment of Reactivity During Oxidation

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### Abstract

The oxidation of biofuel samples with different lignin content (10, 20 and 70 %) was studied. The kinetic parameters of combustion reactions were obtained, which allowed us to consider the process as a two-stage one. The sample with 20 % lignin content was shown to have a high reactivity in oxidation reactions.

**Keywords:** biofuel, lignin, heat of combustion, oxidation kinetics, kinetic equations

### INTRODUCTION

Plant raw materials hold a great but insufficiently used at present energy-bearing potential [1–3]. It is known that there are up to 5 units of irrationally used wastes (straw, husk, fibres and dust of plant origin) per 1 unit of corn [4]. At present, combustion is the main method to utilize the wastes of this kind. Only an insignificant part of the biomass is used for obtaining energy for household purposes [5]. The development of new technologies of combustion to produce energy is held back by the disadvantages characteristic of lignocellulose fuel [6, 7]: instability of composition and heating value, hindered control of combustion rate, difficulties in arranging the uniform supply of fuel, high investment cost of energy-generating installations and boilers.

The majority of these disadvantages are connected with the heterogeneity of plant raw mate-

rial, which may be eliminated only by making a homogeneous mass of pellets and bricks [8, 9] or by fine grinding of the biomass into powder fuel for flare combustion [10, 11]. In both cases, biomass grinding and powder mixing of the components differing from each other in chemical composition are carried out. The product is uniform with respect to dispersion and heat capacity, it is easily transportable and may be dosed.

During the recent years, new methods are under development to enhance the heating value of lignocellulose fuel, first of all those based on an increase in the mass fraction of lignin by means of aerodynamic separation of the tissues of plant raw material differing from each other in chemical composition [12, 13], and those based on the mechanochemical removal of the carbohydrate part of lignocellulose, which is carried out in the cycle of bioethanol production [14]. Thus obtained side product of biotechnological saccharification of

the plant raw material has an increased heat of combustion, small particle size, and may be used as powder fuel directly at the same biotechnological enterprise [12].

In spite of the anticipated progress in the studies of dispersed powder fuel, the information on lignocellulose oxidation is still rather scarce [15] and mainly deals with applied thermal physical aspects of burning [16], methods of homogenization and dosage of fuel [17, 18], the removal of the released heat *etc.* [19].

The goal of the present work was to study the kinetics of the oxidation of powder lignocellulose fuel with different chemical composition, revelation and characterization of the stages of the chemical oxidation process.

## EXPERIMENTAL

### Sample preparation

Wheat straw from the Kozhevnikovskiy District of the Tomsk Region was used as the initial lignocellulose raw material. Its chemical composition was determined according to the procedure described in [20], mass %: lignin 18.3, cellulose 32.9, hemicellulose 33.6, extractive substances 9.4; humidity 5.9 %, ash content 8.5 %. To prepare the samples of powder fuel, wheat straw was ground in a centrifugal roller mill TM-3 (JSC Novits, Russia) with the rotor frequency of 2800 r.p.m.

The samples of powder fuel with lignin content 10, 20 and 70 mass % were obtained by mixing the weighted portions of ground wheat straw with the calculated amount of pure cellulose (Sigma Aldrich, CAS # 9004-34-6) and lignin (Sigma Aldrich, CAS # 8068-05-1). In order to average the composition, the mixtures were thoroughly stirred and attrited in an agate mortar for 5 min.

The heat of combustion (the high heating value) of biofuel samples was determined with the

help of an adiabatic calorimeter ABK-1 (Russia) according to the procedure described in [21]. For this purpose, the samples 0.7–0.8 g in mass were put into a calorimetric vessel and burnt in the atmosphere of oxygen at a pressure of 30 atm. The operation of the calorimeter and determination of the amount of released heat were maintained by the control system based on the personal computer.

### Thermal analysis

Thermogravimetric (TG) analysis was carried out with the help of a Netzsch TG 209 F1 thermal analyzer (Germany). Experiments were carried out in the inert gas medium (helium) and the oxidative environment (80 % argon/20 % oxygen). The heating rate was 5, 10 and 20 K/min. To avoid sample overheating and to decrease the contribution from the gas-phase pyrolysis of volatile substances outside the crucible, small sample masses were involved (~2 mg).

### Kinetic analysis under non-isothermal conditions

Thermogravimetric data were processed with the help of the computer programme NetzschThermokinetics 2 (version 2004.05). A special software module allows processing TG curves recorded with different heating rates, and calculating activation energy ( $E$ ) without preliminary information on the kinetic topochemical equation. To calculate  $E$  for each experimental point of transformation (the transformation degree  $\alpha$  within the range 0.005 to 0.995), Friedmann method was used.

On the basis of the resulting TG data, topochemical equations describing the heterogeneous chemical reactions at the interface were determined: the growth of the nuclei of the new phase, and the diffusion-driven propagation of the reaction front. The calculation was carried out on the basis of the differential procedure proposed by Borchardt–Daniels within the approach with multiple linear regression. The range for  $\alpha$  during calculation was chosen on the basis of the constancy of calculated kinetic parameters from Friedmann's analysis.

The F-test was used to search for the best kinetic description of the process and for the statistical management of the resulting equation. It analyzes the residual dispersion of separate models with respect to each other and reveals the statistical difference between the models. If  $F_{\text{exp}}(1)$

TABLE 1

Chemical composition and heat of combustion of biofuel samples with different lignin content

Parameter	Lignin content, mass %		
	10	20	70
Cellulose content, mass %	63.2	32.2	12.1
Hemicellulose content, mass %	18.5	32.9	12.3
Heat of combustion, MJ/kg	17.0	17.5	22.2

$\approx F_{\text{exp}}(2)$  for two equations, there are no reasons to expect that one of the models is better in characterizing the experiment. The statistical quantile  $F_{\text{crit}}$  was obtained for the significance level 0.05.

If calculation gave two or three kinetic equations with close values in their correlation coefficients but with noticeably different values in kinetic parameters, an equation with  $E$  most close to the value obtained experimentally was chosen.

As a rule, a random error of  $E$  determination for oxidation was  $\sim 10\%$ . After calculation by means of nonlinear regression, the NetzschThermokinetics 2 computer programme allows estimating the contribution from each stage of the multistage process into the error. New studies of non-isothermal kinetics [22–24] were taken into account in the calculations, and general recommendations for carrying out kinetic calculations according to thermal analysis data were used.

## RESULTS AND DISCUSSION

The data of TG analysis of straw samples under variations of experimental conditions (composition of the gas medium and sample heating rate) and sample composition (lignin content) are presented in Fig. 1–4. It turned out that, for other conditions being equal, the temperature range of gas evolution is shifted to lower temperatures in compari-

son with the temperature range of pyrolysis (see Fig. 1). Therefore, accelerated oxidation of the released gases does not occur, and straw oxidation is a solid-phase reaction.

The temperature range of the oxidation process depends on lignin content and shifts to higher temperatures with an increase in lignin content in the sample (see Fig. 2).

The curves of mass loss recorded with different heating rates (5, 10 and 20 K/min), depending on temperature  $T$  (see Fig. 3, 4) and time of reaction (Fig. 5, 6) were used for the kinetic investigation. A comparison of experimental and calculated data is most convincing for the second version. Rather small weighted portion of the sample was used ( $\sim 2$  mg), however, it was impossible to exclude its ignition and overheating, which is evidenced by the inclination of curve 1 (see Fig. 3).

### *Straw sample with lignin content 70 mass % (particle size less than 100 $\mu\text{m}$ )*

The data obtained using the calculation module without the model are shown in Fig. 7. Activation energy may be considered as a variable in agreement with Friedmann's method, so oxidation is a multistage reaction.

The scheme providing the best compliance with the process involves two stages with consecutive ( $A \rightarrow B \rightarrow C$ ) or parallel ( $A \rightarrow B$ ;  $C \rightarrow D$ ) reactions

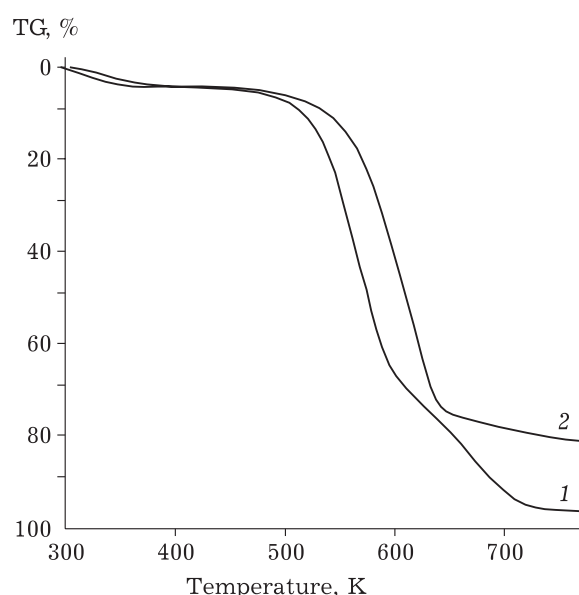


Fig. 1. Data of TG analysis of straw sample (10 mass % lignin) in the flow of argon/oxygen (1) and helium (2). Heating rate: 10 K/min.

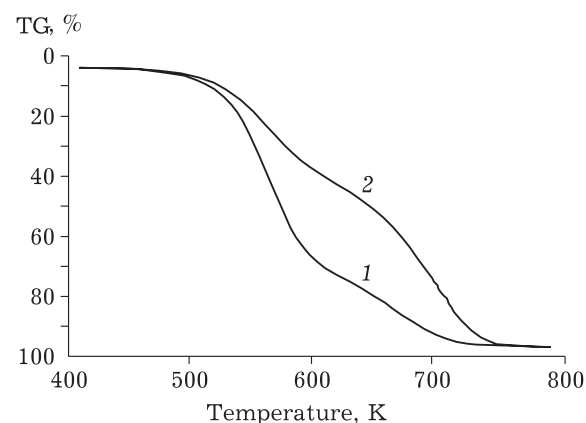


Fig. 2. Data of TG analysis of straw samples with lignin content 20 (1) and 70 (2) mass % in the flow of argon/oxygen. Heating rate: 10 K/min [12].

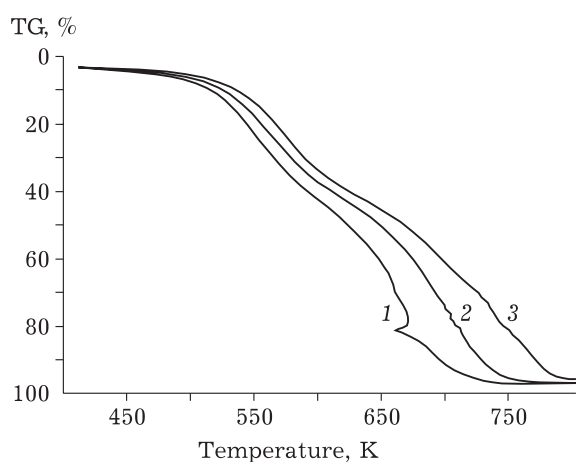


Fig. 3. Data of TG analysis of straw sample (70 mass % lignin) in the flow of argon/oxygen. Heating rate, K/min: 5 (1), 10 (2) and 20 (3).

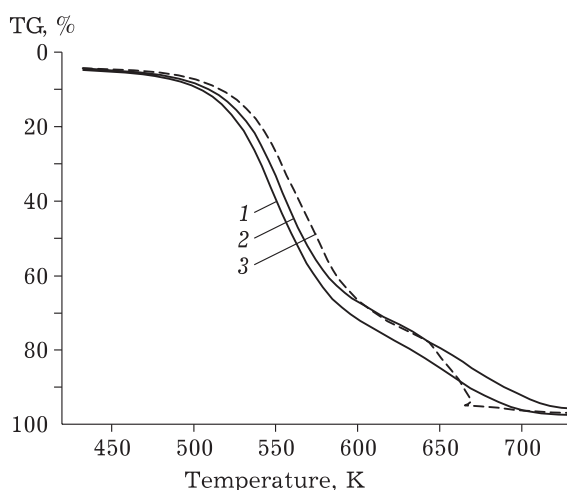


Fig. 4. Data of TG analysis of straw sample (20 mass % lignin) in the flow of argon/oxygen. Heating rate, K/min: 5 (1), 10 (2) and 20 (3).

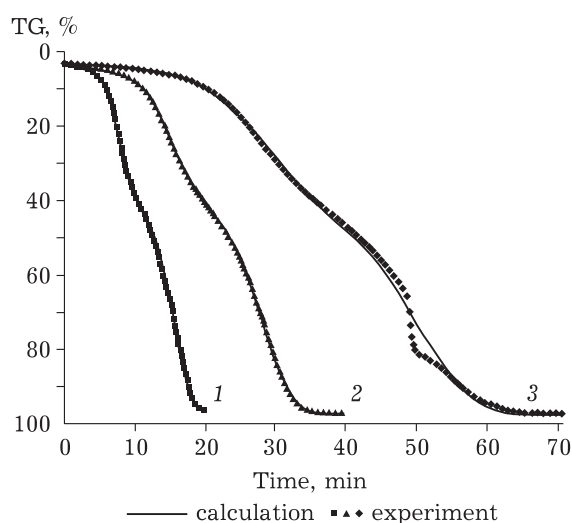


Fig. 5. Processing of the data of TG analysis of straw sample (70 mass % lignin). TG curves of fitting nonlinear regression modeled by two consecutive (A → B → C) reactions (An equations). Heating rate, K/min: 20 (1), 10 (2) and 5 (3).

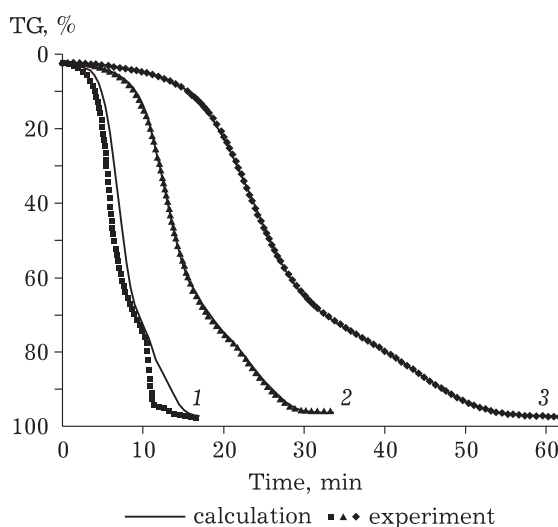


Fig. 6. Processing of the data of TG analysis of straw sample (20 mass % lignin). TG curves of fitting nonlinear regression modeled by two consecutive (A → B → C) reactions (An equations). Heating rate, K/min: 20 (1), 10 (2) and 5 (3).

described by two Avrami–Erofeev equations (An).

A comparison of the experimental calculated curves (lines) according to Avrami–Erofeev equations for the models described by two serial or parallel reactions is presented in Fig. 5 and 8.

Version 1. Two consecutive reactions (see Fig. 5):

I. A → B.  $f_1(\alpha) = (1 - \alpha)/[-\ln(1 - \alpha)]^{1.2}$ ,  $E_1 = 175 \pm 7$  kJ/mol,  $\lg A = 14.0 \pm 0.7$ .

II. B → C.  $f_2(\alpha) = (1 - \alpha)^{0.17}$ ,  $E_2 = 74 \pm 1$  kJ/mol,  $\lg A = 3.1 \pm 0.1$ .

The correlation coefficient is equal to 0.999744.

Here  $f(\alpha)$  is the topochemical equation;  $\alpha$  is the degree of transformation during decomposition

(from 0.00 to 1.00);  $E$  is activation energy;  $A$  is the preexponential factor.

Different topochemical equations  $f(\alpha)$  describe the progress of the reaction within the space of the solid phase: nucleation, chemical reaction at the interface, diffusion processes.

Version 2. Two parallel reactions (see Fig. 8):

I. A → B.  $f_1(\alpha) = (1 - \alpha)/[-\ln(1 - \alpha)]^{1.4}$ ,  $E_1 = 185 \pm 10$  kJ/mol,  $\lg A = 15 \pm 1$ .

II. C → D.  $f_2(\alpha) = (1 - \alpha) \cdot [-\ln(1 - \alpha)]^{0.17}$ ,  $E_1 = 77 \pm 1$  kJ/mol,  $\lg A = 3.3 \pm 0.1$ .

Correlation coefficient is equal to 0.999430.

There are only small differences between the

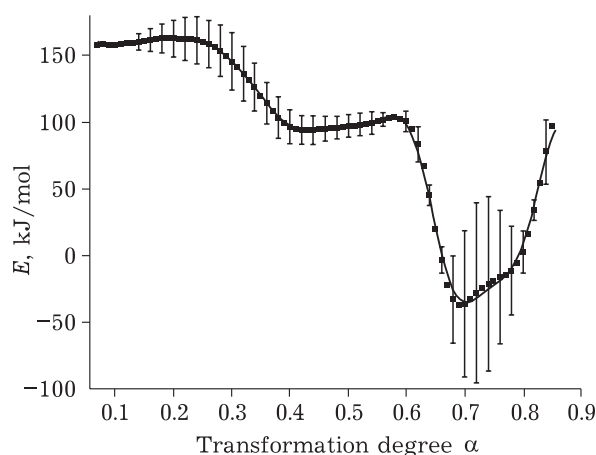


Fig. 7. Friedmann analysis of straw oxidation (70 mass % lignin): dependence of activation energy  $E$  on transformation degree  $\alpha$ . Perpendicular lines show the square mean deviation.

kinetic parameters of these two versions. For the model described by two parallel reactions (see Fig. 8), the computer programme used in this study allows evaluating the contributions from each stage (as a part of mass loss,  $\Delta m$ ) after the calculation of the nonlinear regression. The first stage of mass loss ( $A \rightarrow B$ ) corresponds to 38 mass %, and the second stage of mass loss ( $C \rightarrow D$ ) to 62 mass % of complete oxidation.

It is usually accepted that the three main components of straw start to oxidize within different temperature ranges:  $\approx 450$  K (hemicellulose and lignin);  $\approx 540$  K (cellulose) [24]. A possible explanation is: for a sample with high lignin content, these three main components of straw are oxidized in two steps – the first stage (420–620 K) is the oxidation of hemicellulose, and the second stage (420–800 K) is the oxidation of lignin and cellulose.

#### Straw sample with lignin content 20 mass % (particle size less than 100 $\mu\text{m}$ )

The experimental data (see Fig. 4) for the straw sample with lignin content 20 mass % were processed according to the above-described procedure for the sample with lignin content 70 %. The following equations describing oxidation as a two-stage process with consecutive (see Fig. 6) or parallel (see Fig. 9) reactions.

Two consecutive reactions (see Fig. 6):

I.  $A \rightarrow B$ .  $f_1(\alpha) = (1 - \alpha) / [-\ln(1 - \alpha)]^{0.31}$ ,  $E_1 = 133 \pm 7$  kJ/mol,  $\lg A = 10.0 \pm 1$ .

II.  $B \rightarrow C$ .  $f_2(\alpha) = (1 - \alpha) \cdot [-\ln(1 - \alpha)]^{0.17}$ ,  $E_1 =$

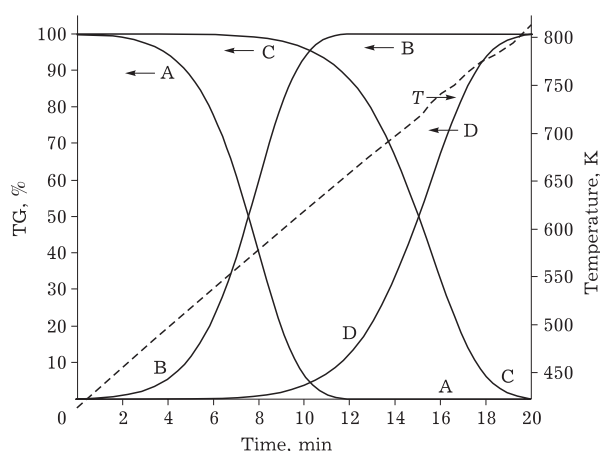


Fig. 8. Oxidation of straw samples (70 mass % lignin). Time dependence of the yield for each reagent during decomposition. Calculation corresponds to the model of a two-stage process described by two parallel reactions ( $A \rightarrow B$ ;  $C \rightarrow D$ ). Heating rate 20 K/min.

$155 \pm 1$  kJ/mol,  $\lg A = 10.0 \pm 1$ .

The correlation coefficient is equal to 0.991363.

Two parallel reactions (see Fig. 9):

I.  $A \rightarrow B$ .  $f_1(\alpha) = (1 - \alpha) / [-\ln(1 - \alpha)]^{0.28}$ ,  $E_1 = 134 \pm 2$  kJ/mol,  $\lg A = 10.3 \pm 0.2$ .

II.  $C \rightarrow D$ .  $f_2(\alpha) = (1 - \alpha) / [-\ln(1 - \alpha)]^{1.22}$ ,  $E_1 = 155 \pm 4$  kJ/mol,  $\lg A = 10.1 \pm 0.3$ .

The correlation coefficient is equal to 0.999779.

A comparison between experimental and calculation data for consecutive processes (see Fig. 6) and the time dependence of oxidation and the appearance of initial and final products (see Fig. 9) is presented as an example. According to the model obtained for parallel reactions, the first stage ( $A \rightarrow B$ ) corresponds to 60 % mass loss, while the second stage ( $C \rightarrow D$ ) accounts for 40 % mass loss during the oxidation.

For the sample with low lignin content, the three main components of straw are oxidized in two steps: the first stage (420–620 K) is the oxidation of hemicellulose and lignin, and the second stage (420–800 K) is the oxidation of cellulose. Unlike for the sample with high lignin content, in this case the oxidation is shifted to lower temperature range. Within temperature range 420–620 K for samples with 20 and 70 mass % lignin content, 60 and 40 % of the biomass are oxidized, respectively.

A comparison between the kinetic parameters obtained for the oxidation of straw samples with low (20 mass %) and high (70 mass %) lignin oxidation allows concluding that the former sample possesses higher reactivity in oxidation reactions.

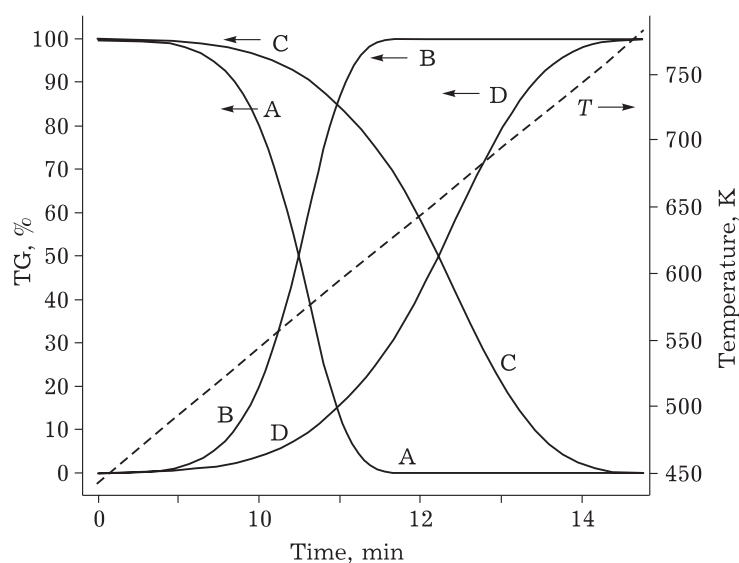


Fig. 9. Oxidation of straw samples (20 mass % lignin). Time dependence of the yield for each reagent during decomposition. Calculation corresponds to the model of two-stage process described by two parallel reactions ( $A \rightarrow B$ ;  $C \rightarrow D$ ). Heating rate is 20 K/min.

## CONCLUSION

It is demonstrated that the kinetics of the oxidation of straw samples with different lignin content may be described using a model of the two-stage process, including two consecutive or parallel reactions. It was established that the kinetic parameters and correlation coefficients are practically independent of the version of calculations with parallel or consecutive reactions. Dependence of the kinetic parameters of biofuel oxidation on its chemical composition was revealed. Within temperature range 420–620 K, for samples with 20 and 70 mass % lignin content, 60 and 40 % of the biomass is oxidized, respectively, which is due to a broad range of lignin oxidation and consecutive oxidation of hemicellulose and cellulose. The kinetic description (topochemical equation, activation energy and the preexponential factor) is formal and may be used for preliminary calculation of the oxidation process for mixtures under isothermal conditions.

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