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# STUDY OF THE KINETICS OF THERMAL DECOMPOSITION OF THE RICE HUSKS PURIFIED FROM CELLULOSE

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## Abstract

**A relevant task of today's materials science is enhancing the characteristics of the materials combined with reducing energy consumption and environmental impact during their synthesis. Silicon dioxide is one of the materials for an extremely wide range of application. Currently, the requirements for the operational characteristics of silicon dioxide concern the production of nanosized amorphous silicon dioxide of high purity. The production of silicon dioxide can be made environmentally friendly by using the rice husks as a renewable and cheap raw material. The technology for production of silicon dioxide from the rice husks is less energy-consuming in comparison with traditional processing of quartz and this technology produces a significantly lower pollution impact on the environment. To obtain high purity silicon dioxide from the rice husks, the authors have proposed to extract the amorphous component of cellulose prior to the heat treatment of plant raw materials. This operation was carried out during 6 hours at a temperature of 100 °C with stirring the pulp in a 15 % sulfuric acid solution. Analysis of the phase composition of silicon dioxide obtained from the rice husks after the acid treatment showed that the amorphous phase of silicon dioxide is obtained in the temperature range of 600–650 °C. Based on the results of studying the kinetics of thermal destruction of rice husks under the non-isothermal conditions, a mathematical model of the process has been proposed, which makes it possible to determine the degree of decomposition of the rice husks, depending on the temperature of their heat treatment. This is necessary in the design of equipment for processing the rice husks in the production of high purity silicon dioxide.**

*Key words*: kinetics of thermal destruction; rice husks; mathematical model; cellulose, decomposition; silicon dioxide

# ДОСЛІДЖЕННЯ КІНЕТИКИ ТЕРМІЧНОГО РОЗКЛАДАННЯ РИСОВОГО ЛУШПИННЯ, ОЧИЩЕНОГО ВІД ЦЕЛЮЛОЗИ

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## Анотація

**Актуальним завданням сучасного матеріалознавства є підвищення характеристик матеріалів при зниженні енерговитрат і екологічного навантаження на навколишнє середовище при їх синтезі. Одним з матеріалів надзвичайно широкого спектру призначення є силіцій (IV) оксид. Вимоги до його експлуатаційних характеристик на сучасному рівні зводяться до отримання нанорозмірного аморфного силіцій (IV) оксиду високої чистоти. Екологізація виробництва силіцій (IV) оксиду може бути досягнута використанням в якості поновлюваної і дешевої сировини відходів рисового виробництва – рисового лушпиння. Технологія отримання силіцій (IV) оксиду з рисового лушпиння є менш енерговитратною в порівнянні з традиційною переробкою кварцу і рівень забруднюючого впливу на навколишнє середовище такої технології істотно нижче. Для отримання силіцій (IV) оксиду з рисового лушпиння з високим ступенем чистоти в даній роботі запропоновано проводити перед термообробкою рослинної сировини екстракційний витяг аморфної складової целюлози. Ця операція проводилась за температури 100 °С протягом 6 годин при перемішуванні пульпи в 15 %-му розчині сульфатної кислоти. Аналіз фазового складу силіцій (IV) оксиду, отриманого з рисового лушпиння після кислотної обробки, показав, що аморфна фаза $SiO_2$ може бути одержана в діапазоні температур 600–650 °С На підставі результатів дослідження кінетики термодеструкції рисового лушпиння в неізотермічному режимі запропонована математична модель процесу, яка дозволяє визначати ступінь розкладання рисового лушпиння в залежності від температури його термообробки. Це необхідно для проектування обладнання з переробки рисового лушпиння в виробництві силіцій (IV) оксиду високої чистоти.**

*Ключові слова:* кінетика термодеструкції; рисове лушпиння; математична модель; целюлоза; розкладання; силіцій (IV) оксид.

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# ИССЛЕДОВАНИЕ КИНЕТИКИ ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ РИСОВОЙ ШЕЛУХИ, ОЧИЩЕННОЙ ОТ ЦЕЛЛЮЛОЗЫ

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Аннотация

**Актуальной задачей современного материаловедения является повышение характеристик материалов при снижении энергозатрат и экологической нагрузки на окружающую среду при их синтезе. Одним из материалов чрезвычайно широкого спектра назначения является диоксид кремния. Требования к эксплуатационным характеристикам диоксида кремния на современном уровне сводятся к получению наноразмерного аморфного диоксида кремния высокой чистоты. Экологизация производства диоксида кремния может быть достигнута использованием в качестве возобновляемого и дешевого сырья отходов рисового производства – рисовой шелухи. Технология получения диоксида кремния из рисовой шелухи является менее энергозатратной по сравнению с традиционной переработкой кварца и уровень загрязняющего воздействия на окружающую среду такой технологии существенно ниже. Для получения диоксида кремния из рисовой шелухи с высокой степенью чистоты в настоящей работе предложено проводить перед термообработкой растительного сырья экстракционное извлечение аморфной составляющей целлюлозы. Эта операция проводилась при температуре 100 °С в течение 6 часов при перемешивании пульпы в 15 %-ном растворе серной кислоты. Анализ фазового состава диоксида кремния, полученного из рисовой шелухи после кислотной обработки, показал, что аморфная фаза $SiO_2$ получается в диапазоне температур 600–650 °С. На основании результатов исследования кинетики термодеструкции рисовой шелухи в неизотермическом режиме предложена математическая модель процесса, которая позволяет определять степень разложения рисовой шелухи в зависимости от температуры ее термообработки. Это необходимо для проектирования оборудования по переработке рисовой шелухи в производстве диоксида кремния высокой чистоты.**

*Ключевые слова*: кинетика термодеструкции, рисовая шелуха, математическая модель, целлюлоза, разложение, диоксид кремния

## Introduction

Today, technological progress is closely related to the use of the unique properties of the nanostructured materials. Nanomaterials have a wide range of applications and are an integral attribute of all science-intensive technologies [1, 2]. One of the multifunctional nanomaterials is nanosized silicon dioxide [3]. Silicon dioxide nanoparticles are used in the production of composite and ceramic materials, drugs, and catalysts [4; 5]. The increased interest in silicon dioxide nanoparticles is due to their large specific surface area, high chemical and physical stability, and low toxicity [6]. High-purity silicon dioxide is the major raw material for the semiconductor industry and for the production of ceramics and polymer materials [7; 8].

The production of nanosized silicon dioxide uses energy- and labor-intensive methods, which reduces its economic efficiency. The industrial synthesis of silicon dioxide is carried out using sodium silicate, which is obtained by melting quartz sand and sodium carbonate at 1300 °C. This technology not only requires a lot of energy and additional operations for purifying the product, but also causes significant damage to the environment [8]. An alternative method for the synthesis of silicon dioxide nanoparticles is the processing of agricultural waste biomass, in particular, rice husks [9]. The ash content of the rice husks is about 20 % by weight. This solid residue of the combustion of the rice husks contains 80–95 wt. % of silicon dioxide [10].

Amorphous silicon dioxide obtained from rice husks has been proposed to be used for the production of ceramics [11], as filler in polymer composites and in the production of zeolites [12]. Adsorbents based on such silicon dioxide can be used to purify wastewater from heavy metal ions and organic pollutants [13]. In [14], an adsorption ceramic membrane was prepared on the basis of nanoparticles of silicon dioxide obtained from the rice husks. By the example of the purification of an aqueous solution of methylene blue from a dye, it has been shown that this membrane can successfully serve as an easily re-generable adsorbent for purifying wastewater from organic pollutants. High-purity amorphous silicon dioxide has a large specific surface area and can be used as an adsorbent or catalyst carrier in fine chemical synthesis [15].

In the synthesis of high purity amorphous silicon dioxide with ultrafine particle size, it is necessary to pretreat the rice husks and ensure proper control of its combustion conditions. To remove impurities of metal oxides from rice husks, it has been proposed to use pretreatment of plant materials with solutions of mineral acids [16; 17]. It was shown in [18] that the purity of silicon dioxide obtained from rice husks without pretreatment was 97.2 wt.%, though its purity reaches 99.7 wt.% after acid treatment of the raw material. The treatment of rice husks with solutions of hydrochloric and sulfuric acids before calcination was discussed in [19; 20]. To reduce the cost and toxic impact on the environment, it was proposed in [21] to use citric instead of hydrochloric acid. It was shown in [22] that the effectiveness of removing calcium impurities from rice husks through the use of citric acid depends not only on the acid concentration, but also on the temperature and time of processing the raw material.

High purity silicon dioxide can be obtained from the rice husks by its alkaline extraction followed by acid treatment and calcination [23]. The use of such a sol-gel method for the synthesis of silicon dioxide makes it possible to achieve the content of the basic substance at the level of 99.9 wt.% [24].

With any method of obtaining silicon dioxide from the rice husks, the temperature and time of heat treatment are the major factors that determine the crystallographic state of the product obtained. In [25; 26] it was shown that the optimal temperatures of the heat treatment of the rice husk for obtaining the amorphous silicon dioxide are close to 600 °C. For controlled synthesis of amorphous silicon dioxide of predicted purity, it is necessary to understand the nature of thermochemical transformations which accompany this process and to operate with their kinetic parameters.

The purpose of this work is to study the kinetics of thermal decomposition of rice husks after the extraction of cellulose from them, to determine the kinetic parameters of this process under non-isothermal conditions and to construct a mathematical model that corresponds to the established thermochemical transformations.

## Research methods

The study of the kinetics of thermal decomposition of the rice husks was carried out using plant raw materials that were pretreated. To obtain silicon dioxide of increased purity, it seems expedient to carry out the purification of the rice husks from cellulose by its extraction prior to their heat treatment. This operation consisted of processing the feedstock with a 15 % aqueous solution of sulfuric acid for six hours. Amorphous cellulose, the so-called hemicellulose, passes into the acidic solution. Crystalline cellulose and cellulose bonded with lignin (celolignin) cannot be removed from the rice husks in this way. Extraction was carried out in a 250 $cm^3$ five-necked flask equipped with a stirrer, a reflux condenser and a thermometer and placed in a thermostatic water bath. The temperature of the extraction process was maintained at 100 ° C. After the process had been finished, the insoluble residue was filtered through a Schott glass filter under the vacuum and rinsed with distilled water. The rinsed residue was dried in a drying oven at a temperature of 90–95 ° C to its constant weight.

The elemental composition of the residue after extraction of the amorphous cellulose was determined by the method of displacement chromatography using a CHNS/O 2400 Seriesll analyzer. The results of the analysis are shown in Table 1.

*Table 1*

**Elemental composition and ash content of the rice husks after extraction of amorphous cellulose**

| Description | Symbol, unit of measurement | Actual value, wt % |
|---|---|---|
| Ash content on dry state | $A^d$,% | 31.88 |
| Mass fraction of carbon | $C^d$,% | 32.06 |
| Mass fraction of hydrogen | $H^d$,% | 4.68 |
| Mass fraction of nitrogen | $N^d$,% | 0.28 |
| Mass fraction of oxygen | $O^d{}_d$,% | 31.10 |

When the mass fraction of bound water removed from the rice husks at 100 °C had been determined, the arbitrary formula of the rice husk molecule free from amorphous cellulose was composed based on the data on the elemental composition (Table 1): $C_{2.67}H_{3.84}O_{1.92}N_{0.02} \cdot 0.53\ SiO_2 \cdot 0.42H_2O$.

The kinetics of thermal decomposition of the rice husks, free from amorphous cellulose, was studied with the use of the derivatographic method. Data on the change in the mass of samples under the non-isothermal heating conditions in combination with the physicochemical methods of analysis of decomposition products made it possible to establish the sequence of chemical transformations corresponding to the destruction of the rice husks and to calculate the kinetic parameters of the process.

Screening of the derivatogram of 200 mg rice husk samples was carried out with the use of the "Paulik F. – Paulik J. – Erdey L." derivatograph in the air in the temperature range of 20–1000 °C at a heating rate of 10 K/min. The system of differential equations was solved by the Runge-Kutta method.

## Results and discussion

Analysis of the thermogram of a sample of rice husks free from amorphous cellulose showed (Fig. 1) that there are three extrema on the DTA curve. The endoeffect corresponds to a temperature of 95 °C and the two exoeffects correspond to temperatures of 330 °C and 603 °C. The observed endoeffect is obviously caused by the loss of water which is part of the structure of the rice husks. The exoeffects correspond to the processes of thermal destruction of crystalline cellulose at a temperature of 330 °C and lignin at a temperature of 603 °C [28].

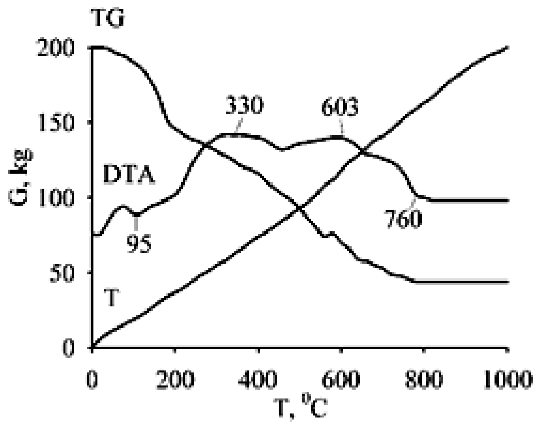


**Fig. 1. Derivatogram of the thermal decomposition of the rice husks, free from amorphous cellulose**

Based on the change in the sample mass and its elemental analysis, it can be said that the destruction of the cellulose, remaining after extraction, proceeds at a temperature of 250 - 470 ° C and leads to the formation of a product of the following arbitrary composition: $C_{2.67}H_{3.84}O_{1.92}N_{0.02}\cdot 0.53\ SiO_2$. In the temperature range of 470 - 730 ° C, the organic component of the rice husks is completely destructed with the formation of silicon dioxide.

The endothermic effect observed at a temperature of 760 ° C (Fig. 1) is not accompanied by a change in the sample mass. Apparently, in this case, there is a change in the structure of silicon dioxide from the amorphous to the crystalline state. To verify this assumption, X-ray phase studies of the products of calcination of the rice husks, free from amorphous cellulose, were carried out; the calcination products were obtained at temperatures of 600, 700, and 800 ° C. As can be seen from Fig. 2, the diffraction pattern 1 does not contain diffraction peaks and, therefore, the silicon dioxide sample is X-ray amorphous. Diffraction pattern 2 shows the weak peaks at $d_{HKL}$ = 3.35; 2.45; 1.98; 1.67, which indicates the impurities of the crystalline phase of silicon dioxide. In diffraction pattern 3, corresponding to a silicon dioxide treatment temperature of 800 °C, these peaks are quite distinct and indicate the transition of amorphous silicon dioxide to the crystalline state. Therefore, the recommended temperature range for obtaining amorphous silicon dioxide is 600–650 °C.

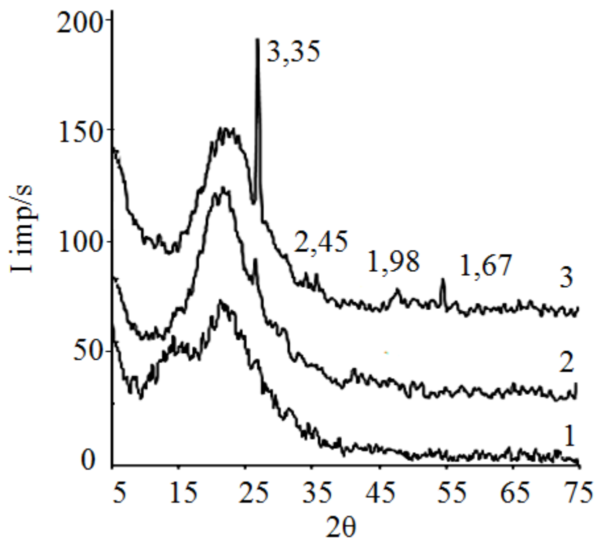


**Fig. 2. X-ray diffraction patterns of the products of calcination of the rice husks, free from amorphous cellulose: 1 – 600 °C; 2 – 700 °C; 3 – 800 °C**

Based on the foregoing, it is possible to present the process of thermal destruction of the rice husks, free from amorphous cellulose, as the form of successive transformations, which occur during the non-isothermal processing of the raw material under study:

$$C_{2,67}H_{3,84}O_{1,92}N_{0,02}\cdot 0.53SiO_2\cdot 0.42H_2O \rightarrow C_{2,67}H_{3,84}O_{1,92}N_{0,02}\cdot 0.53SiO_2 + 0.42H_2O \quad (1)$$

$$C_{2,67}H_{3,84}O_{1,92}N_{0,02}\cdot 0.53SiO_2 + 1.46O_2 \rightarrow C_{1,24}H_{1,72}O_{0,92}\cdot 0.53SiO_2 + 0.01N_2 + 1.06H_2O + 1.43CO_2 \quad (2)$$

$$C_{1,24}H_{1,72}O_{0,92}\cdot 0.53SiO_2 + 1.21O_2 \rightarrow 0.53SiO_2 + 0.86H_2O + 1.24\ CO_2 \quad (3)$$

Equations (1)–(3) contain seven components. The symbols for the number of moles of the participants in the reactions are given in Table 2.

*Table 2*

**Component Symbols**

| Component | Symbols |
|---|---|
| $C_{2.67}H_{3.84}O_{1.92}N_{0.02}\cdot 0.53\ SiO_2\cdot 0.42\ H_2O$ | $n_1$ |
| $C_{2.67}H_{3.84}O_{1.92}N_{0.02}\cdot 0.53\ SiO_2$ | $n_2$ |
| $C_{1.24}H_{1.72}O_{0.92}\cdot 0.53\ SiO_2$ | $n_3$ |
| $N_2$ | $n_4$ |
| $H_2O$ | $n_5$ |
| $CO_2$ | $n_6$ |
| $SiO_2$ | $n_7$ |

We construct a mathematical model describing the process of oxidative thermal destruction of the rice husks, free from amorphous silicon dioxide. The model consists of three differential kinetic and four algebraic material balance equations:

$$\frac{dn_1}{d\tau} = -k_1 n_1 \qquad (4)$$

$$\frac{dn_2}{d\tau} = k_1 n_1 - k_2 n_2 , \qquad (5)$$

$$\frac{dn_3}{d\tau} = k_2 n_2 - k_3 n_3 \qquad (6)$$

$$n_4 = 0,01 n_1^0 - 0,01 n_1 - 0,01 n_2 \qquad (7)$$

$$n_5 = 2,34 n_1^0 - 2,34 n_1 - 1,92 n_2 - 0,86 n_3 \qquad (8)$$

$$n_6 = 2,67 n_1^0 - 2,67 n_1 - 2,67 n_2 - 1,24 n_3 \qquad (9)$$

$$n_7 = 0,53(n_1^0 - n_1 - n_2 - n_3) \qquad (10)$$

where $k_1$ – $k_3$ are the rate constants of reactions (1)–(3), $s^{-1}$;
τ – time, s;
$n_1°$ is the initial number of moles in 100 grams of the rice husks, free from amorphous cellulose;
$n_1$ – $n_7$ are the current numbers of moles of the corresponding components.

To solve the proposed mathematical model, it is necessary to determine the rate constants of the reactions (1)–(3). We use the formal equation of the rate of transformation based on the law of mass action [20], presented in the form:

$$\frac{d\alpha}{d\tau} = k \cdot \alpha^p , \qquad (11)$$

where $\tau$ is the time at which the degree of transformation α has been reached;
$k$ is the reaction rate constant;
p is a quantity, that is formally similar to the order of the reaction.

The degree of transformation was determined by the formula:

$$\alpha = \frac{W_0 - W_s}{W_0 - W_K} \qquad (12)$$

where $W_0$ is the initial mass of the sample;
$W_S$ is the mass of the sample at a temperature T;
$W_K$ is the final mass of the sample.

Suppose that the reaction rate constant is determined in accordance with the Arrhenius equation [8]:

$$k = k_0 \exp\left(-\frac{E}{RT}\right), \qquad (13)$$

where E is the activation energy;
$k_0$ is the preexponential factor;
R is the universal gas constant;
T is the temperature.

Given that the heating rate is constant $u = \frac{dT}{d\tau} = const$ in the thermogravimetric analysis, we can write:

$$\frac{d\alpha}{\alpha^p} = \frac{k_0}{u}\exp(-\frac{E}{RT})dT . \qquad (14)$$

When integrating (14) for the case p = 1, we obtain:

$$\ell n\alpha = \int_0^T \frac{k_0}{u}\exp\left(-\frac{E}{RT}\right)dT . \qquad (15)$$

In accordance with the results of derivatographic studies, we will take as reference the extrema temperatures expressed in Kelvin degrees: $Ts_1$ = 368 K, $Ts_2$ = 603 K, $Ts_3$ = 876 K.

The variable Θ is taken with an arbitrary interval in the temperature and is equal to Θ = T – Ts. Replacing the variable T in equation (15) by Θ and taking into account that $\frac{1}{T} \approx \frac{\left(1-\frac{\theta}{Ts}\right)}{Ts}$, we obtain the integral expression:

$$\ell n\alpha = \frac{k_0}{u}\cdot\frac{RTs^2}{E}\exp\left[-\frac{E}{RTs}(1-\frac{\theta}{Ts})\right] \qquad (16)$$

or $\ell n\ell n\alpha = C + \frac{E\cdot\theta}{RTs^2}$, (17)

where $C = \ln\left(\frac{k_0}{u}\cdot\frac{RTs^2}{E}\right) - \frac{E}{RTs}$ (18)

Dependence (17) is linear, and the slope of the dependence curves plotted in coordinates $W^* = \ln\ln\alpha$ can be used to determine the activation energy of reactions (1)–(3).

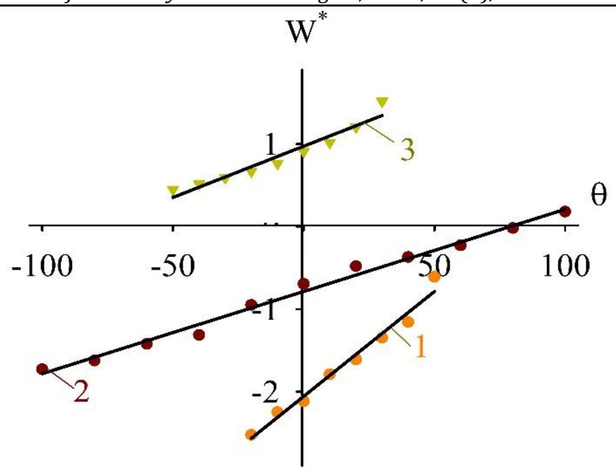


**Fig. 3. Dependences of W * on the temperature difference θ for reactions (1)–(3): 1 - for reaction (1) at a temperature of $T_{S1}$ = 368K, 2 - for reaction (2) at a temperature of $T_{S2}$ = 603K, 3 - for reaction (3) at a temperature of $T_{S3}$ = 876 K**

Based on the graphical dependences shown in Fig. 3 and using the equations (13) and (18), the kinetic parameters of the reactions (1)–(3) were calculated, which are summarized in Table 3.

*Table 3*

**Kinetic Parameters of the Thermal Decomposition of the Rice Husks, Free from Amorphous Cellulose**

| Chemical reaction | T, K | Preexponential factor, $k_0$, $c^{-1}$ | Arbitrary activation energy of the reaction, E, J / mol |
|---|---|---|---|
| 1 | 368 | $1.54 \cdot 10^2$ | $31.75 \cdot 10^3$ |
| 2 | 603 | 1.43 | $33.25 \cdot 10^3$ |
| 3 | 876 | $1.09 \cdot 10^2$ | $79.11 \cdot 10^3$ |

The obtained kinetic parameters of the successive stages of the heat treatment of the rice husks, free from amorphous cellulose, were used to determine the space-time characteristics when solving the system of equations (4–10) by the Runge-Kutta method using the Mathcad 14 software (Fig. 4).

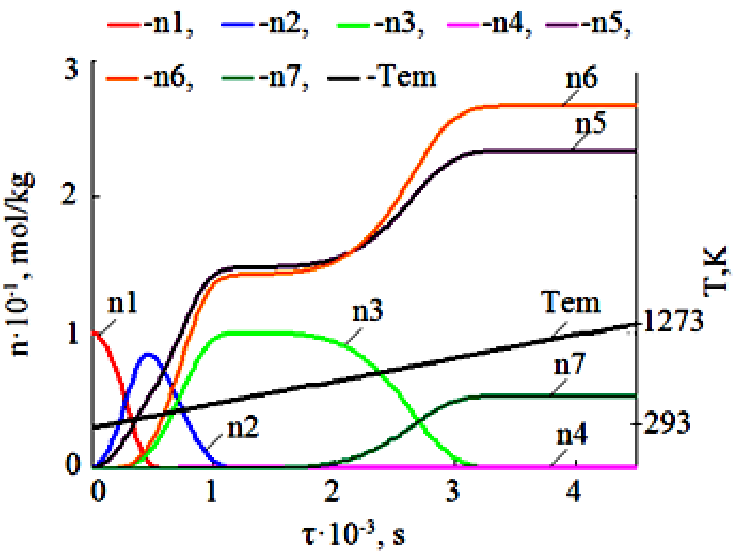


**Fig. 4 Proportion of the components of the reaction mixture in the thermal decomposition of the rice husks, free from amorphous cellulose**

The proposed mathematical model makes it possible to calculate the degree of transformation of the rice husks, free from amorphous cellulose, into silicon dioxide, depending on the temperature of the thermal destruction process. The corresponding dependence, obtained by the calculation with the use of equations (4–10), is shown in Fig. 5 by a solid line. The transformation degree values obtained according to equation (12) based on experimental data are indicated on the graph by dots.

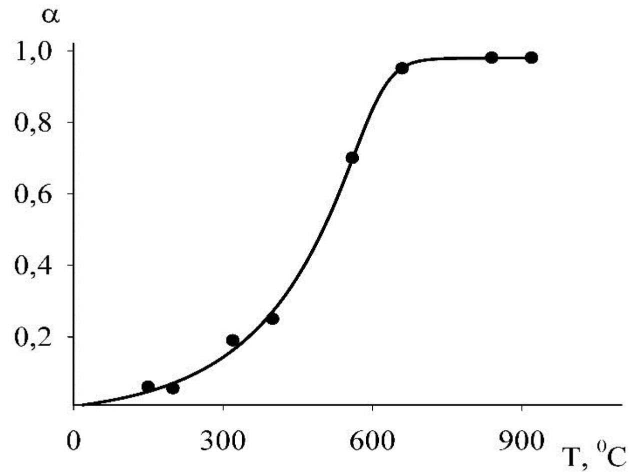


**Fig 5 Dependence of the degree of transformation of the rice husks, free from amorphous cellulose, on the heat treatment temperature:**
**• • • experimental data;**
**— calculated curve.**

Good agreement between the calculated and experimental values of the degree of transformation, corresponding to the certain temperatures of heat treatment of the rice husks, indicates the adequacy of the proposed model and satisfactory accuracy of the obtained kinetic parameters of the process. Consequently, the considered mathematical model can be used in the design of reactors for processing rice husks, free from amorphous cellulose, to obtain amorphous silicon dioxide of increased purity.

## Conclusions

1. To obtain high-purity silicon dioxide from the rice husks, it has been proposed to carry out the preliminary acid treatment of the raw materials with 15 % sulfuric acid. At this stage, the amorphous cellulose is removed, which reduces the contamination of the synthesized silicon dioxide with carbon-containing compounds.

2. On the basis of experimental data on the elemental composition of the products of thermal destruction of the rice husks, free from amorphous cellulose, a chemical scheme of sequential transformations of the feedstock has been established as a function of the processing temperature. It has been shown that the formation of silicon dioxide occurs as a result of successive transformations of arbitrary molecules $C_{2.67}H_{3.84}O_{1.92}N_{0.02}\cdot0.53\,SiO_2\cdot0.42\,H_2O$, $C_{2.67}H_{3.84}O_{1.92}N_{0.02}\cdot0.53\,SiO_2$, $C_{1.24}H_{1,72}O_{0.92}\cdot0.53SiO_2$ at the temperatures of 95, 330 and 603 °C.

3. A mathematical model has been developed that describes the kinetics of thermal decomposition of the rice husks, free from amorphous cellulose. The kinetic parameters of the process were obtained and an experimental verification of the adequacy of the proposed model was carried out. It has been shown that the formation of silicon dioxide with a transformation degree equal to unity occurs at a temperature of 650 °C.

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