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OBTAINING OF HIGH PURITY AMORPHOUS SILICON DIOXIDE FROM RICE HUSK

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Abstract. Using maximum extraction of carbon-containing components the content of amorphous silicon dioxide was increased in the rice husk solid residue. In accordance with the hypothesis about the mechanism of extracting carbon-containing components from rice husk by liquid extractants, proper extractants were selected. The effect of main technological factors including a process temperature, time and concentration of the extractants was determined.

Keywords: amorphous silicon dioxide, rice husk, extraction, lignin, cellulose, mechanism, hypothesis.

1. Introduction

In search of alternative and renewable sources of energy and raw materials for the chemical industry [1, 2] the waste of rice production – rice husk (RH) – is of special attention. RH is the carrier of amorphous silicon dioxide and may be used for the production of silicon carbide, furfural, cellulose, lignin, rice bran oil, cutin.

RH consists of lignin (~40 wt % [3]), cellulose (~36 wt % [3]), silicon oxides and metals (about 24 wt % [4, 5]).

To produce the amorphous silicon dioxide of high purity the rice husk is grinded and chemically treated in order to remove carbon-containing components as much as possible [4, 5]. The resulting material is calcined in an oxygen environment.

We analyze the extracting process of carbon-containing components from a solid material (rice husk) using a liquid extractant and take into account the structural and chemical peculiarities of the solid phase.

The organization of the solid plant material structure, as well as that of the solid fossil fuels, which is the result of continuous transformation (metamorphism) of phytogenic raw materials, conditionally can be represented by the following three levels:

– at the microlevel the material state and properties are determined by the movement of the molecules of various organic and inorganic substances;

– at the macrolevel the material state and properties are determined by a complex of molecules of various substances (macromolecules), bonded by intermolecular interaction forces of different nature;

– at the level of the solid particles the material state and properties are determined by association of macromolecules, which are bounded by different polyconjugations (hydrogen bonds, EDA interactions, strong C–C bonds).

Taking the above-mentioned mechanism into account, the conversion of carbon-containing component into liquid state is represented as follows:

– liquid selective extractant penetrates into the pores of the solid particle and contacts with the carbon-containing component;

– the relationship between polyconjugations on the 3rd level and intermolecular forces on the 2nd level of structural and chemical organization of solid particles is changed as a result of interference of the electron shells of extractant and carbon-containing component molecules;

– the structure is destroyed due to the weakening of bonds between its elements (the structure moves to the 2nd or even 1st levels of the structural organization, which corresponds to a liquid state) at the same consumption of energy supplied from the outside (at the same temperature) under which the structure was quite stable before liquid extractant impact;

– the increase in extractant concentration increases to the highest possible extraction degree of carbon-containing component converted into liquid state; at the same time a new level of the result depends not only on the extractant concentration, but also on the previously achieved level.

The above-described phenomena, occurring simultaneously at a great number of points in the solid particles, facilitate the mass transfer in the solid-liquid

system, "loosening" particles macrostructure and increasing the content of non-extractable substances (in our case, the target product) in it.

Within the presented hypothesis about the mechanism of extracting process for the solid particle component by liquid extractant it is possible to formulate a number of practical recommendations for technological process operations and regime, as well as to formulate an equation model of the process, establishing the relationship between the extraction degree of carbon-containing component and main technological factors.

In particular, the following operations should be performed:

1. Grinding of solid material into particles with a maximum total surface;
2. Intensive mixing of the phases for the efficient use of their contact surfaces;
3. Selection of the liquid phase with a low surface tension value.

The technological factors are:

- process temperature;
- process time;
- extractant concentration.

2. Experimental

2.1. Theoretical Part

To derive the equation relating to the solid component extraction degree and the mentioned factors, we introduce the following designations:

y – the extraction degree, wt %; x – extractant concentration, vol %; $\frac{dy}{dx}$ – change of extraction degree in response to changes in the extractant concentration (for simplicity, we denote this ratio as an extraction rate).

In accordance with the hypothesis of the process mechanism, let us write the expression:

$$\frac{dy}{dx} = f(x, y) \quad (1)$$

which means that the extraction rate depends not only on the extractant concentration, but on already achieved values of extraction degree as well.

As a particular case we consider the simplified Eq. (1) in the form of Eq. (2) or (3):

$$\frac{dy}{dx} = f_1(y) \cdot f_2(x) \quad (2)$$

$$\frac{dy}{f_1(y)} = f_2(x) dx \quad (3)$$

Integrating Eq. (3) we obtain Eq. (4):

$$F_1(y) = F_2(x) \quad (4)$$

which determines the y value as a function of x .

To proceed from the general to the specific results of the solid component extraction by liquid extractant let us note that the previous state of the system is determined by both extracted and non-extracted amount of the solid component. Therefore, taking into account the dependence of extraction rate on extracted and non-extracted (residual) amount of the component, we introduce the expression (5) as f_1 function:

$$f_1(y) = y(y_{\max} - y) \quad (5)$$

where y_{\max} – the highest possible extraction degree.

Substituting (5) into (2), we obtain:

$$\frac{dy}{dx} = y(y_{\max} - y) \cdot f_2(x) \quad (6)$$

After conversion of Eq. (6) we get:

$$d \ln y - d \ln(y_{\max} - y) = y_{\max} \cdot f_2(x) \cdot dx \quad (7)$$

Eq. (7) can be easily integrated (see Eqs. (3) and (4))

$$\ln y - \ln(y_{\max} - y) = y_{\max} \cdot F_2(x) + c_1 \quad (8)$$

From Eq. (8) we get:

$$y = \frac{y_{\max}}{1 + b \cdot e^{-y_{\max} F_2(x)}} \quad (9)$$

where $b = e^{-c_1}$; the constant of integration can be found according to the given value (x, y).

If we assume that $f_2(x)$ is a linear function, i.e. $f_2(x) = bx$, then:

$$F_2(x) = b \int x dx = \frac{1}{2} bx^2 \quad (10)$$

Substituting (10) into (9) and assuming that

$$y_{\max} = a \quad (11)$$

$$\frac{1}{2} \cdot y_{\max} \cdot b = c \quad (12)$$

we finally find the dependence of the solid component extraction degree on extractant concentration in the form of Eq. (13):

$$y = \frac{a}{1 + b \cdot e^{-cx^2}} \quad (13)$$

The parameters of Eq. (13) can be found from the experimental data, bearing in mind that:

- according to (11) $a = y_{\max}$;
- according to (13) at $x = 0$ and $y_{x=0} \neq 0$:

$$b = \frac{a}{y_{x=0}} - 1 \quad (14)$$

- according to (13) at $x = 1$, $y_{x=1} \neq 0$ and $y_{x=0} \neq 0$:

$$c = -\ln \frac{a - y_{x=1}}{b \cdot y_{x=1}} \quad (15)$$

Thus, for determining the parameters a , b and c the work should include experiments at $x = 0$, $x = 1$ and x , under which y_{\max} is achieved.

It can be assumed that a , b and c are the functions of the temperature and process time. In the case of determining these functions they may be included in Eq. (13) and then the equation turns into dependence of the extraction degree on both technological factors.

2.2. Experimental Part

Before carbon-containing components extraction the rice husk was washed by hot water and then grinded using a horizontal mill of impact-centrifugal type; the particles size were 40–150 μm .

The experiments were conducted at the laboratory plant, shown in Fig. 1.

The sample of grinded RH (5 g) was placed into a thermostated reactor, then 50 ml of concentrated hydrochloric acid as an extractant were added [3, 4]. To reduce the surface tension of hydrochloric acid ($\sigma = 0.0596 \text{ N/m}$ [6]), and provide conditions for its penetration into solid particles, the acid was added in admixture with 96 % ethanol ($\sigma = 0.0173 \text{ N/m}$ [6]). The content of hydrochloric acid in the ethyl alcohol was varied from 0 to 3.5 wt %.

The range of investigated temperatures was within 293–1073 K. The process time varied from 0.5 to 6 h. The reaction mixture was vigorously stirred with a propeller stirrer.

After the end of the experiment the insoluble residue was filtered and repeatedly washed until pH = 7. The washed residue was dried at 1173–1223 K in air till the constant weight.

In the absence of accurate data about the content of lignin in the starting sample of RH its extraction degree was evaluated indirectly with regard to the weight of the whole sample according to the formula:

$$a = \frac{G_i - G_f}{G_i} \cdot 100\% \quad (16)$$

where a – the extraction degree of lignin from RH, wt %; G_i – initial weight of the sample, g; G_f – weight of the residue after extraction.

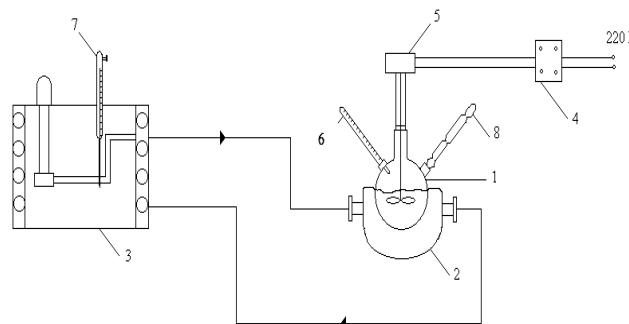


Fig. 1. Laboratory plant for lignin extraction from RH: thermostated reactor (1); reactor jacket (2); thermostat (3); autotransformer (4); stirrer with electrical motor (5); alcohol thermometer (6); contact thermometer (7) and water cooler (8)

It should be taking into account that the direct determination of the extraction degree gives much higher values. So if we assume that the lignin content in the sample is 40 wt %, and the value defined by Eq. (16) is equal to 30 wt %, the actual extraction degree of lignin is 75 wt %.

The experiments concerning the extraction of cellulose from RH were carried out in the same way. Aqueous solution of sulfuric acid was used as the extractant. The temperature was varied from 293 to 373 K, time – from 0.5 to 6 h.

RH characteristics are represented in Tables 1 and 2.

Table 1

Technical analysis and elemental composition of RH

Index	Analysis method	Symbol and unit	Actual value
Analytical moisture	ISO 589-81	W^d , %	1.90
Ash content for dry matter	ISO 1171-97	A^d , %	20.90
Weight content of total sulfur	ISO 334-92	S_t^d , %	0.001
Yield of volatiles	ISO 562-81	V^{adj} , %	75.00
Weight content of carbon	ISO 625-96	C^d , %	35.51
Weight content of hydrogen		H^d , %	5.70
Weight content of nitrogen	ISO 333-83	N^d , %	0.31
Weight content of oxygen	ISO 1994-76	$O_{d,}^d$, %	37.54

Table 2

Composition of mineral (ash) part of RH

Substance	Symbol and unit	Actual value	
		RH ash	RH ash after extraction
Silicon dioxide	SiO_2 , %	91.96	99.09
Aluminium oxide	Al_2O_3 , %	0.67	0.21
Iron oxide	Fe_2O_3 , %	4.15	0.21
Magnesium oxide	MgO , %	0.14	0.05
Calcium oxide	CaO , %	1.09	0.19
Sodium oxide	Na_2O , %	0.20	0.09
Potassium oxide	K_2O , %	1.61	0.07
Sulfur trioxide	SO_3 , %	0.18	0.08

Note: All analyses were carried out in accordance with state standard 10538-87

Table 3

Data on degree of lignin extraction from RH

Concentration of hydrochloric acid in ethyl alcohol	Lignin extraction degree			
	293 K	313 K	333 K	353 K
Process time – 4 h				
0	1.9	3.9	6.4	8.2
0.5	2.5	4.6	7.5	9.6
1	4.6	7.5	11.0	13.9
1.5	12.1	16.0	18.9	26.6
2	12.8	17.0	20.3	28.3
2.5	12.9	17.1	20.5	28.8
Process time – 6 h				
0	2.1	5.3	7.5	8.5
0.5	2.6	5.9	8.2	10.0
1	5.8	8.5	12.5	15.0
1.5	14.0	18.0	22.6	31.0
2	14.7	21.0	25.4	33.0
2.5	14.7	21.2	25.6	33.0

Table 4

Data on degree of cellulose extraction from RH

Concentration of sulfuric acid aqueous solution	Cellulose extraction degree			
	293 K	313 K	333 K	373 K
Process time – 4 h				
0	0	0	0	0
5	2.0	3.4	5.9	7.8
10	7.3	10.2	17.2	22.0
15	11.5	15.3	22.0	25.7
Process time – 6 h				
0	0	0	0	0
5	2.5	3.8	6.4	8.0
10	10.0	15.2	21.1	26.0
15	14.2	18.9	25.2	29.9

Table 5

Parameters of Eq. (13) for the process of lignin extraction

Regime		Coefficients in Eq. (13)			Residual standard deviation
T, K	τ, h	a	b	c	S_r
293	4	10.9707	51.7183	2.8635	0.1299
	6	12.6000	38.43917	2.657247	0.2168
313	4	13.1648	36.4083	2.6309	0.0914
	6	15.8152	36.344	2.218453	0.0989
333	4	14.0248	19.224	2.24012	0.0855
	6	17.9552	25.344	2.208191	0.34192
353	4	20.3803	29.2457	2.4616	0.2467
	6	24.5653	38.43917	2.657247	0.2168

Table 6

Parameters of Eq. (13) for the process of cellulose extraction

Regime		Coefficients in Eq. (13)			Residual standard deviation
T, K	τ, h	a	b	c	S_r
293	4	11.684	9.549091	0.690646	0.030022
	6	14.28	10.22	0.797	0.0744
313	4	15.6264	6.74975	0.635435	0.010613
	6	18.952	9.544	0.908	0.163637
333	4	22.176	5.5764	0.73607	0.196727
	6	25.376	6.758	0.867	0.3578
373	4	25.76853	5.225581	0.84892	0.2394
	6	29.832	6.317073	0.933575	0.151974

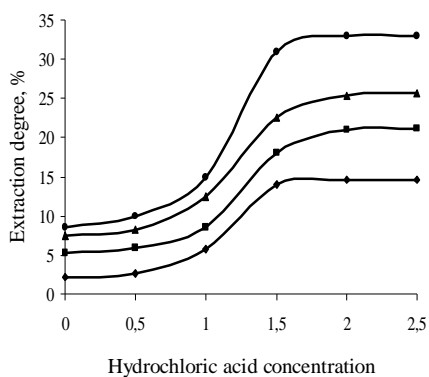


Fig. 2. Dependence of lignin extraction degree on temperature and hydrochloric acid concentration at $\tau = 6$ h: \blacklozenge – 293 K; \blacksquare – 313 K; \blacktriangle – 333 K; \bullet – 353 K

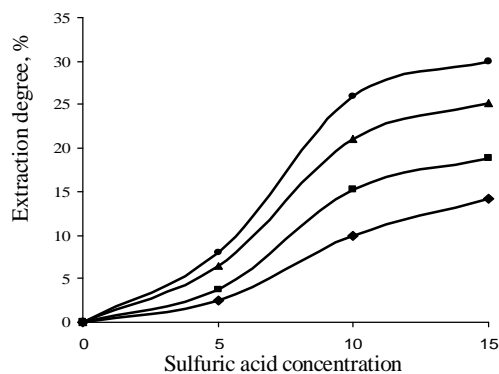


Fig. 3. Dependence of cellulose extraction degree on temperature and hydrochloric acid concentration at $\tau = 6$ h: \blacklozenge – 293 K; \blacksquare – 313 K; \blacktriangle – 333 K; \bullet – 373 K

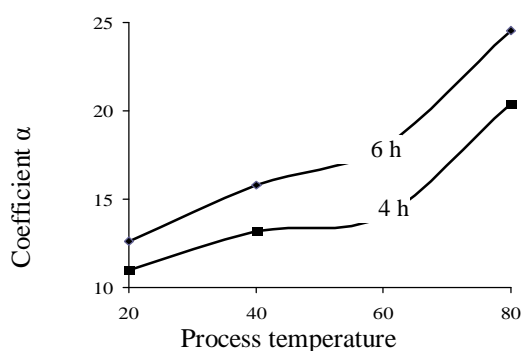


Fig. 4. Dependence of coefficient α on temperature and process time for lignin extraction

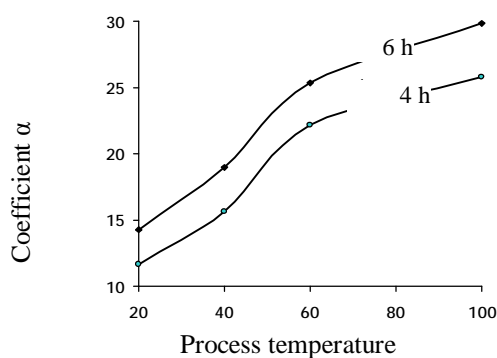


Fig. 5. Dependence of coefficient α on temperature and process time for cellulose extraction

Fig. 6. Degree of lignin and cellulose extraction (2-stage process) vs. process time

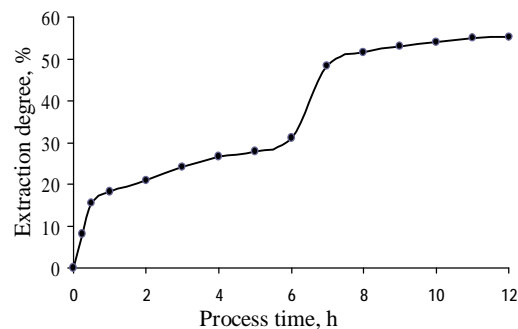


Table 7

Data on degree of lignin and cellulose extraction from RH (2-stage process)

Concentration of sulfuric acid aqueous solution	Degree of lignin and cellulose extraction			
	293 K	313 K	333 K	373 K
Process time – 4 h				
0	30.0	30.0	30.0	30.0
5	32.0	34.3	35.5	40.0
10	36.4	39.1	42.1	48.1
15	41.4	44.5	47.8	54.0
Process time – 6 h				
0	30.0	30.0	30.0	30.0
5	33.6	35.9	38.1	41.3
10	39.0	42.0	45.5	49.1
15	43.2	46.8	49.9	55.4

3. Results and Discussion

Table 3 shows averaged experimental data on the degree of lignin extraction from RH depending on the concentration of hydrochloric acid in ethyl alcohol and process temperature. When processing the cellulose by concentrated acids, we observe the formation of a gel-like precipitate which is difficult to be separated from RH insoluble part. That is why we used diluted aqueous solutions of sulfuric acid in the experiments. Averaged experimental data on the degree of cellulose extraction from RH depending on the sulfuric acid concentration, temperature and process time are presented in Table 4.

In accordance with the hypothesis about the mechanism of carbon-containing components extraction from RH we experimentally found the values of a , b , c in Eq. (13). These values for lignin and cellulose extraction are shown in Tables 6 and 7, respectively. To estimate the accuracy of Eq. (13) while using the values of a , b , c , in the last column of Tables we show the values of the residual standard deviation. Figs. 2 and 3 show the dependence of lignin and cellulose extraction degrees, respectively, on the temperature and acids concentration.

The proximity of the calculated (solid lines) and experimental (dots) reveals the adequacy of the model (13) and, as a consequence, on the validity of the hypothesis about the mechanism of the developed process.

Figs. 4 and 5 present data which show a dependence of the coefficient α on temperature and process time. It is obvious that the decisive role here belongs to the temperature, its effect is 3–5 times higher than the effect of process time. At the same time it is clear that to describe the plots shown in Figs. 4 and 5, additional experimental studies are needed. For more complete extraction of carbon-containing components from RH the intermediate product obtained after lignin extraction was treated by acidic extractant (2-stage process).

Averaged experimental data on the degree of lignin and cellulose extraction at different temperatures and times are presented in Table 7.

The obtained experimental results were the basis for the implementation of lignin and cellulose extraction process, as consecutive stages of the same process. The extraction degree increases to 55 % (see Fig. 6).

Based on the hypothesis that the amorphous silicon dioxide extract actually is not extracted with carbon-containing components of RH, we conclude that SiO₂ content in the solid residue is increased to the value of $\frac{20.9 \cdot 91.96}{45} = 42.71$ wt %, as a result of two-stage process.

At the same time while comparing the ash compositions of initial RH and its solid residue after extraction we conclude that a significant contribution to the growth of SiO₂ content (7.13 wt %) is provided by a selective extraction of all mineral components of RH (except SiO₂). This conclusion allows to suggest that the mentioned components are distributed in lignin and cellulose, whereas SiO₂ is associated with a carbon-containing condensed structures, not converted into liquid state under the investigated conditions.

In this connection, to obtain high-purity SiO₂ it is necessary to include in the process the burning stage of the solid residue of 2-stage RH extraction.

4. Conclusions

1. The hypothesis about the mechanism of amorphous SiO₂ obtaining by extraction of carbon-containing components (lignin and cellulose) from rice husk was formulated. On this basis we derived an equation associating the extractant concentration and extraction degree of carbon-containing components and define the requirements for the extractant and experimental conditions.

2. The effect of extractants concentrations (hydrochloric acid in ethanol and sulfuric acid aqueous solution), temperature and process time on the degree of lignin and cellulose extraction from RH was studied.

3. It was shown that equation $y = \frac{a}{1 + b \cdot e^{-cx}}$ adequately describes experimental data under any temperature and time within the ranges of $293 \leq T \leq 373$ K and $0.5 \text{ h} \leq \tau \leq 6 \text{ h}$.

4. Investigation of the resulting model showed that:
– using RH fraction of 40–150 μm and lignin extraction by hydrochloric acid in ethanol the averaged maximum extraction degree of lignin (33 wt %) is achieved at 353 K for 6 h;

– using RH fraction of 40–150 μm and cellulose extraction by 15% aqueous solution of sulfuric acid the averaged maximum extraction degree of cellulose (29.9 wt %) is achieved at 373 K for 6 h.

5. Consecutive implementation of these stages allows to increase the extraction degree of carbon-containing components to 55 % and thereby increases the content of amorphous silicon dioxide in RH solid residue from 20.90 to 42.71 wt %.

References

- [1] Drozdник I., Boriskina N. and Balaeba Y.: Uglekhim. Zh., 2015, **1-2**, 12.
- [2] Gordienko M.: Uglekhim. Zh., 2015, **1-2**, 21.
- [3] Nikitin V., Obolenskaya A. and Schegolev V.: Khimiya Drevesiny i Cellulosa. Lesnaya Prom., Moskva 1978.
- [4] Gridneva T., Soroka P., Tertyshnyi O *et al.*: Vopr. Khim. i Khim. Techn., 2007, **6**, 212.
- [5] Gridneva T., Soroka P., Tertyshnyi O *et al.*: Naukova Praci Odessa Nats. Acad. Kharch. Techn., 2008, **32**, 139.
- [6] Pavlov K., Romankov P. and Noskov A.: Primery i Zadachi po Kursu Processov i Apparatov Khimicheskoi Technologii. Khimiya, Moskva 1987.

**ОДЕРЖАННЯ АМОРФНОГО СИЛІЦІЙ(IV)
ОКСИДУ ПІДВИЩЕНОЇ ЧИСТОТИ
ІЗ РИСОВОГО ЛУШПИННЯ**

Внаслідок максимального вилучення карбон-вмісних компонентів, підвищено вміст аморфного силіцій(IV) оксиду у твердому залишку рисового лушпиння. Вибрано екстрагенти відповідно до гіпотези про механізм екстрагування карбон-вмісних компонентів з рисового лушпиння рідкими екстрагентами. Встановлено вплив основних технологічних чинників: температура, час процесу та концентрація екстрагенту.

Ключові слова: аморфний силіцій(IV) оксид, рисове лушпиння, екстрагування, лігнін, целюлоза, механізм, гіпотеза.