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OXIDATIVE-ORGANOSOLVENT DELEGIFICATION OF WHEAT STRAW

Urgency of the research. *Expansion of the raw material base of the pulp and paper industry of Ukraine takes place through the use of alternative types of vegetable raw materials, namely wheat straw, and the improvement of environmentally friendly oxidative-organosolvent technology for the production of straw pulp.*

Target setting. *Methods for the delignification of vegetable raw materials using the oxidant – hydrogen peroxide – are currently available. The disadvantage of these methods is the high consumption of the oxidant, which constitutes 90 % by weight of absolutely dry raw material that significantly increases the cost of technical cellulose. Therefore, it is necessary to improve the technological parameters of the delignification process of wheat straw with hydrogen peroxide in acetic acid.*

Actual scientific researches and issues analysis. *Recent open-access publications have been reviewed, including literature on oxidative-organosolvent delignification methods of plant material using peroxoacids.*

Uninvestigated parts of general matters defining. *Investigation of technological parameters of oxidative-organosolvent delignification for the reduction of oxidant consumption and determination of optimal values of temperature and duration of the delignification process of wheat straw with the mixture of hydrogen peroxide in acetic acid.*

The research objective. *Investigation of straw pulp production method in order to reduce the consumption of cooking reagents while increasing the physical- mechanical properties and yield of the target product.*

The statement of basic materials. *A method of obtaining straw pulp from wheat straw shreddings in acetic acid media with the hydrogen peroxide consumption 50 % by weight of absolutely dry raw material was investigated. The content of the main components in the raw vegetable material was determined. The effect of the delignification conditions, namely the temperature and cooking duration, on the yield of the fibrous semi-finished product, the content of residual lignin and the content of cellulose was studied. It was shown that the increase of temperature from 70 °C to 90 °C and duration of vegetable raw materials processing from 60 to 180 min lead to the decrease in yield by 28 %, the content of residual lignin by 6.5 %, while the cellulose content in the fibrous semi-finished product increased by 21 %. Calculated regression equations adequately described the experimental data and could be used as a mathematical model of the delignification process of wheat straw by hydrogen peroxide in acetic acid media. Optimal values of technological parameters of the wheat straw cooking process were determined using the method of multicriterion optimization of the delignification conditions.*

Conclusions. *Calculated regression equations adequately described the production process of straw cellulose by hydrogen peroxide delignification in acetic acid. Established optimal technological parameters provided obtaining a final product with high quality indicators (yield 78.2%, residual lignin content 3.6%, cellulose content 65.4%, breaking length – 6200 m, punching resistance 210 kPa, tearing resistance – 425 mN, folding endurance 625 n.d.b.).*

Keywords: *wheat straw; hydrogen peroxide; acetic acid; delignification; yield; residual lignin content; cellulose; regression equation.*

Table: 1. Fig.: 4. References: 10.

Urgency of the research. Scientists are developing new environmentally friendly technologies that are based on the use of non-toxic delignifying reagents [1]. In particular, the processes of oxidative-organosolvent delignification of vegetable raw materials with hydrogen peroxide in the organic acids media are intensively investigated [2]. Such cooking is characterized by a greater selective effect on lignin, which makes it possible to increase the cellulose yield by preserving the polysaccharides (cellulose and hemicelluloses) of vegetable raw materials, by the possibility of using simple schemes of chemicals regeneration with smaller negative environmental impact [2].

Target setting. Today, highly selective methods of delignification, such as cooking of vegetable raw materials with peroxoformic (PFA) and peroxoacetic (PAA) acids, have been widely used [3]. It should be noted that the delignification by superacids generated during the cooking process does not lead to the destruction of the high-molecular component of a vegetable material. The disadvantage of such methods of obtaining fibrous semi-finished products is the significant consumption of oxidizer (H_2O_2) up to 90 % by weight of absolutely dry (abs. dry) raw materials. This factor of the process greatly increases the cost of technical pulp. Therefore, there is a need to improve the technology of the delignification process of vegetable raw materials with hydrogen peroxide in acetic acid media.

Actual scientific researches and issues analysis. Recent years scientists have conducted a large amount of research on oxidative-organosolvent cooking of vegetable raw materials, primarily agricultural waste [4-6]. Delignification of raw materials was carried out at different consumption of the oxidant (H_2O_2) from 5 to 60 % in an organic solvent at pH = 2-4 [7]. At

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the beginning of the process of cooking by peroxoacids, a heterolytic reaction of protonation of an oxygen atom of a hydroxyl group into an α-ether group occurs with the participation of a solvent. The use of oxidant at 50 % by weight of abs. dry raw materials makes possible to run the delignification of vegetable raw materials at temperatures of 90-100 ºC [7]. In addition, it should be noted that the technology of oxidative-organosolvent cooking involves the integrated processing of vegetable raw materials and the utilization of waste alkali liquor.

Uninvestigated parts of general matters defining. The absence of defined optimal parameters (temperature and cooking duration) of the wheat straw delignification process with hydrogen peroxide in acetic acid media requires further studies to obtain straw pulp with high quality indicators with minimal energy and chemical expenses.

The research objective. The purpose of this work is to study the process of oxidative-organosolvent delignification of wheat straw and to define the optimal values of its carrying out.

To achieve this goal, the following tasks were set:

– to determine the chemical composition of wheat straw shreddings;

– to investigate the impact of main factors of the delignification process on the properties of the final product;

– to make mathematical processing of the experimental data and to optimize the parameters of the straw pulp production basised of the obtained regression equations.

The experimental part

Wheat straw stalk (Triticum vulgare), harvested after the growing season and air-dried afterwards, were used for straw pulp research. Wheat straw was sorted from leaves and ears, crushed to a size of 15-20 mm and stored in a desiccator to maintain constant humidity and chemical composition. The chemical composition of wheat straw stems was performed according to TAPPI standard techniques [8]. Oxidative cooking of wheat straw was carried out with a cooking solution containing glacial acetic acid and water at a ratio of CH_3COOH : H_2O – 75:25 % by volume with the addition of hydrogen peroxide 50 % by weight of abs. dry raw material, at concentrations of H_2O_2 – 50 %. The delignification process was carried out at a temperature from 70 to 90±2 °C, cooking duration from 60 to 180 minutes, the water duty 10:1.

To save the cooking solution, the delignification process was carried out in heat-resistant flasks connected to backflow condenser. After processing, the fibrous semi-finished product was separated from the solution, rinsed with running water to neutral pH of the wash water, dehydrated and dried to a moisture content 6-8%. The yield of the product was determined gravimetrically. The quality indicators of the obtained cellulose – yield and residual lignin content were determined according to standard methods [8]. Physical-mechanical characteristics: breaking length, punching resistance, tearing resistance, folding endurance were determined according to ГОСТ 14363.4-89 [9].

The statement of basic materials. First of all, the chemical composition of the feedstock was determined. As a result of the research, the following chemical composition of wheat straw was obtained: content of cellulose – 50.1 %; lignin – 21.6 %; resins, fats and waxes (RFW) – 2.2 %; pentosans – 26.7 %; water solubility – 10.1 %; solubility in 1 % NaOH solution – 28,5 %; ash – 6.6 %. The obtained results indicated that the chemical composition of wheat straw stems is close to that of the hardwood, except content of minerals, which consists mainly from silicon oxide SiO_2. The ash content of wheat straw is several times higher than that of timber due to cereal growing conditions.

In order to obtain straw pulp, a series of laboratory cookings were conducted and the results are shown in Fig. 1.

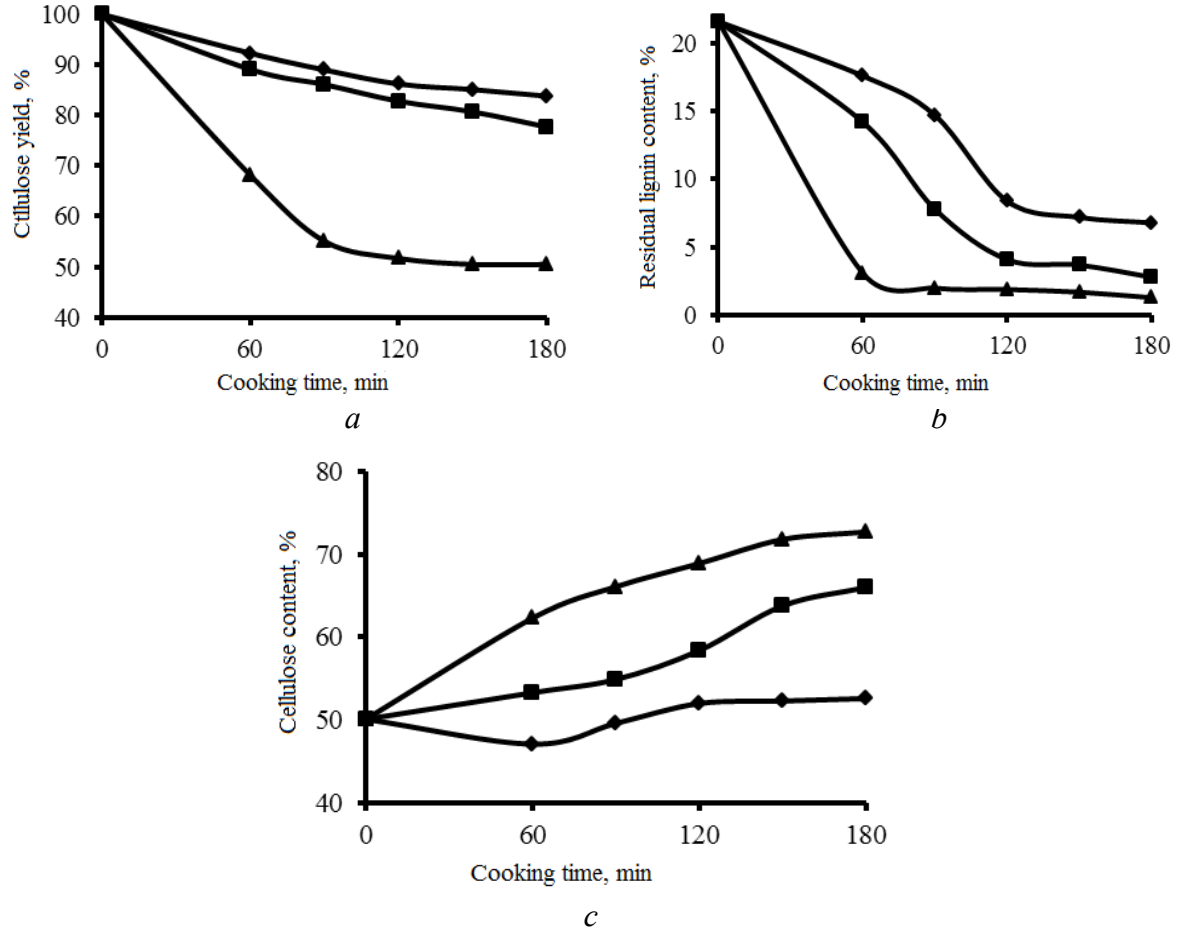


Fig. 1. Straw pulp quality indicators:
a – cellulose yield; b – residual lignin content; c – cellulose content
(– ♦ – – 70 ºC, – ■ – – 80 ºC, – ▲ – – 90 ºC)

As can be seen from the graphical dependencies at Fig. 1 (a), straw pulp yield of decreases with the increase of temperature and duration of cooking. This is due to the intensification of the process of lignin destruction because of the acidic decomposition of α-ether bonds of lignin with the formation of intermediate benzyl carbocations (Fig. 2). This explains the easier delignification of non-wood plant material, in which the proportion of non-cyclic α-aryl ether structures, which are responsible for lignin destruction, is almost as much as twice higher, than that of coniferous lignins. The organic solvent, as a weak nucleophile, blocks the active centers of lignin and impedes the process of its condensation. It should be noted that peroxide delignification of wheat straw is accompanied by partial destruction of polysaccharides, which also leads to a decrease in the yield of technical cellulose. Arabinans content changes the most quickly. The amount of glucans and xylans, which are the main components of the solid residue, decreases evenly throughout the cooking process. The cellular tissue in the straw is resistant to the components of the cooking solution.

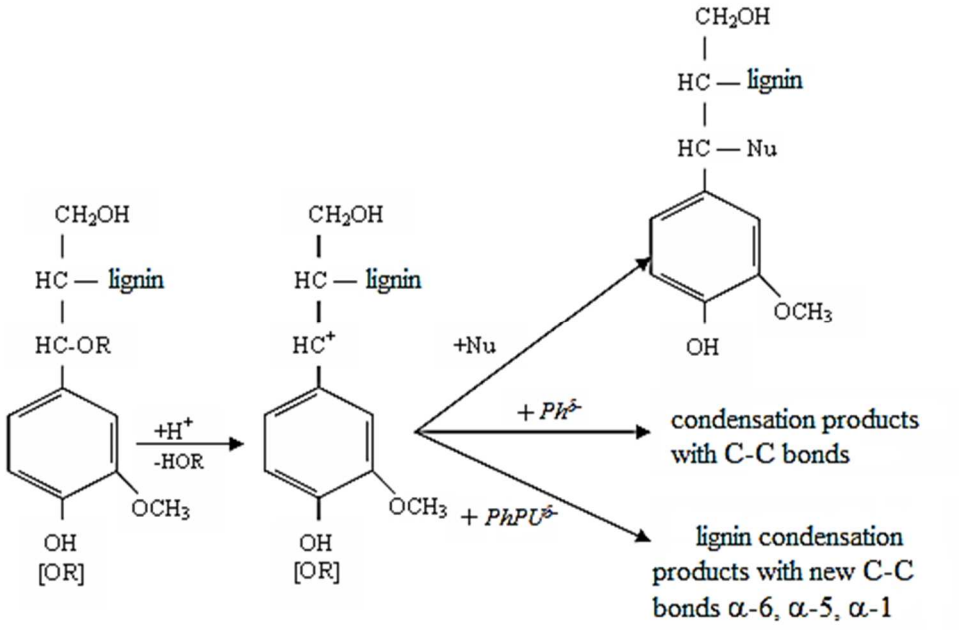


Fig. 2. The decomposition of α-ether bonds of lignin by organosolvent cooking of plant raw materials in acidic media:
Nu – an external nucleophile (HOH, C_2H_5OH, CH_3OH etc.); $PhPU^{\delta-}$ – an internal nucleophile (phenylpropane structural unit of lignin); $Ph^{\delta-}$ – an external nucleophile of the phenolic type (phenol, cresols etc.)

In organosolvent cooking in acidic media, β-ether lignin bonds (primarily the β-O-4 bond at Fig. 3) are also subject to destruction, which also leads to a decrease in the yield of straw fibrous semi-finished products.

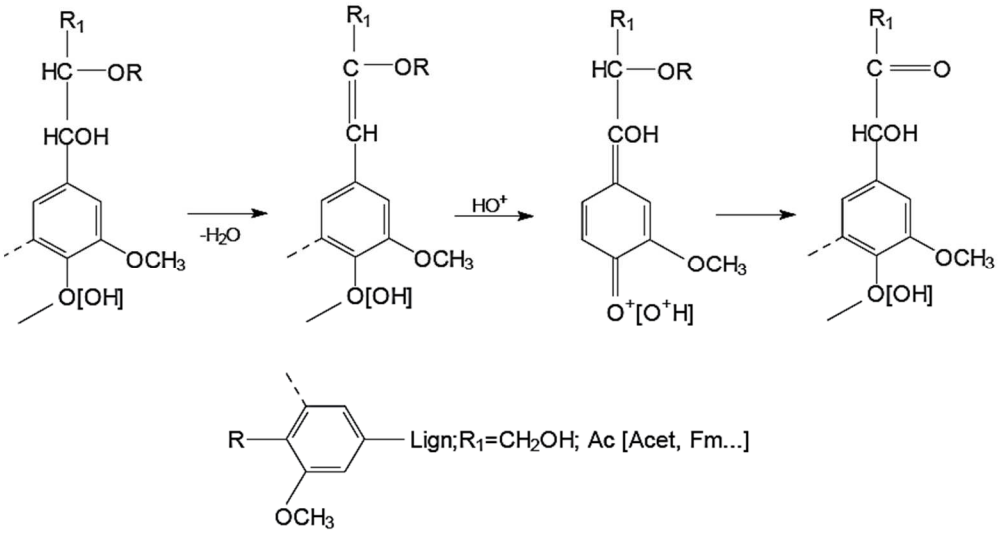


Fig. 3. The mechanism of decomposition of β – O – 4 bond

Similar dependencies are observed at Fig. 1 (b), namely with regard to the residual lignin content in straw pulp on changes of technological parameters. It should be noted that the bulk of lignin is removed from the plant material during the first 60 minutes.

The cellulose content increases due to the transition of soluble carbohydrate part of the plant raw materials – hemicelluloses and a considerable amount of pentosans – into cooking solution.

To obtain the mathematical dependence of the quality indicators of straw pulp on the main technological factors, a second-order polynomial was used, which has the following form for two independent variables:

$$y_i = b_0+b_1X_1+b_2X_2+b_3X_1X_2+b_4X_1^2+b_5X_2^2,$$

where y_i – a quality index of straw pulp

b_0, b_1, b_2, b_3, b_4, b_5 – coefficients of mathematical model

x_1 i x_2 – the values of the factors.

The following indicators of cellulose quality were determined as variable functions (y_i): y_1 – yield, %; y_2 – content of residual lignin, %. The optimization of technological parameters was performed by the multicriteria estimation method using the generalized Harrington function of desirability. According to the chosen method, the values of the parameters y_1 and y_2 were converted into the corresponding desires d_1 and d_2 [10].

As an outcome of mathematical processing of the results of cooking, regression equations were calculated that adequately describe the experimental data and can be used as a mathematical model of oxidative-organosolvent cooking, namely the production of cellulose with predetermined quality parameters.

a) mathematical model for cellulose yield, %

$y = -696.29 + 0.005155 \cdot X_1 + 21.189 \cdot X_2 + 0.00093917 \cdot X_1^2 – 0.0041333 \cdot X_1 \cdot X_2 – 0.1391 \cdot X_2^2$

b) mathematical model for residual lignin content, %

$y = +92.62 – 0.57747 \cdot X_1 – 0.761 \cdot X_2 + 0.00062697 \cdot X_1^2 + 0.0045333 \cdot X_1 \cdot X_2 – 0.0015 \cdot X_2^2$

c) mathematical model for cellulose content, %

$y = +49.826 – 0.033267 \cdot X_1 – 0.846 \cdot X_2 + 0.00032806 \cdot X_1^2 + 0.0024833 \cdot X_1 \cdot X_2 – 0.0098 \cdot X_2^2$.

In the process of mathematical modeling on the basis of the obtained regression equations the technological parameters of the cooking process were determined and the values of the pulp quality indicators in the form of the optimal point were obtained: $X_1 = 90$ ºC, $X_2 = 180$ min.

Using the obtained mathematical dependences, the quality indicators of straw pulp were calculated according to the determined technological parameters and compared with the obtained experimental data. The results are shown in Table 1.

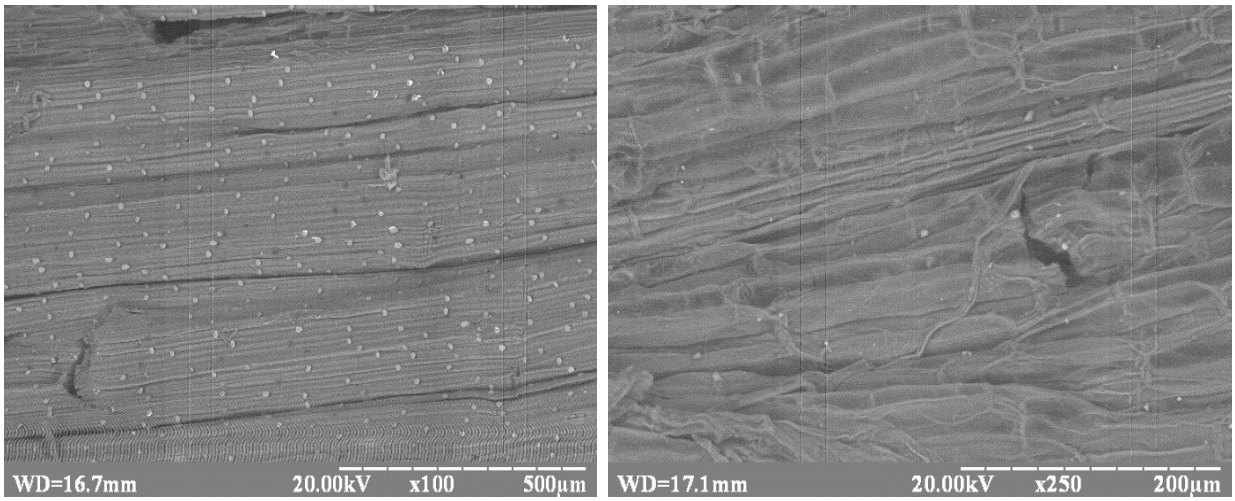
Table 1

Quality indicators of straw pulp obtained by cooking of wheat straw with hydrogen peroxide in acetic acid media

Quality indicators	Theoretical data	Practical data
Cellulose yield, %	51,6	50,5
Residual lignin content, %	1,4	1,3
Cellulose content, %	71,2	72,7

Physical-mechanical parameters of straw technical pulp obtained under optimal conditions of the delignification process were determined in accordance with the accepted methods [9]: breaking length, m – 6200, punching resistance, kPa – 210, tearing resistance, mN – 425, folding endurance, n.d.b. – 625. In terms of strength, obtained cellulose is not inferior to sulfite bleached coniferous pulp of quality class C-II according to GOCT 3914-89.

The samples of wheat straw and straw cellulose were investigated by scanning electron microscopy (Fig. 4).



a *b*

Fig. 4. Photographs of SEM samples of wheat straw (a) and straw cellulose (b) obtained by cooking with hydrogen peroxide in acetic acid at 90 °C during 180 min

As can be seen from the SEM images, cooking of wheat straw with hydrogen peroxide in acetic acid media leads to a significant change in the length of the fibers.

Conclusions. The possibility of delignification of wheat straw shreddings with hydrogen peroxide at its consumption 50 % by weight of abs. dry raw material in acetic acid media is shown.

The effect of temperature and duration of cooking on the quality of straw pulp was investigated. An increase of these parameters was found to reduce the yield of straw pulp and residual lignin content by 39 and 16.3 %, respectively.

Calculated regression equations adequately described the experimental data and could be used as a mathematical model for the oxidative-organosolvent cooking of wheat straw. The optimal technological parameters of the delignification process – temperature 90 °C, cooking time 180 min, and straw pulp quality indicators at the optimum point were determined by the multicriteria optimization method.

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ОКИСНО-ОРГАНОСОЛЬВЕНТНА ДЕЛІГНІФІКАЦІЯ ПШЕНИЧНОЇ СОЛОМИ

Актуальність теми дослідження. *Розширення сировинної бази целюлозно – паперової галузі України за рахунок використання альтернативних видів рослинної сировини, а саме пшеничної соломи та вдосконалення екологічно безпечної окисно – органосольвентної технології одержання солом'яної целюлози.*

Постановка проблеми. *Нині наявні методи делігніфікації рослинної сировини з використанням окисника – пероксиду водню. Недоліком таких способів є високі витрати окисника, а саме 90 % від маси абсолютно сухої сировини, що значно збільшує собівартість технічної целюлози. Тому необхідно вдосконалити технологічні параметри процесу делігніфікації пшеничної соломи пероксидом водню в середовищі оцтової кислоти.*

Аналіз останніх досліджень. *Були розглянуті останні публікації що є у відкритому доступі, включаючи літературу щодо окисно–органосольвентних способів делігніфіації рослинної сировини з використанням пероксокислот.*

Виділення недосліджених частин загальної проблеми. *Дослідження технологічних параметрів окисно– органосольвентної делігніфікації - зменшення витрат окисника та визначення оптимальних значень температури і тривалості процесу делігніфікації пшеничної соломи пероксидом водню в середовищі оцтової кислоти.*

Постановка завдання. *Дослідження способу одержання солом'яної целюлози з метою зниження витрат варильних реагентів за одночасного збільшення фізико–механічних показників і виходу цільового продукту.*

Виклад основного матеріалу. *Досліджено спосіб одержання солом'яної целюлози із січки пшеничної соломи в середовищі оцтової кислоти за витрат пероксиду водню 50 % від маси абсолютно сухої сировини. Визначено вміст основних компонентів у вихідній рослинній сировині. Вивчено вплив умов делігніфікації, а саме температури та тривалості варіння на вихід волокнистого напівфабрикату, вміст в ньому залишкового лігніну та вміст целюлози. Показано, що зростання температури від 70 ºС до 90 ºС і тривалості обробки рослинної сировини від 60 до 180 хв. призводить до зменшення виходу на 28 %, вмісту залишкового лігніну на 6,5 %, при цьому вміст целюлози у волокнистому напівфабрикаті зростає на 21 %. Розраховано рівняння регресії, які адекватно описують експериментальні дані і можуть бути використані в якості математичної моделі процесу делігніфікації пшеничної соломи пероксидом водню в середовищі оцтової кислоти. Методом багатокритеріальної оптимізації умов делігніфікації визначено оптимальні значення технологічних параметрів процесу варіння пшеничної соломи.*

Висновки відповідно до статті. *Розраховано рівняння регресії, що адекватно описують процес одержання солом'яної целюлози делігніфікацією пероксидом водню в середовищі оцтової кислоти. Встановлено оптимальні технологічні параметри, які забезпечують одержання кінцевого продукту з високими показниками якості (вихід 78,2 %, вміст залишкового лігніну 3,6 %, вміст целюлози 65,4 %, розривна довжина – 6200 м, опір продавлюванню 210 кПа, опір роздиранню – 425 мН, міцність на злам під час багаторазових перегенів 625 к.п.п.).*

Ключові слова*: пшенична солома; пероксид водню; оцтова кислота; делігніфікація; вихід; вміст залишкового лігніну; целюлоза; рівняння регресії.*

Рис.: 4. Табл.: 1. Бібл.: 10.

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