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RESOURCE-SAVING OXIDE-ORGANSOLVENT TECHNOLOGY OF STRAW FIBER SEMI-FINISHED PRODUCTS

Suggested method of obtaining cellulose from wheat straw stalks is substantiated. The influence of catalyst – citric acid costs on the quality indicators of straw fibrous semi – finished products has been studied. The influence of technological parameters, duration and temperature of oxidative delignification of vegetable raw materials on cellulose strength indicators is established. The developed technology allows to obtain cellulose with high quality indicators: yield from 55.1 to 84.7%, and residual lignin content from 1.0 to 6.7%, breaking lengthfrom 3000 to 7000 m and tear resistance from 275 to 520 mN. The regression equation of the process of oxidative-organosolvent cooking of wheat straw stalks using the method of full factorial experiment is obtained. The optimal parameters of the process of delignification of vegetable raw materials are obtained using optimization method and generalized Harrington desirability function. In contrast to traditional long-term and time-consuming methods of obtaining cellulose-containing fibrous semi-finished products, the developed method of delignification can reduce energy consumption and reduce negative impact on the environment. Technological parameters of the obtained straw cellulose allow its use in the production of bleached types of cardboard and paper products.

Key words: *wheat straw, peroxoacetic acid, catalyst, delignification, cellulose, mathematical models.*

Formulation of the problem. Pulp and paper industry of Ukraine has shown quite positive results in recent years. At the same time, reserves of intensive development remained only in medium and small enterprises. Opportunities to increase production at large enterprises due to intensive factors are almost exhausted. Development of the pulp and paper industry in the country depends primarily on the consumption of its products. Production facilities of pulp and paper enterprises of Ukraine are loaded by only 30%, and about 50% of cardboard and paper products, imported into the country [1-2]. Today products of domestic enterprises in the industry are 80% made from secondary raw materials, which negatively affectsits quality. This problem is due to the lack of own production of cellulose semi-finished products. This problem can be solved by using annual plants and agricultural waste for the production of cellulose-containing materials for various purposes.

Over the last 20 years, principles of evaluating cellulose production methods in the world have changed significantly. Tighter requirements for the composition of effluents and gaseous emissions of industrial enterprises raised the question of the need to abandon technologies that involve usage of chlorine and sulfur compounds. This stimulated research for alternative ways of delignification of plant raw materials that would be more environmentally friendly. Nevertheless, problem of contamination with hydrogen sulfide, organic sulfides and other harmful compounds can`t be solved only by improving the auxiliary processes and equipment (absorption, evaporation, washing, sodoregeneration).

One of the ways to solve environmental problems is to develop fundamentally new ways to produce cellulose. First of all, it can be catalytic oxidative methods of delignification of vegetable raw materials with hydrogen peroxide in an acidic environment[3-4].

Analysis of recent researches and publications. Effective catalysts for the reaction of lignin oxidation by hydrogen peroxide are compounds of transition metals – chromium, molybdenum, tungstate. They interact with hydrogen peroxide with the formation of intermediate peroxocomplexes [5-6]. Peroxocarboxylic acids, like most hydroperoxides, are chemically unstable, mainly due to influences of metals of variable valence. The addition of citric acidis significantly more effectiveto improve the stability of peroxyacids(0.3% by volume, which is 1.5% by weight of absolutely dry wood) [7-9]. Therefore, such oxidative-organosolvent technologies are one of the promising areas for obtaining cellulose from non-woody vegetable raw materials.

Agriculture which produces significant amount of grain, industrial and other crops annually, has a large resource of by-products. Of all types of agricultural waste, cereal stalks are recognized as suitable for the production of fibrous semi-finished products [10-12].

Formulation of the goals of the article. The aim of the work is to develop resource-saving and cost-effective catalytic oxidative-organosolvent technology for pulp production from Ukraine's own raw materials.

Presentation of the main material of the research. Distinctive features of the fibrous mass of wheat straw determines its chemical composition. Stems of wheat straw contain large amount of pentosans 26.7%, lignin content lower than 17.7% and total ash content and content of silicon compounds compared to deciduous wood (for birch the corresponding figures are 23.3%, 19.4% and 0.5%) are several times higher – 6.6%.

Study of the process of obtaining cellulose from wheat straw chips in the system "acetic acid – water-hydrogen peroxide" was based on technological modes developed by authors [13]. In order to reduce the cost of cellulose for the cooking process, it is proposed to use citric acid as a catalyst, which is many times less expensive than molybdenum and tungstate and has a multi-ton production.

There was made a number of experimental researches of the process of delignification of wheat straw chaff with a cooking solution containing glacial acetic acid and water, at a ratio of 75:25 by volume, with the addition of 50% H_2O_2 by weight of absolutely dry raw materials, and citric acid at a cost of 0.5 to 3.0% by weight of absolutely dry raw materials. Delignification was performed at constant temperature and duration (100 °C, 90 min.) in glass flasks at atmospheric pressure. The results of cooking were characterized by the yield of solid residue (as a percentage of the mass of absolutely dry raw materials) and the mass fraction of lignin in the solid residue (as a percentage) of Fig. 1.

Investigation has found (Fig. 1) that the usage of citric acid leads to an increase in the yield of straw cellulose by 1.5 – 4.1%, content of residual lignin decreases by 0.46 – 0.58% by weight of absolutely dry cellulose. Such changes in the quality of the solid residue are associated with the acceleration of the process of dissolution of lignin macromolecules and its transfer to the cooking solution and the stabilization of the carbohydrate component of vegetable raw materials.

It should be noted that with the usage of citric acid more than 0.5% compared to the weight of dry raw

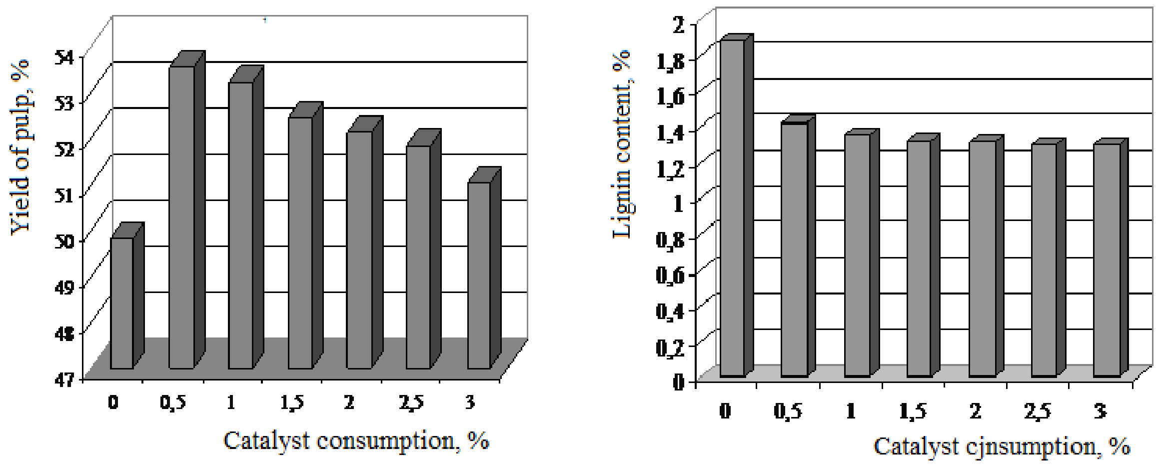

Figure 1. Dependence of yield and residual lignin content of oxidative-organosolvent straw cellulose on the catalyst content in the cooking solution

materials, the yield decreases with almost the same degree of delignification compared to similar cooking of wheat straw without usage of chemical impurities. The optimal values of these parameters of the process of delignification of wheat straw are achieved at a consumption of citric acid 0.5% by weight of absolutely dry raw materials.

Oxidative cooking of wheat straw with a cooking solution containing glacial acetic acid and water in the ratio CH_3COOH : H_2O – 75 : 25 volume % with the addition of hydrogen peroxide 50% by weight of absolutely dry raw material are used to establish the optimal cooking parameters – temperature and duration of the delignification process,. The delignification process was carried out at a temperature starting from 80 to 100 ± 2 ° C, duration from 60 to 180 minutes, hydromodule 10: 1, catalyst consumption 0.5% by weight of absolutely dry raw material Quality indicators of acetic – peroxide straw cellulose are given in table 1.

The process of delignification of vegetable raw materials in the studied system takes place in mild conditions with significant swelling of plant fibers. The growth of technological parameters, especially temperature, accelerates the process of delignification, which allows to obtain cellulose with high yield and low residual lignin.

Indicators of strength of the obtained organosolvent straw cellulose are shown in Fig. 2. Fibrous semi-finished product obtained at a temperature of 80 °C with the duration of the delignification process 60-120 minutes is failed to grind due to the large amount of indigestion.

Due to the better paper-forming properties of straw cellulose due to the formation of additional hydrogen bonds between polysaccharides and high content of hemicelluloses, with increasing cooking time to 120 minutes, the physical and mechanical properties of the obtained fibrous semi-finished products increase. Further increase in cooking time doesn`t improve strength to the large extend. As the resultthis pulp is recommended for the production of mass bleached paper.

For the mathematical processing of the results, a complete factorial experiment was used. The follow-

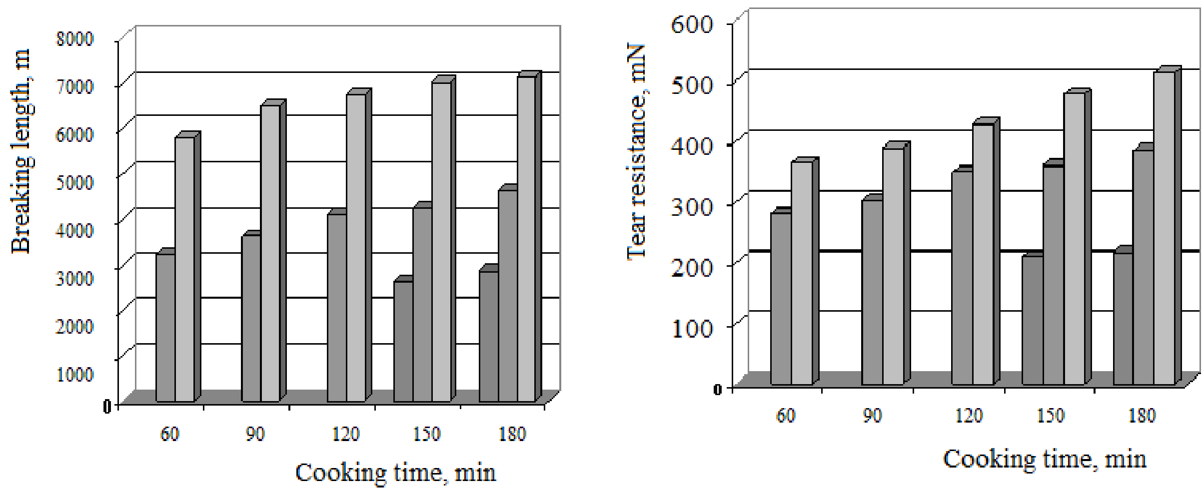

Figure 2. Dependence of breaking length and tear resistance of straw cellulose on the duration of the cooking process wheat straw at different temperatures: ■ – 80ºC, ■ – 90ºC, ■ – 100ºC

Table1

Quality indicators of straw fibrous semi-finished products

Delignification temperature, ºC	Quality indicators of fibrous semi-finished products by cooking time, min				
	60	90	120	150	180
Yield of fibrous semi-finished products,% of absolutely dry raw materials					
80	-	84,7	80,4	78,6	73,2
90	76,9	74,7	73,3	65,6	62,1
100	68,7	57,5	56,9	55,6	55,1
Residual lignin content, %					
80	-	6,7	5,6	5,5	5,3
90	6,7	5,5	4,6	4,1	4,0
100	2,4	2,2	1,7	1,5	1,0

ing variables were considered as the main technological parameters influencing the quality indicators of oxidative-organosolvent straw cellulose (x_i), which after ranking according to the degree of influence on the output variables (Y_i), are located in the following row: cooking temperature, ° C (x_1); cooking time, min. (x_2); pH of the medium (x_3); hydraulic module of cooking (x_4); degree of compaction (x_5); humidity of raw materials (x_6); chemical composition of raw materials (x_7).

Since vegetable raw materials with the same humidity and chemical composition, degree of compaction, hydromodule and pH of the medium were used for cooking, the factors $x_1 – x_7$ are constant in the study and therefore weren`t taken into account when obtaining regression equations. The following cellulose quality indicators were selected as optimizing parameters: cellulose yield,%, (Y_1); residual lignin content,% (Y_2); tear resistance, mN (Y_3); breaking length, m (Y_4).

The mathematical model, in accordance with its purpose, should reflect the mechanisms of the studied processes with the greatest degree of accuracy. That is why the purposeful usage of information in order to study the pattern of changes in the mentioned properties should be done by the development and further study of mathematical models. As a result of mathematical processing, regression equations were obtained, which adequately describe the dependences of the initial variables Y_i on technological factors x_i:

a) mathematical model for cellulose yield, %

$$Y_1 = + 70,422 – 10,2x_1 – 7,25x_2 + 0,375x_1x_2 – 0,33333x_1\hat{}2 + 0,51667x_2\hat{}2$$

b) mathematical model for the content of residual lignin, %

$$Y_2 = + 4,7544 – 2,215x_1 – 1,0483x_2 + 0,2025x_1x_2 – 1,1817x_1\hat{}2 + 0,51833x_2\hat{}2$$

c) mathematical model in terms of tear resistance, mN

$$Y_3 = + 340,22 + 117,33x_1 + 47,833x2 + 28x_1x_2 – 20,333x_1\hat{}2 – 3,8333x_2\hat{}2$$

d) mathematical model in terms of breaking length, m

$$Y_4 = + 4071,1 + 2068,3x_1 + 593,33x_2 + 120x_1x_2 + 508,33x_1\hat{}2 – 146,67x_2\hat{}2$$

The optimum point is observed under conditions when factors x_1 and x_2 acquire the following values: cooking temperature x_1 = 100 °C; cooking time x_2 = 90 minutes.The optimum quality indicators of the obtained straw cellulose has the following values: yield – 63.8%, residual lignin content – 1.98% by weight of absolutely dry cellulose, tear resistance – 394 mN, breaking length – 6210 m.

According to the found statistical regression equations $Y_1 – Y_4$, multicriteria optimization was performed using the Gauss – Seidel method, and also determined the compromise area of delignification of wheat straw depending on the main technological parameters (x_i), which is shown in Fig. 3 (the area is located on the plane $x_1 – x_2$).

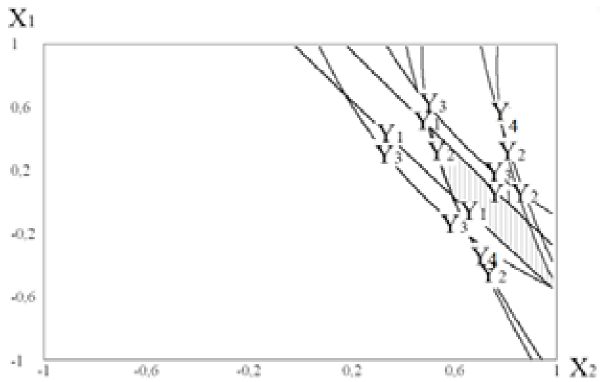

Figure. 3.Compromise area of oxidative-organosolvent delignification of wheat straw: 1 – cellulose yield; 2 – residual lignin content; 3 – tear resistance; 4 – breaking length

The analysis of the obtained regression equations allows us to state that the indicators of cellulose quality are more influenced by the temperature of the delignification process.

Conclusions. On the basis of the conducted theoretical and experimental researches the usage of citric acid as a catalyst is offered as a resource-saving way of reception of cellulose from stalks of wheat straw. Using the method of experimental planning and analysis of experimental data, the optimal mode of oxidative low-temperature delignification of vegetable raw materials was determined. The proposed cooking is an alternative and environmentally friendly way to obtain cellulose.

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Трембус І.В., Гондовська А.С., Тінницька Е.Ю., Михайленко Н.В. РЕСУРСООЩАДНА ОКИСНО-ОРГАНОСОЛЬВЕНТНА ТЕХНОЛОГІЯ ОДЕРЖАННЯ СОЛОМ'ЯНИХ ВОЛОКНИСТИХ НАПІВФАБРИКАТІВ

Обгрунтовано запропонований спосіб одержання целюлози із стебел пшеничної соломи. Вивчено вплив витрат каталізатора – лимонної кислоти на показники якості солом'яних волокнистих напівфабрикатів. Встановлено вплив технологічних параметрів, тривалості і температури окисної делігніфікації рослинної сировини, на показники міцності целюлози. Розроблена технологія дозволяє отримати целюлозу з високими показниками якості: виходом від 55,1 до 84,7 %, та вмістом залишкового лігніну від 1,0 до 6,7 %, розривною довжиною від 3000 до 7000 м та опором роздиранню від 275 до 520 мН. Отримано рівняння регресії процесу окисно-органосольвентного варіння стебел пшеничної соломи з використанням методу повного факторного експерименту. Методом оптимізації з використанням узагальненої функції бажаності Харінгтона одержано оптимальні параметри проведення процесу делігніфікації рослинної сировини. На відміну від традиційних довготривалих і трудомістких способів отримання целюлозовмісних волокнистих напівфабрикатів, розроблений метод делігніфікації дозволяє зменшити енерговитрати і знизити негативний вплив на навколишнє середовище. Технологічні параметри одержаної солом'яної целюлози дають можливість її використання у виробництві вибілених видів картонно-паперової продукції.

Ключові слова: *солома пшенична, пероксооцтова кислота, каталізатор, делігніфікація, целюлоза, математичні моделі.*