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USED PULPING LIQUORS APPLICATION IN OXIDATIVE – ORGANOSOLVENT TECHNOLOGY OF STRAW CELLULOSE PRODUCTION

The study demonstrated the production of oxidative pulp from wheat straw stalks using the acetic acid-water-hydrogen peroxide system with the addition of 0.5% citric acid by weight of dry raw materials as a catalyst. The cooking solution consisted of 75% ice-cold acetic acid and 25% water by volume, with the addition of 50% hydrogen peroxide by weight of dry raw materials. The delignification process of non-woody plant material was studied at a hydraulic module of 10:1, using different temperatures and durations (80-100°C, 60-180 minutes, respectively). The straw pulp obtained has high-quality indicators. The yield ranges from 55.1% to 84.7%, with residual lignin content of 1.2% to 6.7% by weight of absolute dry raw material. Additionally, it has a tearing resistance of 200-510 mN and a tensile strength of 2500-7000 m. This pulp can be used in the composition of various types of cardboard and paper products. The research analysis revealed that a method of regenerating spent cooking solutions during oxidative-organosolvent cooking of non-woody plant material involves returning a portion of the spent cooking solution for re-cooking. The residual concentrations of delignifying substances in the spent cooking solution were measured. It was discovered that the primary delignifying reagent, peroxoacetic acid, was only used in amounts ranging from 37-53%. Experimental results have shown that adding a spent solution, comprising 10% of the fresh solution, does not significantly reduce the quality of the resulting straw pulp. In fact, it increases the yield by 1.3% while only increasing the residual lignin content by 0.52% by weight. The infrared spectra of oxidized lignin and straw pulp were obtained with and without the addition of spent pulp to the fresh cooking solution. It was found that the precipitated oxidative lignin contains a small amount of polysaccharide component.

Key words: *oxidative-organosolvent delignification, wheat straw, cellulose, lignin, regeneration, spent cooking solution, infrared spectrum.*

Formulation of the problem. The environmental and technological evaluation of existing methods for obtaining technical cellulose has changed significantly all over the world. Strict requirements for industrial effluents composition and gaseous emissions in pulp and paper industry fundamentally raised the question of necessity to abandon technologies using chlorine and sulfur compounds [1]. Non-wood plant raw materials, namely the straw of cereal crops, are processed into fibrous semi-finished products mainly by alkaline cooking methods – sodium and sulfate. Taking into account high ash content of raw material, short fiber length, macro and microstructure heterogeneity, number of technological complications arise during such raw materials delignification [1, 2]. During alkaline delignification of cereal crops straws almost all mineral substances are transferred to used cooking liquors which causes difficulties in evaporation, causticization processes and burning of lime sludge [3].

Catalytic oxidation delignification methods of plant material using hydrogen peroxide in acidic environment are being considered at the moment [4, 5]. Oxidative-organosolvent methods are environmentally friendly and resource-saving that make possible to obtain fibrous semi-finished products with high yield, low energy consumption and absence applying harmful substances in process. It should be noted that oxidative-organosolvent technologies include complex processing of plant raw materials. They make possible to utilize hemicelluloses and isolate reactive lignin from pulp liquors which further processed into valuable chemical products [6].

Peracetic acid is one of the promising reagents for vegetable raw materials delignification. Plant raw materials cooking with this acid take place at temperatures up to 100°C, without excess pressure and with high delignification process selectivity [7, 8]. The pulp which obtained in this way characterized by high yield and whiteness, which indicates low lignin content in solid residue. Peracetic acid can be prepared in various ways including from acetic acid which is multitonnable and relatively cheap product of wood chemistry and other chemical synthesis [9]. The issue of used cooking solutions regeneration remains unresolved in proposed technologies of oxidizing-organosolvent pulp production.

Analysis of recent research and publications. Most studies of plant raw materials processing into cellulose are devoted to research chemical processes, delignification kinetics, technical cellulose properties and components of destruction in lignocarbon complex. Only some works consider the issue of processing and multiple application used cooking solutions [10, 11]. Acetic acid working solution after cooking plant raw materials does not contain mineral components, which simplifies its complex processing and allows it to be partially returned to technological cycle in contrast to sulfite and sulfate pulp obtaining methods. In the study [10] it is proposed to regenerate acetic acid using azeotropic distillation method in wood processing with aqueous environment of ethanol and acetic acid mixture. Used cooking solution is regenerated in vacuum evaporator during wheat straw processing [12, 13]. The regenerated clear distillate is returned to technological process while low molecular weight lignin is isolated from the cubic residue. However, components removal from cubic residue is complicated by resinous substances accumulation. Oxidative-organosolvent process with using returned solutions for further cookings with insufficient amount replenishment of delignifying reagents can be considered promising from the point of view of regeneration [14]. Therefore, improving cellulose obtaining technology by oxidation-organosolvent delignification methods from non-wood plant materials with used cooking solutions recovery is urgent task today.

Setting objectives. The work purpose is to evaluate possibility of using spent cooking solutions after oxidative-organosolvent cooking of wheat straw to obtain technical cellulose.

Presentation of main research material. The characteristic features of fibrous mass from wheat straw are primarily determined by its chemical composition. Its definition was carried out in accordance with the existing TAPPI standards [15] for various plant raw materials components, namely: T-222 – for lignin; T-257 – for substances extracted with hot water; T-212 – for substances extracted with 1 % NaOH; T-204 – for substances extracted with alcohol-benzene solution; T-211 – for determination of ash content (Fig. 1).

During the study of obtaining straw cellulose process in the system "acetic acid–water–hydrogen peroxide", the technological indexes developed by authors [12] were taken as basis. Citric acid was used as catalyst in amount of 0,5 % by weight of absolute dry raw material. It was conducted number of experi-

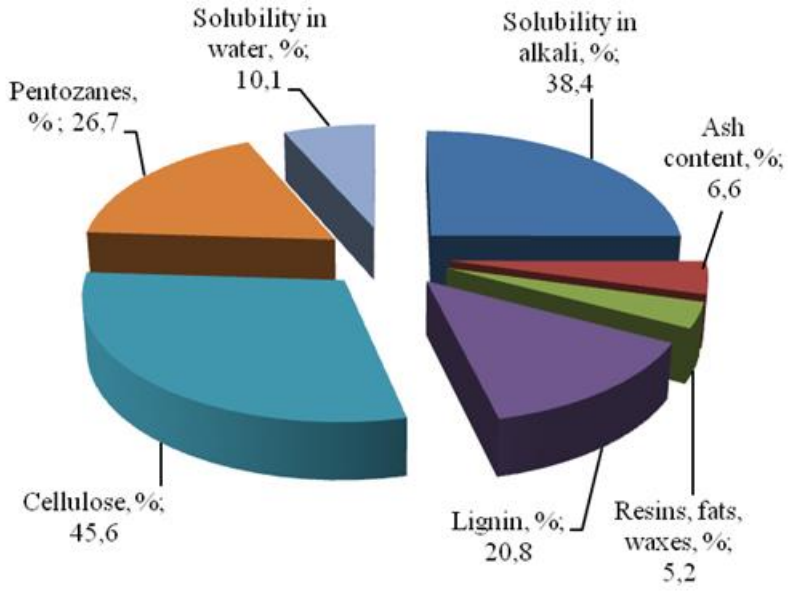

Fig. 1. Chemical composition of wheat straw stalks

mental studies of wheat straw delignification process with cooking solution containing glacial acetic acid and water in their ratio 75:25 % by volume, with addition 50 % H_2O_2 by weight of absolute dry raw material. Process took place at hydromodule 10:1, at different temperatures (80–100°C) and durations (60–80 min.) in glass flasks at atmospheric pressure.

The delignification process of plant raw materials in studied system takes place in mild conditions with significant swelling of plant fibers. Increasing technological parameters, primarily temperature, accelerates delignification process, which allows obtain cellulose with high yield 55,1–84,7 %, low residual lignin content 1,2–6,7 % and high strength indicators (tear resistance 200–510 mN, breaking length 2500–7000 m).

Used cooking solution is subject of regeneration after peroxoacetic delignification method of plant raw materials, but it should be noted that there are certain disadvantages associated with solvent regeneration [14]:

– high boiling point of acetic acid (118,1°C);

– azeotrope formation during rectification process of acetic acid with insufficient content for direct usage for cellulose obtaining process (azeotrope boiling temperature is 124,1°C).

These problems not only complicate solvent regeneration, but also lead to its loss. Most of hydrogen peroxide spent on peroxyacid formation with subsequent oxidation of lignin. The remainder is lost during its decomposition with molecular oxygen formation and cannot be regenerated [12, 14].

After analyzing used solution it was established that peracetic acid concentration in solution decreases from 4,3 to 2,8 %, depending on temperature and process duration. It was experimentally established that during hot peroxyacetic acid preparation, its maximum concentration is at level 7,3–7,9 %. It is advisable to reuse spent cooking solution for wheat straw cooking process based on fact that main delignifying reagent was used only in the amount 37–53 %.

It is worth noting that in delignification process cooking solution affects entire plant raw materials complex. At the same time, main lignin destruction products mass, part of hemicelluloses, extractive substances and cellulose is also partially destroyed. Complex of substances accumulates in reactor, which are very difficult to isolate and identify as a result of all these reactions.

To determine lignin content in dry residue organic part composition it was used a technique consists of leaching lignin compounds with sulfuric acid with concentration 30 % at pH 1–2 [16]. The solid residue was not treated with acid as pH of used cooking solution was 2. The lignin sediment formed in settling process was filtered through glass filter and used for further research. The settled liquor was used for adding to fresh cooking solution in delignification process of wheat straw stalks.

Cooking with the system "acetic acid-water-hydrogen peroxide-citric acid" was carried out in order to study the effect of using spent cooking solution in composition with fresh one. The process was carried out at temperature 100°C and duration 90 minutes with content of used filtered cooking solution in composition with fresh one from 5 to 25 %. The results of the research are shown in Table 1.

The research results make it possible to state that increasing amount of spent cooking solution leads to slight increase in yield. But it is worth noting that used liquors addition simultaneously leads to increasing residual lignin amount in obtained technical cellulose.

It was experimentally established that this tendency is much less pronounced in case of adding filtered cooking solution. Increasing content of used solution by more than 15 % worsens the delignification process. It was established that lignin content increases sharply by 1,8 % and the whiteness of pulp visually decreases. Used cooking solution should be apply only in small quantities of 10–15 % and in filtered state for re-cooking despite the fact that it contains sufficient amount of delignifying reagent.

The IR spectroscopy was utilized to examine structure of cellulose samples derived from oxidative delignification of wheat straw and residual solid matter left after processing (Fig. 2). Spectra were collected in the range of 400–4000 cm^{-1}. Sample 1 consisted of oxidized lignin, while sample 2 represented cellulose obtained through cooking in acetic acid-wa-

Table 1

Quality indicators of straw semi-finished fibre products from the content of spent cooking solution in the composition of fresh cooking solution

Quality indicators, %	Fraction of spent cooking solution/spent and filtered, %					
	0	5	10	15	20	25
Yield	63,8	64,2/63,9	65,1/64,1	66,3/65,8	66,1/66,2	68,2/67,8
Content of residual lignin	1,98	2,2/2,0	2,5/2,1	3,0/2,3	3,8/2,8	4,9/3,0

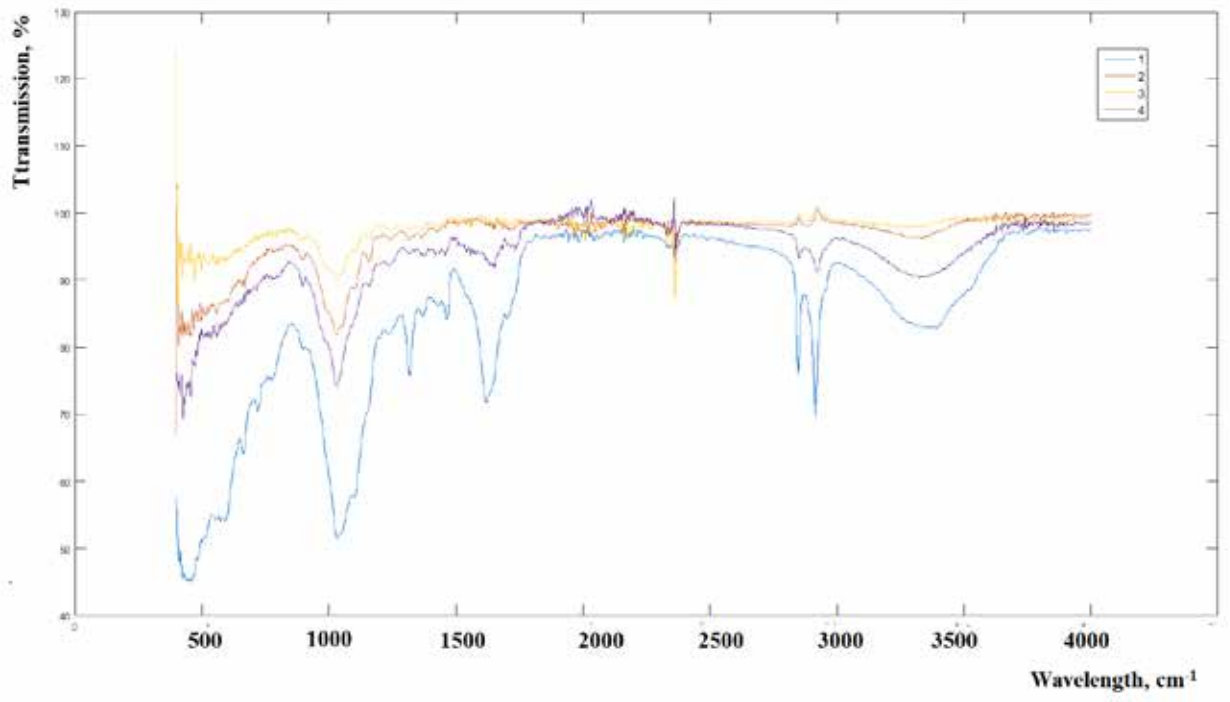

Fig. 2. IR spectrum of laboratory organosolvent lignin and straw cellulose samples

ter-hydrogen peroxide-citric acid system. Samples 3 and 4 were prepared similarly but using 10 % spent cooking solution and spent filtered cooking solution, respectively. All samples exhibited a broad absorption band in the 3000–3600 cm^{-1} range, attributed to O-H vibrational oscillations, along with absorption bands at 2838 and 2914 cm^{-1} corresponding to C-H oscillations. These bands are present due to hydroxyl groups and C-H bonds found in cellulose, hemicellulose, and lignin. However, higher intensity of the band in 3000–3600 cm^{-1} range for sample 1 is indicative of higher moisture content. The presence of absorption band at 1745 cm^{-1} is attributed to stretching vibrations of C=O in hemicelluloses and lignin. Moreover, this band is more prominent in sample 1, suggesting higher lignin and hemicellulose content in its structure. Treatment of raw material with peroxyacid resulted in removal of these components, leading to significant reduction in intensity of the 1745 cm^{-1} band for samples 2, 3, and 4.

The absorption peak at 1618 cm^{-1} corresponds to asymmetric vibrations of carboxyl group of glucuronic acid in hemicelluloses and C=O vibrations within lignin's structure. Following treatment, there's notable decrease in intensity of this peak, further confirming delignification process. Additionally, absorbed H_2O presence contributes partially to band at 1618 cm^{-1} in samples IR spectra. The absorption bands at 1457, 1424, 1370, and 1317 cm^{-1} are indicative of samples containing lignin and stem from C-H deformation vibrations in CH_2 and CH_3 groups. It's evident that sample 1 exhibits higher lignin content compared to samples 2, 3, and 4. Across all samples, bands at 1160 and 896 cm^{-1} arise from C-O-C stretching in β-(1→4)-glycosidic bonds within cellulose and hemicellulose. Due to its lignin content, sample 1 also presents absorption band at 846 cm^{-1}, corresponding to C-H fluctuations in aromatic structure of lignin.

Conclusions. It was determined that straw cellulose with high quality indicators was obtained by cooking in acetic acid – hydrogen peroxide – water system of hay straw with citric acid addition in the amount 0,5 % according to the results of comprehensive research.

The chemical composition of spent cooking solution after wheat straw delignification was analyzed. It was determined that application of used solutions and solutions after oxidized lignin planting in amount of 10 % in composition work cooking solution does not deteriorate obtained straw cellulose quality indicators.

It was established that planted oxidized lignin contains small amount of polysaccharide component in its composition with using IR spectroscopy.

Bibliography:

1. Cybulska I., Brudecki G. P., Zembrzuska J. Organosolv delignification of agricultural residues (date palm fronds, Phoenix dactylifera L.) of the United Arab Emirates. *Applied Energy*. 2017. No. 185, P. 1040-1050.
2. Dapia S., Santos V., Parajo J. C. Formic acid-peroxyformic acid pulping of Fagussylvatica. *Journal of Wood Chemistry and Technology*. 2000. No. 20, P. 395-413.
3. Nakano J., Kitanaka Y. Chemical Pulping of Straws (III). Properties of ash fnd Behaviors of Ash in Alkaline Cooking. *Japan Tappi Journal*. 1996. Vol. 50, No. 4, P. 692-696.
4. Barbash V.A., Trembus I.V., Nagorna J.M. Pulp obtaining from ornstalks. *Chemistry &chemical technology*. 2012. No. 1, P. 83–87.
5. Poppius–Levlin K., Mustonen R., Huovila T., Sundquist J. MILOX pulping with aceticacid/peroxyacepticacid. *Paper ija Puu*. 1991. No. 2, P. 154–158.
6. Oral J., Sikula J., Puchy R., Hajny Z., Stehlik P., Bebar L. Processing of waste from pulp and paper. *Journal of Cleaner Production*. 2005. No. 13, P. 509-515.
7. Kham L., Bigot Y.L., Delmas M., Avignon G. Delignification of wheat straw using amixture of caroxylicacid andperoxo acids. *Industrial cropsand products*. 2005. No. 5, P. 9–15.
8. Barbash V., Trembus I., Sokolovska N. Performic pulp from wheat straw. *Cellulose chemistry and technology*. 2018. Vol. 7-8, No. 52, P. 673-680.
9. Constant S., Basset C., Dumas C., Renzo F. Di, Robitzer M. Reactive Organosolv Lignin Extraction from Wheat Straw: Influence of Lewis Acid Catalysts on Structuraland Chemical Properties of Lignins. *Industrial Crops and Products*. 2015. Vol. 65, P.180-189.
10. Barbash VA, Makarenko AA, Bondar RV, Bondar SE, Trembus IV. Poluchenye voloknystykh polufabrykatov yz sorho sakharnoho. *Enerhotekhnolohyy y resursosberezhenye*. 2010. No. 2, S. 38-41.
11. Edel R. M., Brunow G. Reactions of β-aryl ether lignin model compounds under formic acid and peroxyformic acid pulping conditions. *The Intern. Symp. on Wood and Pulping Chemistry.* Raleigh, USA. 1989. May 22–25.
12. Trembus I.V., Sokolovska N.V. Delihnifikatsiia pshenychnoi solomy v systemi CH_3COOOH-H_2O-H_2O_2. *Wshodnioeropejskie Czasopismo Naukowe East European Scientific Journal.* 2018. No. 2, S. 61-66.
13. Abad S., Santos V., Parajo J. C. Formic acid-peroxyformic acid pulping of aspenwood: an optimization study. *Holzforschung*. 2000. No. 54, P. 544-552.
14. Trembus I., Trophimchuk J., Deykun I., Cheropkina R. The catalytic delignification of sunflower stalks with hydrogen peroxide in the environment of acetic acid. *Journal of Chemical Technology and Metallurgy.* 2021. Vol. 56, No. 2. P. 296-301.
15. TAPPI test methods. *Tappi Press.* Atlanta, Georgia. 2004.
16. Trembus I.V., Hondovska A.S., Tinytska Ye.Yu., Mykhailenko N.V. Resourse-saving oxide-organo-solvent technology of straw fiber semi-finished products. *Вчені записки Таврійського національного університету імені В.І. Вернадського. Серія: Технічні науки.* 2022. Т. 33 (72). № 2, С. 80-84.

Трембус І.В., Михайленко Н.В., Гондовська А.С. ВИКОРИСТАННЯ ВІДПРАЦЬОВАНИХ ЩОЛОКІВ В ОКИСНО-ОРГАНОСОЛЬВЕНТНІЙ ТЕХНОЛОГІЇ ОДЕРЖАННЯ СОЛОМ'ЯНОЇ ЦЕЛЮЛОЗИ

Показано можливість отримання окисної целюлози із стебел пшеничної соломи в системі «оцтова кислота-вода-пероксид водню» з додаванням в якості каталізатора лимонної кислоти в кількості 0,5 % від маси абсолютно сухої сировини. Варильний розчин містив льодяну оцтову кислоту та воду у співвідношенні 75 : 25 об'ємних %, з додаванням 50 % пероксиду водню від маси абсолютно сухої сировини. Процес делігніфікації недеревної рослинної сировини досліджувався за гідромодуля 10 : 1, різної температури та тривалості (80–100 ^{0}C, 60–180 хв, відповідно).Одержана солом'яна целюлоза має високі показники якості: вихід 55,1–84,7 %, вміст залишкового лігніну 1,2–6,7 % від маси абс. сух. сировини, опір роздиранню 200–510 мН, розривну довжину 2500–7000 м і може бути використана в композиції масових видів картонно-паперової продукції. Аналіз досліджень показав, що для регенерації відпрацьованих варильних розчинів за окисно-органосольвентного варіння недеревної рослинної сировини використовують спосіб повернення частини відпрацьованого розчину на повторне варіння. Визначено залишкові концентрації делігніфікуючих речовин у відпрацьованому варильному розчині. Встановлено, що основний делігніфікуючий реагент, пероксооцтова кислота, використана лише у кількості 37–53 %. Експериментально встановлено, що додавання

відпрацьованого розчину у кількості 10 % у складі свіжого розчину не значно погіршує показники якості одержаної солом'яної целюлози (вихід зростає на 1,3 %, при цьому збільшується вміст залишкового лігніну на 0,52 % від маси. абс. сух. сировини). Отримано ІЧ спектри окисного лігніну та солом'яної целюлози, одержаної з додаванням і без додавання до свіжого варильного розчину відпрацьованого щолоку. Встановлено, що висаджений окисний лігнін містить у своєму складі незначну кількість полісахаридної складової.

Ключові слова *окисно-органосольвентна делігніфікація, пшенична солома, целюлоза, лігнін, регенерація, відпрацьований варильний розчин, ІЧ-спектроскопія.*