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PREPARATION OF PULP FROM SUNFLOWER STALKS USING PEROXY ACIDS

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Wood fibers are the most common material for the production of paper and cardboard. However, forest resources are decreased rapidly nowadays due to their use in cellulose and papermaking industry and in some competing industries, such as building and furniture productions. It is necessary to propose new resources of raw materials and new environmentally friendly methods for obtaining pulp to produce different paper products. In this study, the methods for the cooking of sunflower stalks were developed using peracids, in particular peracetic and performic acids. The chemical and physical properties of pulps were investigated. High-quality pulps were obtained with a yield in the range from 46 to 94% and with the content of residual lignin from 1.2 to 9.6%. The effects of temperature and duration of the delignification process on the quality indices of the obtained pulp were investigated. The lignin-carbohydrate diagram of delignification of sunflower stalks by different methods was developed. The regression equations for the process of peracetic cooking of sunflower stalks were derived. The optimal parameters of the oxidative-organosolv delignification of sunflower stalks were obtained with the application of Harrington's desirability function.

Keywords: peroxy acid, delignification, quality indices, regression equation, optimization.

Introduction

The growth of the needs in cardboard and paper products and the shortage of wood raw materials in pulp and paper industry escalate the problem of expanding the raw material base through the use of plant agricultural wastes. Ukraine is one of the leaders in world exports of sunflower seed processing products, and Ukraine's share in world trade of sunflower oil is estimated to be 56%, so a large number of fields are occupied with sunflower crops. Most of the sunflower stalks are not applied for further processing. Using only 25% of this amount will allow receiving from 1 to 3 million tons of pulp for the production of cardboard and paper products, which will increase the use of paper and cardboard per capita in Ukraine [1].

The processing of non-wood materials (NWM) into pulp for cardboard and paper products is associated with the specific features of the anatomical structure and chemical composition of these materials, the requirements for the quality of pulp and the technical and economic indicators of the certain method of delignification [2].

An important fact for a further development of the pulp and paper industry is the reduction of the negative impact on the environment. One of the ways to solve environmental problems of the industry is to develop new and modernization of existing methods for pulp obtaining, in particular organosolv methods of delignification. These methods are environmentally friendly and allow obtaining pulp with a high yield at relatively low energy consumption providing the absence of sulfur-containing by-products and wastes [3] and chlorine compounds [4]. As an alternative method, catalytic oxidation methods, for instance delignification of plant materials with hydrogen peroxide in acidic medium, have been proposed [5]. Hydrogen peroxide is a strong oxidizer and considered to be one of the most promised and environmentally acceptable reagents for the delignification process [6]. Peracids (often called peroxy acid) can be obtained by the reaction of hydrogen peroxide with organic acids; peracetic and performic acids are of special interest because they are characterized by a high delignification activity and can be generated during cooking. The use of organic peracids with the concentration of 4–10 wt.% allows delignifing plant material at atmospheric pressure and temperature lower than 100°C and reducing the consumption of fresh water [7,8]. The use of peracids does not lead to the degradation of the high molecular weight polysaccharides of plant material, pulp is characterized by a high value of brightness and can be used in the composition of paper and cardboard without the application of an additional stage of bleaching. Hemicelluloses can be eliminated and reactive lignin, which can be processed into valuable chemical products, can be isolated [9].

The technologies of oxidative-organosolv cooking of softwoods and hardwoods are widely represented in literature, unlike plant agricultural waste, in particular sunflower stalks. Therefore, the purpose of the work was to study the process of obtaining pulp from stalks of sunflower by performic and peracetic acids and to characterize its chemical and physical properties.

Materials and methods

Sunflower stalks were used for obtaining pulp. The content of the main chemical components in the initial raw material is as follows: cellulose 40.6%, lignin 21.8%, hot-water solubility 4.8%, NaOH solubility 35.8%, ethanol-benzene extractives 2.1%, and ash 2.9% of oven-dry raw material. The chemical properties were determined according to the corresponding standards of the Technical Association of the Pulp and Paper Industry (TAPPI) for the different components: T–222 for lignin, T–257 for hot-water solubility, T–212 for 1% NaOH solubility, T–204 for ethanol-benzene extractives and T–211 for ash. Air-dried stalks of sunflower were grinded to a size of 15–20 mm and stored in a desiccator to achieve permanent humidity and chemical composition.

In order to obtain pulp, a series of cooking of sunflower stalks with peracetic acid (PAA) and performic acid (PFA) were done. Cooking of stalks with PFA was carried out with a solution of formic acid (with a concentration of 60 wt.%) and hydrogen peroxide (with a concentration of 30 wt.%) at a ratio of 50:50 vol.%. Cooking of stalks with PAA was performed with a solution of acetic acid (with a concentration of 99.8 wt.%) and hydrogen peroxide (with a concentration of 35 wt.%), a ratio of chemical reagents being 70:30 vol.%. In both cases, the mixing of organic acids and hydrogen peroxide was done immediately before cooking, so the formation of the peracids occurred directly in the processes of delignification of the plant material. The delignification process was carried out at the ratio of liquid to solid equal to 10:1 during 30–120 minutes, the temperature being from 70 to 90^{0}C. To prevent the loss of cooking solution components, the delignification process was carried out in heat-resistant flasks with reflux condenser. At the end of the cooking, the flasks were cooled with tap water, pulp was washed and air-dried. The yield of pulp and the content of residual lignin were estimated in accordance with the standard techniques of TAPPI.

To determine physical properties, obtained pulp was pre-milled in a centrifugal-grinding apparatus at 6% consistency to 60±2^0 SR and pulp handsheets of 75±1 g/m^2 were produced. The strength properties were determined according to the TAPPI standards.

Such parameter as cooking temperature (X_1) and cooking time (X_2) of PAA were selected in this study as the main technological parameters of obtaining pulp from sunflower stalks; they were optimized using 2^2 full factorial design by means of statistical software STAT-SENS, which was developed at the Department of Cybernetics of Chemical Technology Processes of National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute». The yield of pulp (Y_1), the content of residual lignin (Y_2), the breaking length (Y_3) and tear index (Y_4) were selected as quality indices. A second-order polynomial was used to describe studied process, it is represented as follows:

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

where Y_i is the indicators of sorbents, b_0–b_5 are the coefficients of mathematical models, X_1 and X_2 are the parameters of the process.

Regression equations that adequately describe the process of PAA of sunflower stalks were obtained using the statistical Cochran and Fisher criteria. The optimization of the technological parameters of the PAA pulping of sunflower stalks was accomplished by the method of multicriterion optimization using the Harrington desirability function.

Results and discussion

Delignification of sunflower stalks

To study the influence of temperature and cooking duration on the quality of pulp prepared from sunflower stalks, a series of cooking with peracids were conducted and the results are shown in Fig. 1.

As can be seen, the yield of pulp and the content of residual lignin decrease with increasing the temperature and duration of cooking. This can be associated with the intensification of the processes of cleavage of α- and β-etheric alkyl-aryl bonds of lignin macromolecules and with the transferring of lignin degradation products as well as extractive and mineral substances of plant material to the cooking solution.

The yield of pulp during PFA cooking is higher than that of PAA and the difference is 3.7–8.4%, but the content of the residual lignin in PAA pulp is

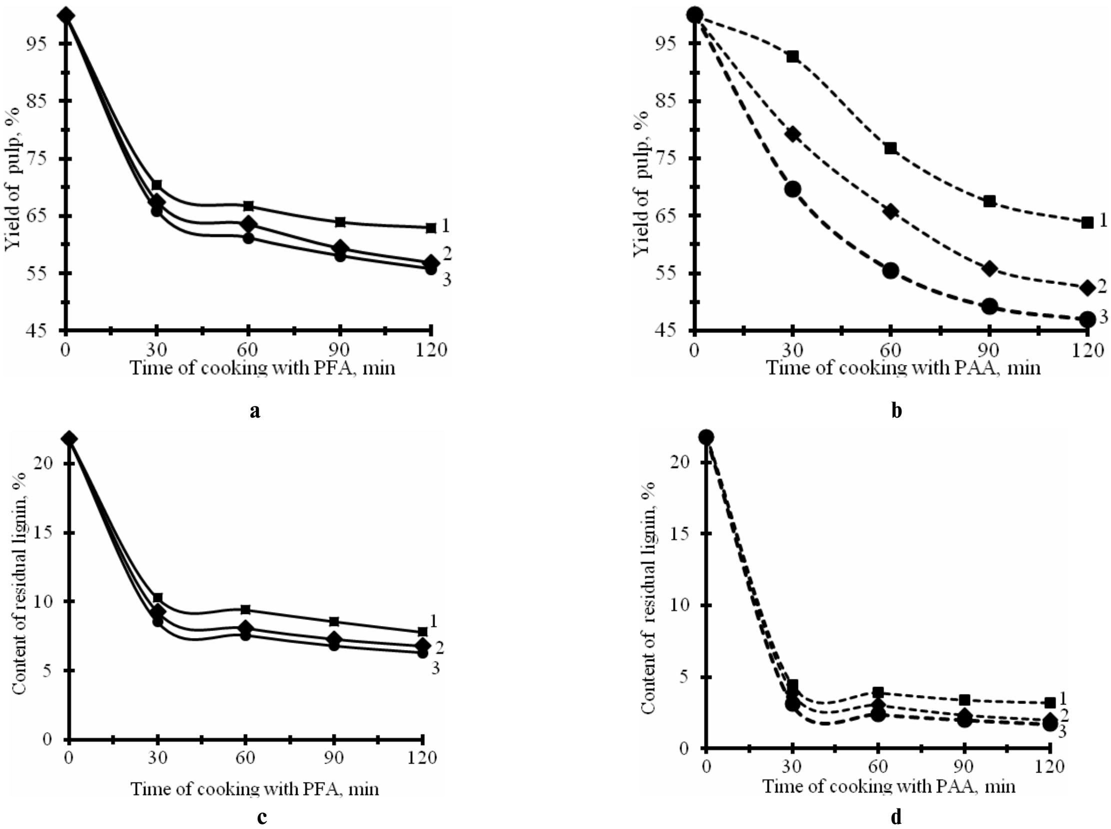

Fig. 1. The influences of duration of cooking of sunflower stalks with peracids at different temperatures on the yield of pulp (a, b) and the content of residual lignin (c, d): 1 – 70^{0}C; 2 – 80^{0}C; 3 – 90^{0}C

much lower than that of PFA pulp (4.6% and 5.8%, respectively).

It should be noted that PAA pulp is characterized by lower content of residual lignin (Fig. 1 d). This can be explained by the fact that the destruction of the structure of lignin occurs in the medium of acetic acid as a result of acid splitting of α-etheric bonds with the formation of intermediate carbocations. In this case, an organic solvent, like a weak nucleophile, blocks the active lignin centers and prevents its condensation. With the use of formic acid acidolysis and acid fragmentation of lignin, splitting of lignin-carbon bonds, destruction and dissolution of hemicelluloses take place. The hydrolytic degradation of the cellulose also occurs during pulping with peracids. However, the contribution of these reactions is very insignificant, otherwise the deterioration of the physical properties of the pulps would be observed with an increasing the duration and temperature of processes (Table).

The brightness value of pulp of PAA cooking is 68–72%, and the brightness of pulp of PFA cooking is 40–44%.

The results of experimental studies show that PAA affects lignin more selectively than PFA which promotes the dissolving of a large part of hemicelluloses.

The strength characteristics of the obtained pulps are given in Table. As can be seen from the data, the physical properties of pulps are improved with increasing the temperature and cooking time. This can be explained by the higher paper-making properties of pulp due to the formation of additional hydrogen bonds between polysaccharides because of

Strength properties of pulp from sunflower stalks after PFA and PAA cooking

Time of cooking, min	Temperature, ^{0}C	Breaking length, m		Tear index, mN	
		PFA	PAA	PFA	PAA
30	70	2860	3050	102.0	140.1
60		4260	5240	142.1	205.5
90		5020	5750	176.4	262.3
120		5520	7070	215.8	287.8
30	80	4090	4350	128.1	157.2
60		5230	5850	137.3	216.5
90		5730	6700	235.4	275.3
120		6160	8650	274.6	314.4
30	90	4390	5100	137.3	272.4
60		5390	5900	296.2	325.3
90		5960	8050	313.9	379.4
120		6870	9050	402.0	478.9

the higher hemicelluloses content, especially, in the case of PAA cooking.

The parameters of strength properties of pulp from sunflower stalks after PAA cooking are higher than those of PFA pulp. The difference is in the range of 7–36%.

As concerns the physical properties, pulp after oxidative-organosolv cooking of sunflower stalks is not inferior to softwood sulfite pulp [10] which indicates the prospects of the use of sunflower pulp in papermaking industry for the production of different types of paper and cardboard.

To characterize the selectivity of the processes of obtaining pulp (the ratio of the amount of dissolved lignin to dissolved carbohydrates), Ross's [11], Schmidt's [12], and Girce's [13] diagrams have been proposed. To compare the effectiveness of different methods of cooking of sunflower stalks, a diagram, which describes the dependence of the yield of the resulting pulp on the content of residual lignin, was plotted (Fig. 2).

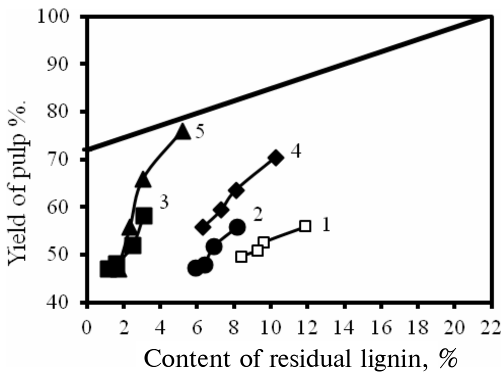

Fig. 2. The influence of residual lignin content on the yield of pulp at different methods of delignification: 1 – soda cooking [14]; 2 – neutral sulfite cooking [14]; 3 – alkaline sulfite anthraquinone and ethanol cooking [14]; 4 – PFA; 5 – PAA

The inclined straight line of «perfect delignification» (Fig. 2) describes the maximum content of polysaccharides in pulp at a given content of residual lignin. Therefore, if the line of the particular delignification process is close to the line of «perfect delignification» at a certain residual lignin, then the yield of pulp is higher due to the preservation of polysaccharides (cellulose and hemicelluloses). It can be concluded that the efficiency of obtaining pulp from sunflower stalks by different methods of delignification increases in the following sequence: soda – neutral sulfite – alkaline sulfite anthraquinone and ethanol – PFA – PAA. The results indicate that PAA cooking is characterized by a high selectivity during obtaining pulp from sunflower stalks.

Optimization of PAA cooking of sunflower stalks

To obtain the mathematical dependences of the quality indices of the sunflower pulp, Y_i, on the main technological parameters, X_i, a full factorial experiment with 2 factors was performed, which is widely used for constructing mathematical models of such objects as technological properties [15].

As a result of the mathematical processing of the experimental data, regression equations that adequately describe the dependence of the quality indices of pulp obtaining from sunflower stalks on the main technological parameters were derived. The adequate regression equations are as follows:

The yield of pulp, %:

$$Y_1=+59.509-11.214x_1-9.0637x_2+ \\ +0.146x_1x_2+6.1222x_1^2+1.0688x_2^2;$$

The content of residual lignin, %:

$$Y_2=+2.6925-0.67467x_1-0.68625x_2-0.065x_1x_2+ \\ +0.22x_1^2+0.15875x_2^2;$$

The breaking length, m:

$$Y_3=+5840.3+3183.3x_1+998.75x_2+ \\ +150x_1x_2-1004.4x_1^2+63.75x_2^2;$$

The tear index, mN:

$$Y_4=+251.89+70.267x_1+61.x_2-2.1x_1x_2- \\ -18.222x_1^2+44.5x_2^2.$$

A compromise area for the PAA delignification of sunflower stalks (Fig. 3), depending on the main technological parameters (X_i), was identified by

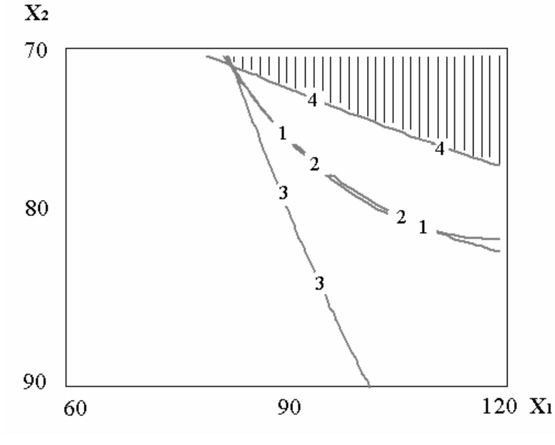

Fig. 3. Compromise area for the PAA delignification of sunflower stalks: (1) – the yield of pulp, %; (2) – the content of residual lignin, %; (3) – the breaking length, m; (4) – the tear index, mN

means of the multicriterion optimization using the Harrington desirability function. The estimated value of the generalized function of the desirability is 0.6 which indicates a good coherence of quality indices with the values of technological parameters.

The following values of parameters are defined as the optimum ones: x_1=80^{0}C (cooking temperature) and x_2=120 min (cooking duration). The quality indices of the obtained oxidative-organosolv pulp at the optimum point are the following: the yield is 55.1%; the content of residual lignin is 2.2%; the breaking length is 7930 m, and the tear index is 299.7 mN.

Conclusions

The expediency of the application of sunflower stalks as an alternative raw material for the pulp and paper industry and peracids as cooking solutions of plant raw materials is substantiated in this work.

The processing of sunflower stalks with solutions of peracetic and performic acids was studied to obtain pulp which is not inferior to wood technical pulp and can be used for the production of different types of cardboard and paper products.

The efficiency of lignin removal from sunflower stalks increases in the following sequence of various methods of cooking: soda – neutral sulfite – alkaline sulfite anthraquinone and ethanol – PFA – PAA.

The regression equations were obtained which adequately describe the experimental data and can be used as mathematical models of peracetic cooking of pulp from sunflower stalks. A compromise area of the PAA delignification of stalks of sunflower and the quality indices of pulp at the optimum point were determined by the method of multicriterion optimization.

The strength properties of the PAA pulp prepared from sunflower stalks were found to be close to those of softwood. Sunflower stalks can be recommended for peracids pulping, paper and board production.

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ОДЕРЖАННЯ ЦЕЛЮЛОЗИ ІЗ СТЕБЕЛ СОНЯШНИКУ З ВИКОРИСТАННЯМ ПЕРОКСОКИСЛОТ

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Найбільш поширеним матеріалом для виробництва паперу та картону є деревні волокна. Наразі лісові ресурси швидко скорочуються через потреби целюлозно-паперової промисловості, а також через конкуруючі галузі, зокрема будівельну та виробництво меблів. Необхідно запропонувати нові сировинні ресурси та нові екологічно чисті способи отримання волокнних напівфабрикатів для виробництва різноманітної паперової продукції. У цьому дослідженні було розроблено методи варіння стебел соняшнику з використанням пероксикислот, зокрема пероцтової та пермурашиної. Досліджено хімічні та фізичні властивості целюлози. Одержано волокнисті напівфабрикати високої якості з виходом в діапазоні від 46 до 94% та вмістом залишкового лігніну від 1,2 до 9,6%. Вивчено вплив температури та тривалості процесу делігніфікації на показники якості отриманої целюлози. Запропоновано лігнін-вуглеводну діаграму делігніфікації стебел соняшнику різними методами. Виведені рівняння регресії для процесу пероцтового варіння стебел соняшнику. Оптимальні параметри окисно-органосольвентної делігніції стебел соняшнику були отримані з використанням функції бажаності Харрінгтона.

Ключові слова: пероксокислота, делігніфікація, показники якості, рівняння регресії, оптимізація.

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