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Valerii Barbash, Irina Trembus and Julia Nagorna

PULP OBTAINING FROM CORN STALKS

National Technical University of Ukraine "Kyiv Polytechnical Institute"
v.barbash @ kpi.ua

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Abstract. The influence of basic technological parameters of the organosolvent delignification of corn stalks process on the pulps quality has been investigated. The adequate regression equations of the process of obtaining pulps using the method of full factorial experiment have been obtained. The optimal values of technological parameters of organosolvent delignification of corn stalks have been calculated. The possibility of bleaching the organosolvent pulp obtained from corn stalks by hydrogen peroxide without the use of chlorine compounds to whitenees more than 80 % has been proved by the experiments.

Keywords: organosolvent delignification, corn stalk, pulp, bleaching, a regression equation, optimization.

1. Introduction

One of the indices of every country development and determination of standard of its citizens is consumption of paper and paperboard per capita. The world consumption of paper and cardboard is growing, especially in western Europe and North America [1]. According to this indicator Ukraine holds one of the last places in Europe (32 against 135 kg per person in Europe [2]). In order to improve this situation the pulp and paper industry of Ukraine needs to increase manufacturing of its own pulps which are obtained both by traditional and alternative methods of the plant raw materials delignification.

The application of traditional methods of the plant raw materials delignification (sulphate and sulphite) leads to pollution of the environment by harmful sulphur and chlorine compounds and increases the morbidity of population [3]. In the sphere of alternative pulping technologies the scientists propose to carry out delignification of the plant raw materials in organic solvents, which are called organosolvent pulping. They are characterized by lower energy capacity and more selective action on lignin, which enables to increase pulp yield due to the greater saving of polysacharides (cellulose and chemicellulose) of the raw plant materials [4]. One of the most effective organosolvent delignification methods is the alkali-sulfite-alcohol cooking of plant raw materials [5].

For the countries which do not have large reserves of free wood stalks of crops and other kinds of non-wood plant materials can be used as the alternative raw materials for producing pulps. Technical and grains plants, the stalks of which can be successfully processed in pulps after harvesting various kinds of cardboard and paper products are widely cultivated in Ukraine. For example, only corn crops occupy 1.9 million hectares of agricultural lands in Ukraine [6]. The corn stalks can be regarded as alternative plant raw material for obtaining pulps.

The aim of this investigation is to determine the optimal values of technological parameters of obtaining pulps from corn stalks, suitable for manufacturing of paper and cardboard.

2. Experimental

In this work the corn stalks from the Cherkasy region were used. Corn (Latin *Zea mays*) is one-year cereal which is grown in all regions of the world and has a gross rounded stalk up to 6 m, thickness 2–7 cm with core, which is filled by parenhyma cells. The average yield of corn was 27.1 kg/ha of grain and 61.0 kg / ha of green mass in Ukraine in 2010 [6]. The air-dry corn stalks were cut to 15–20 mm size in the laboratory and stored in exicators in order to maintain constant humidity in further research. The chemical properties of the corn stalks were determined according to the corresponding TAPPI standards for different components, namely: T-222 for lignin, T-257 for hot-water solubles, T-212 for 1% NaOH solubles, T-204 for ethanol-benzene extractable, T-211 for ash. The chemical composition of corn stalks is shown in Table 1.

According to the data of Table 1 the chemical composition of corn stalks is close to the most common kinds of non-wood plant materials (wheat straw, reed) and differs from hardwood of higher mineral content (ash) and of extracted substances content with hot water and alcohol-benzene mixture.

Table 1

Chemical composition of plant materials, %

Plant material	Solubility in:		Extractable ethanol-benzene	Ash	Pentosanes	Cellulose	Lignin
	hot water	1% soda					
Corn stalk	11.8	19.6	3.5	4.7	25.6	41.6	17.9
Wheat straw	10.1	38.4	5.2	4.2	26.4	46.2	18.6
Reed	6.7	23.6	5.6	4.4	22.7	41.8	21.0
Birch	2.2	11.2	1.8	0.5	28.0	41.0	21.0
Spruce	7.3	18.3	2.9	0.2	10.7	46.1	28.5

In order to obtain pulps under the laboratory conditions the series of cooking by alkali-sulphite-antragunone-ethanol method (ASAE) was carried out in steel autoclaves (volume of 400 ml) in glycerol bath at a given temperature and liquid to solid ratio 5:1. The solutions of sodium sulphite and caustic soda (20 and 5 % mass body dry (b.d.), respectively) at the ratio of ethanol to water 35:65 vol %, antraqunone consumption – 0.1 % mass b.d. raw materials were used as a cooking solution. Cooking temperature varied from 383 to 443 K, duration – from 60 to 150 min. The autoclaves were cooled by running water and the pulp was washed by distilled water for removing residual cooking liquor after cooking and then dried in the air. Yield of pulp and residual lignin content in pulp were determined according to standard TAPPI methods.

To determine the physical and mechanical properties the pulps obtained from corn stalks were processed in centrifugal grinding machine for achieving the degree of 60 ± 2 ^{o}Shopper-Rigler and sent for sheets manufacturing of 1 m^2 at weight of 75 ± 1 g. Physico-mechanical values of pulp and characteristics of waste liquid (residual SO_2, dry matter content and ash content) were measured by standard TAPPI methods.

The bleaching of organosolvent pulps obtained from corn stalks without the use of harmful chlorine compounds were carried out according to the following scheme: chelating processing (Q) – hydrogen peroxide bleaching (P) – acid processing (A). The first stage of bleaching, so called chelating cellulose processing, was carried out at 323 K for 60 min by the solution of the following compounds: trilon B, boric acid, iron and copper sulphate with its consumption of 0.2 % mass b.d. cellulose. The second stage of bleaching was peroxide bleaching, which was carried out by the H_2O_2 consumption of 5 % mass b.d. cellulose at 363 K for 60–80 min. In order to achieve the desired value pH = 9–10, $MgSO_4$, NaOH and Na_2SiO_3 solutions were added immediately before bleaching. Acid processing was carried out by sulphite acid with the SO_2 consumption of 0.5 % mass b.d. cellulose, at room temperature for 60 min. Every stage of pulp bleaching was completed by washing the cellulose in distilled water till the neutral reaction.

3. Results and Discussion

3.1. Delignification of Plant Material

To study the influence of cooking temperature and cooking time on quality of pulp obtained from corn stalks the series of alkali-sulphite-antraqunone-ethanol pulping was carried out. The results are shown in Table 2.

According to the data of Table 2, the pulp yield and residual lignin decrease with the increase of temperature and duration of corn stalks delignification. This is connected with the intensification of splitting processes of α- and β-ether alkylaryl bonds of lignin macromolecules and transfer of lignin decomposition products and also the extractive and mineral contents into cooking solution.

The physical and mechanical indices of organosolvent pulps increase with the increase of the technological parameters (cooking temperature and time). It is explained by better fiber properties of pulps, which create additional hydrogen bonds between polysacharides and high maintenance of hemicelluloses in them improving mechanical indices [7]. However carrying out alkali-sulphite-antraqunone-ethanol delignification of corn stalks for more than 90 min at 443 K leads to hydrolytic degradation of polysaccharides, that brings to some reduction of the mechanical indices of organosolvent pulps. Therefore we can confirm that organosolvent pulps obtained from corn stalks at temperatures from 403 to 443 K are similar to hardwood sulphate pulp and can be used for manufacturing of paper and cardboard.

To find the ways of further utilization of spent cooking liquors we determined the characteristics of chemical composition of black liquors after cooking of corn stalks. The influence of cooking temperature and cooking time on content in black liquors of residual SO_2, dry solid and ash were investigated. The results of conducted researches are presented in Table 3.

Table 2

Quality indices of organosolvent pulps from corn stalks

Cooking temperature, K	Cooking time, min	Yield of pulp, %	Residual lignin, %	Breaking length, m	Burst index, kN/g	Tear index, mN·m^2/g
383	60	78.5	11.6	3800	3.1	2.6
	90	75.0	8.8	4200	3.2	2.9
	120	74.8	8.2	4900	3.7	3.8
	150	78.5	7.6	5600	4.1	4.0
403	60	67.4	7.1	5000	3.5	3.8
	90	65.3	6.6	5100	3.7	4.0
	120	62.5	5.5	5700	3.9	4.3
	150	59.2	5.3	6500	4.3	4.9
423	60	66.8	4.0	6700	4.5	5.9
	90	64.2	3.5	7400	4.7	6.1
	120	61.8	2.8	7600	4.8	7.0
	150	57.3	2.7	7900	5.1	7.4
443	60	62.0	2.6	7300	4.7	6.4
	90	61.7	2.4	7900	5.1	7.6
	120	56.0	2.1	7800	4.5	5.7
	150	53.9	2.0	6500	4.3	5.2

Table 3

Characteristics of spent black liquors after ASAE cooking of corn stalks

Cooking temperature, K	Cooking time, min	SO_2 content, g/l in		Dry resudue,kg/m^3	Ash, %
		cooking solution	spent liquor		
383	60	21.8	13.4	45.6	33.8
	90		12.1	50.0	33.0
	120		11.2	55.3	31.5
	150		9.4	60.1	30.1
403	60	22.9	10.9	50.3	37.6
	90		8.9	58.1	35.9
	120		8.3	63.0	35.0
	150		7.0	67.2	34.9
423	60	21.5	9.1	54.8	41.5
	90		7.7	66.2	41.1
	120		7.0	67.1	38.8
	150		6.1	70.3	36.2
443	60	22.4	8.6	61.3	49.1
	90		5.7	68.5	48.1
	120		4.5	76.9	41.9
	150		3.8	83.6	40.8

Table 4

Characteristics of bleached organosolvent pulp from corn stalks using various reagents for chelating processing (bleaching scheme Q - P - A)

Chelating reagent	Yield of bleached pulp, %	Resudial lignin, %	Breaking length, m	Burst index, kN/g	Tear index, mN·m^2/g	Whitenes s, %
Trilon B	96.6	0.7	7100	4.1	6.0	82.2
Boric acid	97.1	0.5	7000	4.3	6.1	80.7
Copperas	95.6	1.1	6200	3.7	5.3	78.7
Bluestone	85.4	1.2	6700	3.5	5.2	77.1

According to the data of Table 3 the increase of cooking temperature and cooking time leads to the increase of dry residual concentration due to the transition into solution of more amounts of lignin, hemicellulose dissolution products and mineral substances. Also organosolvent cooking at higher temperatures leads to the increase of ash in spent black liquors. The increase of cooking time for each temperature decreases the ash content. This fact may be explained by the prevailing transfer of organic substances (lignin, polysaccharides) than mineral substances to the solution.

3.2. Bleaching of Organosolvent Pulp

For bleaching organosolvent pulp obtained from corn stalks the schemes without chlorine contents reagents were investigated. The hydrogen peroxide was used as the bleaching reagent and chelating reagents which allow to reduce maintenance of cations of variable valency metals in a cellulose (mainly Mn, Fe, Cu), were used for preventing catalytic decomposition of hydrogen peroxide. The cellulose obtained by ASAE method at cooking time of 60 min and temperature of 443 K with whiteness of 53.0 % and quality indices listed in Table 2 was used for investigation. The effect of different compounds as a chelating reagent with consumption of 0.2 % mass b.d. cellulose before peroxide bleaching on quality bleached organosolvent pulp is given in Table 4.

According to the data of Table 4, the use of trilon B and boric acid as a chelating reagent is more effective than copperas or bluestone. The use of trilon B and boric acid are better for bonding of variable valency metals and delignification, increasing writeness of cellulose without substantial change for the worse of its quality indices. The low loss of cellulose indicates that during the peroxide bleaching the minimal degradation of carbohydrate components of plant material takes place and the basic reactions at H_2O_2 bleaching are directed to the oxidation of chromophore groups of lignin and extractive substances due to this the increase of the pulp whiteness without the significant reducing of its yield takes place.

3.3. Determination of Regression Equations and Optimization of Quality Pulp Indices

The full factorial experiment type 2^n as a mathematical method of planning for determination of mathematical dependencies of quality organosolvent pulp indices from their main technological parameters was used. This method is widely used for the construction of experimental-statistical mathematical models for property technology objects [8].

The general view of the regression equations for two variables of pulping process of organosolvent pulp from corn stalks is as follows [8]:

$$Y_i = b_0 + b_1 \cdot x_1 + b_2 \cdot x_2 + b_3 \cdot x_1 \cdot x_2 + b_4 \cdot x_1^2 + b_5 \cdot x_2^2$$

where: Y_i – quality index of organosolvent pulp; b_0, b_1, b_2, b_3, b_4, b_5 - coefficients for the relevant techological parameters; x_1 and x_2 - the value of technological parameters in coded form.

The cooking temperature (x_1) and cooking time (x_2) were selected as the main technological parameters that affect the quality of ASAE pulp from corn stalks. Quality indices Y_i which determine physical and mechanical characteristics of organosolvent pulp are: Y_1 – yield pulp; Y_2 - burst index; Y_3 - residual lignin; Y_4 - tear index; Y_5- breaking length.

The regression equations were calculated by mathematical processing of obtained experimental data. They adequately describe the dependences of the basic quality on selected process parameters and can be used as mathematical models of alkali-sulphite-antraqunone-ethanol method of corn stalks delignification. The determined adequate regression equations are as follows:

Yield, %
$Y_1 = 62.866 - 3.6338x_1 - 7.1813x_2 - 0.30825x_1x_2 - 0.63281x_1^2 + 4.9359x_2^2$
Burst index, kN/g
$Y_2 = 4.2412 + 0.1612x_1 + 0.5615x_2 - 0.4269x_1x_2 - 0.0855x_1^2 - 0.171x_2^2$
Residual lignin, %
$Y_3 = 5.3875 - 1.0106x_1 - 3.7481x_2 + 0.72338x_1x_2 + 0.50766x_1^2 + 0.049219x_2^2$
Tear index, $mN \cdot m^2/g$
$Y_4 = 5.4166 + 0.1134x_1 + 1.4776x_2 - 0.7403x_1x_2 - 0.3504x_1^2 - 0.5559x_2^2$
Breaking length, m
$Y_5 = 6891.2 + 453x_1 + 1539.7x_2 - 618.75x_1x_2 - 466.87x_1^2 - 669.37x_2^2$

The compromise area of ASAE delignification of corn stalks according to the main process variables (x_i) was defined by multiobjective optimization with using the desirability Harinhton´s function. This is shown in the figure (region located in the plane $x_1 - x_2$). The calculated value of the generalized desirability function equals to 0.69, that reveals good coordination of quality indices from values of technological parameters.

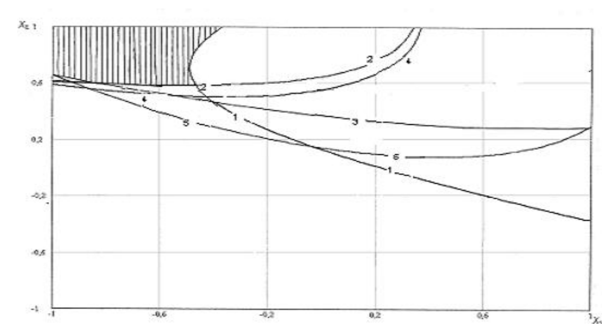

Fig. Compromise area of ASAE delignification of corn stalks: yield of pulp, % (1); burst index, kN/g (2); residual lignin, % (3); tear index, $mN \cdot m^2/g$ (4); breaking length, m (5)

The following values of parameters x_1 and x_2 were determined as a point of optimum:

– In coded form: x_1 = -0.99756 and x_2 = 1;

– In natural units: x_1 (cooking temperature) = = 443 K, x_2 (cooking time) = 60 min.

The quality indices of obtained organosolvent pulp in the optimum point have the next values: yield 63.9 %; burst index 4.8 kN/g; residual lignin 2.5 %; tear index 6.6 mN·m^2/g; breaking length 7462 m.

4. Conclusions

The possibility of treatment the corn stalks by alkaline sulphite-antraqunone-ethanol method of delignification on pulps was shown. These pulps are similar to hardwood pulp and can be used for manufacturing of common kinds of paper and cardboard products.

The possibility of bleaching organosolvent pulp obtained from corn stalks without the use of harmful chlorine compounds was shown.

The regression equations that adequately describe the experimental data and can be used as mathematical models of organosolvent pulping with specified quality parameters were calculated. The compromise area of the ASAE delignification of corn stalks process and quality indices of the organosolvent pulp at the optimum point were determined by the multiobjective optimization method.

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ОДЕРЖАННЯ ВОЛОКНИСТИХ НАПІВФАБРИКАТІВ ІЗ СТЕБЕЛ КУКУРУДЗИ

Анотація. *Досліджено вплив основних технологічних параметрів процесу органосольвентної делігніфікації стебел кукурузи на показники якості волокнистих напівфабрикатів. Отримано адекватні рівняння регресії процесу одержання волокнистих напівфабрикатів з використанням методу повного факторного експерименту, які використано для розрахунку оптимальних значень технологічних параметрів. Експериментально доведено можливість вибілювання органосольвентної целюлози із стебел кукурудзи пероксидом водню до білості більше 80 % без використання сполук хлору.*

Ключові слова*: органосольвентна делігніфікація, стебло кукурудзи, целюлоза, волокнистий напівфабрикат, вибілювання, рівняння регресії, оптимізація.*