Statistic Simulation of the Delignification Process

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Abstract

The paper presents a mathematical formalization of regularities during the alkaline treatment of rice straw as one of the stages of oxidation-organosolvent pulping. The purpose of the research is to maximize the yield of technical pulp, to extract minerals and to remove lignin. It has been found out that the following input values are optimal: the duration of alkaline treatment of rice straw is 240 minutes; the concentration of alkali is 0.69 N. Under the given conditions of alkaline treatment with oxidation-organosolvent pulping, commercial pulp is produced with a yield of 58.8%, the mineral content being 0.05%, and residual lignin being 2.5% of bone dry raw materials.

Introduction

Currently, many studies are focused on the production of budget-friendly sorbents produced from natural materials, the functional groups of which are able to retain reagents on the surface of the carrier without interfering with the visual identification of the metal ion content [1,2]. Sorbents produced from commercial cellulose pulp meet these requirements perfectly due to the structural features of the elementary components of cellulose molecules containing hydroxyl and carboxyl groups [3-7]. The increasing scarcity of pinewood and hardwood resources has created the problem of expanding the raw material base of the pulp and paper, as well as chemical industry. This problem can be solved by using annual plants as a raw material [8,9], for example, the biomass of graminaceous plants [10,11] such as rice straw (RS).

One of the aims of processing RS is to obtain commercial cellulose pulp. As is known, in its composition RS contains from 10 to 30% of mineral components, the remaining part being bone dry raw materials (BDRM). To remove the mineral component from the RS during the oxidation-organosolvent pulping, an alkaline treatment stage is introduced. The action of the alkaline solution on the lingo-carbohydrate complex leads to the removal of the mineral component and part of the lignin, as well as to the degradation of the polysaccharides, reducing the yield of commercial cellulose pulp [12].

Thus, the purpose of this paper is to study the regularities of alkaline RS processing in order to maximize the yield of commercial pulp, to extract the mineral part and remove lignin. To achieve the goal, the following tasks were set:

- to carry out preliminary studies of alkaline RS treatment with various ratio of sodium hydroxide to BDRM and various processing time; to conduct analysis of fibrous material;
- on the basis of realization of a two-level two-factor full factorial experiment, to obtain experimental statistical models of the yield of fibrous material and the content of lignin and mineral components in it;
- to solve the optimization problem of searching for optimal values of technological factors that ensure a high yield of fibrous material from the RS with a minimum content of mineral components in it;
- to conduct oxidation-organosolvent delignification of the fibrous material obtained under optimal conditions to produce technical pulp and perform its analysis.

Methodology

As an object of research, the RS from Krasnodar region, harvest of 2015, was used. The composition of the raw material: the content of Kürshner-Hoffer cellulose is 47.5 ± 1% [13], lignin - 25.5 ± 0.2% [USSR State standard specification 11960], resin (extraction with alcohol-benzene mixture) - 5.1 ± 0, 5 [USSR State standard specification 6841], substances soluble in hot water - 3.7 ± 0.5 [13], mineral substances - 15.7 ± 0.05% [13]. Air-dry RS was subjected to pulping.

Obtaining technical pulp from RS was carried out in two stages: the first stage was alkaline treatment, the second was oxidation-organosolvent pulping [14,15]. Both stages were carried out in the laboratory reactor system LR-2.ST.

Stage 1. RS treatment with aqueous NaOH solution under the following conditions: 1:10 hydromodule; NaOH concentration 0.2 ... 1 N; the consumption of alkali 9.6 ... 48.0% of the BDRM, treatment temperature of 90^{o}C; the duration of the temperature rise is 15 minutes; duration of alkaline treatment is 60 ... 240 minutes. The obtained fibrous material was washed to neutral state, dried in air and analyzed.

Stage 2 (oxidation-organosolvent pulping). Treatment of fibrous material with equilibrium peracetic acid under the following conditions: liquid module - 1:10; treatment temperature of 90 ^{o}C; the temperature rise time is 20 minutes; processing time - 90 min; the consumption of the pulping composition in recalculation for the equilibrium peracetic acid is 0.8g per 1g of the mass of the BDRM. The content of the pulping composition: equilibrium peracetic acid, decomposition stabilizer of peroxide compounds in an amount of 0.01% of the mass of the BDRM, water. At the end of pulping, the used pulping composition was separated from the commercial pulp through the drain valve of the reactor system. Distilled water was fed to the reactor and the obtained commercial pulp was washed until the state of a neutral reaction of the washings was achieved. The analysis of cellulose obtained as a result of pulping showed the following characteristics: humidity - USSR State standard specification 16932; lignin content - USSR State standard specification 11960; content of mineral substances (ash content) - USSR State standard specification 18461.

Results

The results of preliminary studies of alkaline treatment of RS in single-factor experiments are shown in Fig. 1, 3 and 4.

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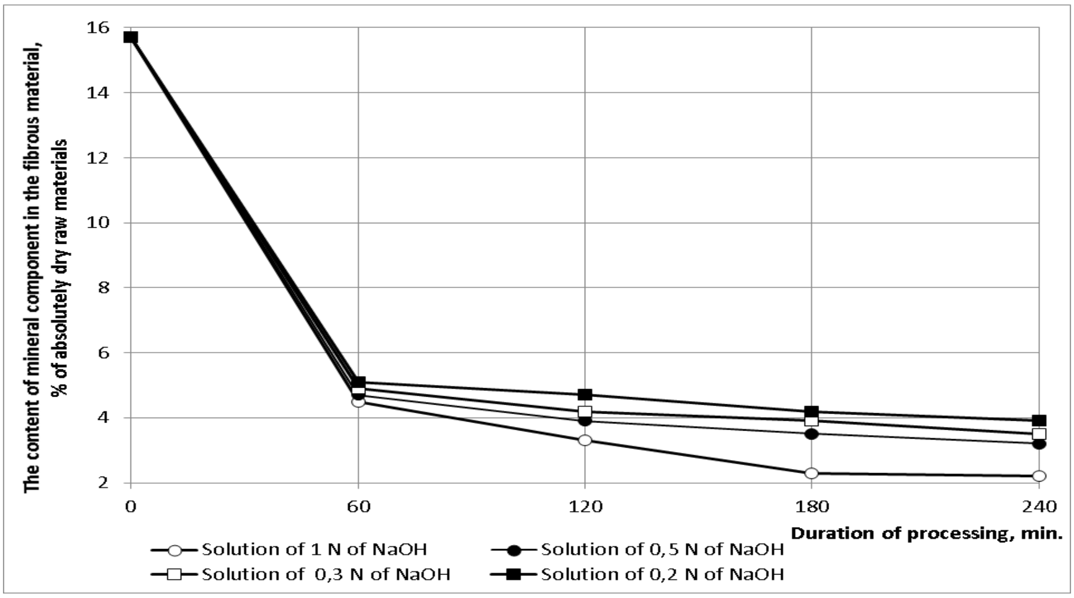
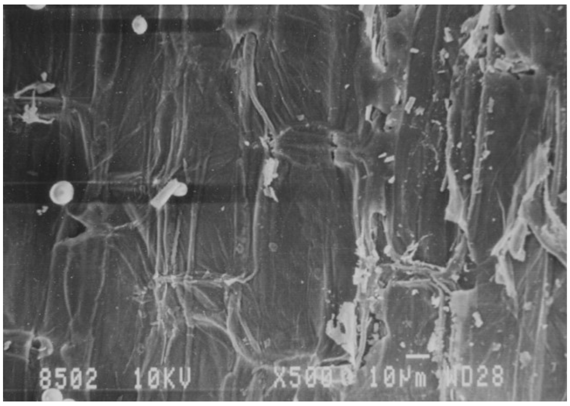


Figure 1: Dependence of mineral content in fibrous material

It can be seen from Fig. 1 that, the higher the concentration of alkaline solution, the more effective the mineral substances are removed from the plant raw material. During the first hour of processing of mineral substances, 67.3 to 71.3% of BDRM is removed depending on the concentration of alkali. For concentrations of 0.2 ... 0.5 N, further processing is performed with the same intensity and allows to remove from 6.0 to 9.5% of BDRM of the mineral component. The process is most effective at the maximum concentration of alkali when 14.5% more of BDRM are removed. Thus, when using 1 N concentration of alkali, 86% of mineral substances are removed from the fibrous material, and in other cases - 73.5 ... 79.6%.

One of the features of RS is the presence of a lipid layer on the outer and inner surfaces of the stem. The lipid layer has hydrophobic properties and performs a protective function. The hydrophobic layer prevents the penetration of chemical agents into the ligno-carbohydrate matrix and makes it difficult to extract other components. Alkali saponifies and partially dissolves the resins and fats in the lipid layer, making the ligno-carbohydrate complex accessible (Figure 2).



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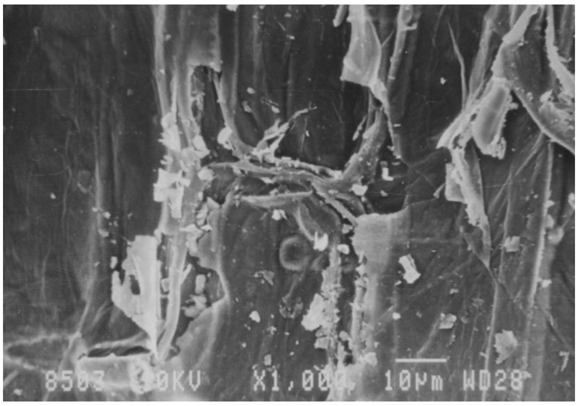

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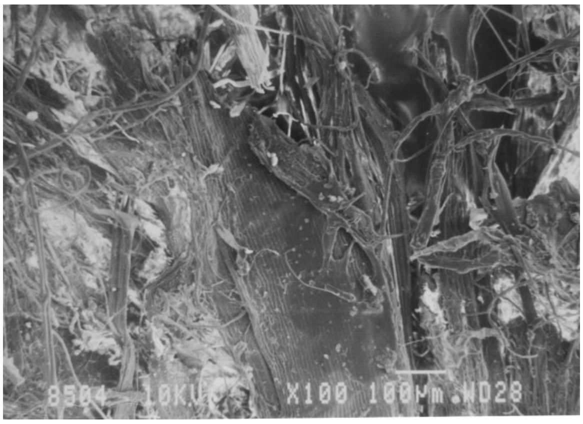
the inside of the stem



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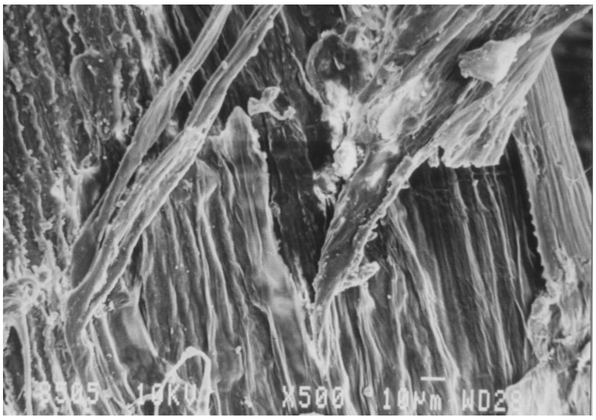

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the outer side of the stem

Figure 2: Internal and external side of the stem of rice straw after alkaline treatment 1N. alkali solution

This creates favorable conditions for the effective separation of minerals and partly lignin. However, aggressive and prolonged alkaline treatment negatively affects the carbohydrate component and, accordingly, the yield of the fibrous product (Figure 3).

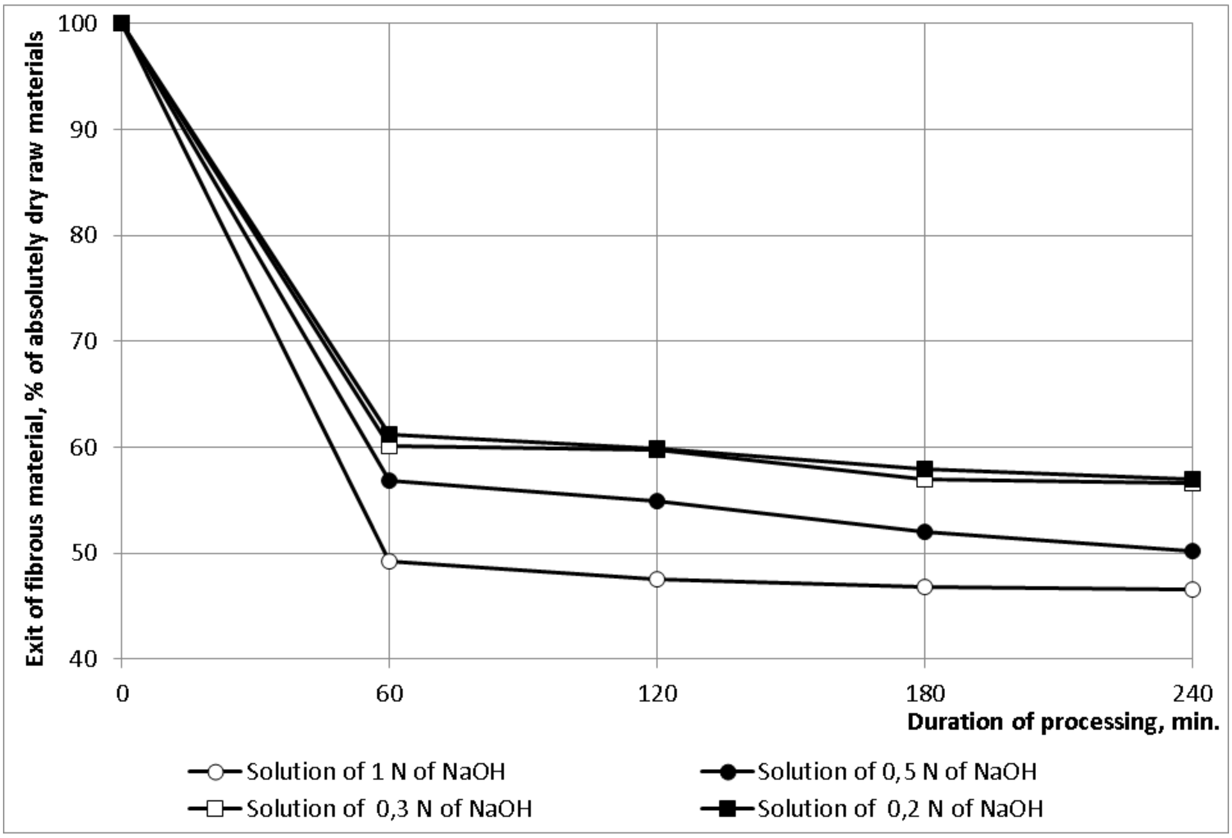

Figure 3: Dependence of the yield of fibrous material on the concentration of alkali and the duration of treatment

Figure 3 shows the dependence of the yield of the fiber product on the concentration of alkali and the duration of treatment. Figure 2 shows that during the first hour of treatment at 1 N concentration of alkali, the reduction in yield is more than 50% of the initial BDRM. During treatment at 0.5 N concentration, the yield is 56.8% of the initial BDRM; at 0.2 and 0.3 N the yields of the fibrous product are almost identical and amount to 56 ... 57% of the original BDRM.

The reduction of the yield of fibrous material when using 1N alkali is due not only to the removal of mineral substances and lignin, but also with the destruction of the carbohydrate part of the RS by reducing the selectivity of the process.

Removal of lignin during alkaline treatment is a concomitant process. Figure 4 shows the dependence of the residual lignin content in the fiber product on the concentration of alkali and the duration of treatment.

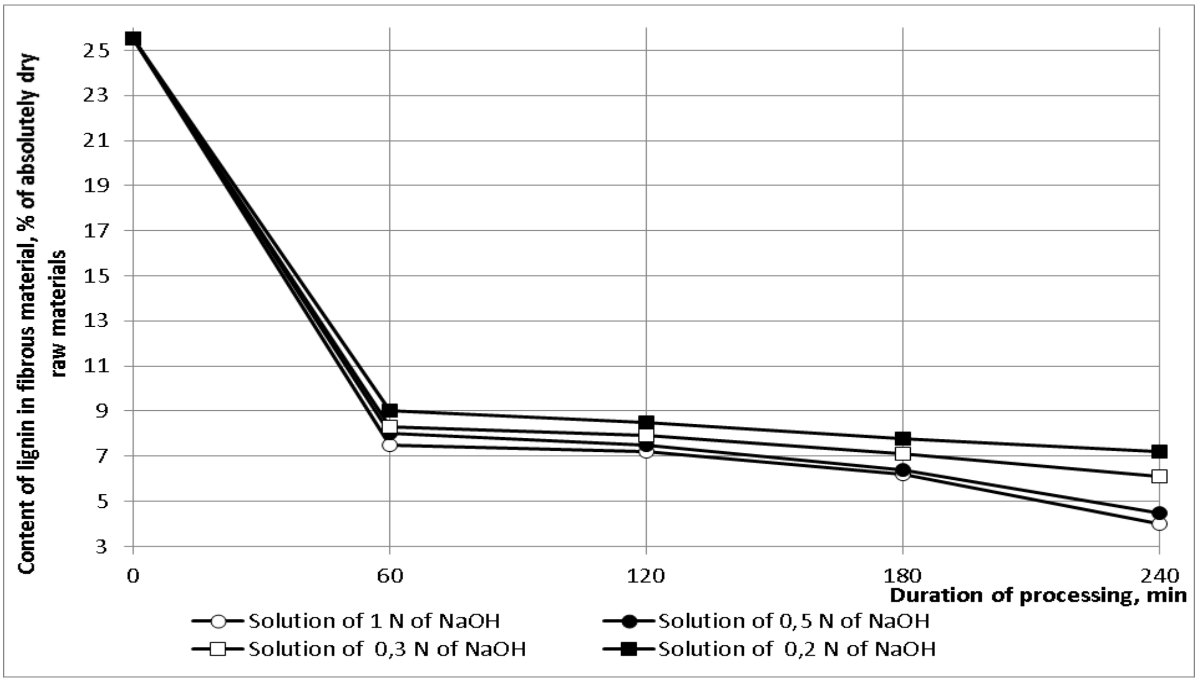

Figure 4: Dependence of lignin content in fibrous material as a function of alkali concentration and processing time

Fig. 4 shows that the bulk of lignin amounting to 64.7 ... 70.6% of the initial lignin content in BDRM is removed in the first hour of processing. Subsequent 180 minutes of treatment allow to remove from 71.8 to 84.3% of the initial lignin content in BDRM depending on the concentration of alkali.

From the data presented, it can be concluded that when the alkali concentration is 1 N, and the treatment time is 240 minutes, a significant degradation of the carbohydrate component is observed, and further increase in the concentration of alkali and the duration of treatment is not advisable. Treatment at an alkali concentration of 0.2 ... 0.3N even with a duration of 240 minutes does not reach the required values for the yield, the content of minerals and the content of residual lignin.

In order to find the optimal values for the concentration of alkali and the duration of RS treatment, a two-level two-factor complete factoral experiment 2^2 was planned and implemented, with a three-fold repetition of each iteration.

Based on preliminary studies of alkaline RS treatment, the following areas of variation of the natural values of the factors (Z_i) were chosen: the concentration of alkali (Z_1) from 0.5 up to 1 N (with the hydromodule 1:10), the duration of RS treatment from 60 up to 240 min.

Areas of change in input factors are presented in Table 1.

Table 1: Areas of change in input factors

Name of input factors	The natural values of the input factors at their next normalized values (xi)		
	x_i = -1	x_i = 0	x_i = 1
Duration of alkaline treatment, min. (Z1)	60	150	240
Concentration of alkali NaOH, N. (Z2)	0,5	0,75	1,0

The following properties (Y_j) were taken as output parameters:
Y_1 - yield of fibrous material,%,
Y_2 - content of residual lignin,%;
Y_3 - content of mineral substances in the fibrous material,%, of the initial BDRM,%.

To obtain the experimental statistical model, a regression analysis of the experimental results was carried out for the first-order plan 2^2 [16].

According to this plan, an experimental statistical model with normalized values of input factors can be presented in the form of a polynomial:

$$y_j = b_0 + b_1x_1 + b_2x_2 + b_{12}x_1x_2,$$

where b_0 is the free term equal to the value of the output parameter at the center of the factor domain for $x_1 = x_2 = 0;$

b_1 and b_2 are effects of linear influence on the output parameter of the corresponding input factors;

b_{12} is the nonlinear effect of the combined influence of both input factors on the output parameter.

The matrix of the plan with the normalized and natural values of the input factors and the experimental results obtained after a three-fold repetition of each experiment are given in Table 2.

Table 2: Plan and results of the experiment

Number of experience	Normalized values of input factors			Natural values of input factors		Arithmetic mean values of input parameters			Dispersion of unit values of output parameters		
	x_1	x_2	$x_1 \cdot x_2$	Z_1, min.	Z_2, N.	y_1, %	y_2, %	y_3, %	S_1^2, $(\%)^2$	S_2^2, $(\%)^2$	S_3^2, $(\%)^2$
1	1	1	1	240	1	46,3	4,8	3,1	0,02	0,0002	0,0017
2	1	-1	-1	240	0,5	56,8	6,5	4,2	0,01	0,0002	0,0007
3	-1	1	-1	60	1	49	7,5	7	0,01	0,0001	0,0004
4	-1	-1	1	60	0,5	59,1	9,4	8,4	0,02	0,0002	0,0002

Statistical analysis of the results of "manual" calculations [17] and calculations performed by the computer program Statgraphics [16] has shown that for the confidence probability of 0.95 the following experimental statistical models of process parameters with normalized values of input factors are adequate:

$y_1 = 52{,}8 - 1{,}25x_1 - 5{,}15x_2;$

$y_2 = 7{,}05 - 1{,}4x_1 - 0{,}9x_2 + 0{,}05x_1 \cdot x_2;$

$y_3 = 5{,}675 - 2{,}025x_1 - 0{,}625x_2 + 0{,}075x_1 . x_2.$

Replacing the normalized values of input factors by natural ones [17] has resulted in the following mathematical models of output parameters: $y_1 = 70{,}3 - 0{,}0139Z_1 - 20{,}6Z_2;$

$y_2 = 12{,}3 - 0{,}016Z_1 - 3{,}6Z_2 + 0{,}002Z_1 \cdot Z_2;$

$y_3 = 11{,}3 - 0{,}023Z_1 - 2{,}5Z_2 + 0{,}003Z_1 \cdot Z_2.$

To test the applicability of the experimental statistical models obtained in practice, an additional experiment was carried out at the center of the investigated factor domain at $Z_1 = 150$ min. and $Z_2 = 0.75$N. A comparison of the values of the output parameters for this experiment showed their good convergence with the calculated values (not more than 5% discrepancy), except for the lignin content (Table 3).

Table 3: Results of practical verification of the obtained experimental statistical models

Output parameter values	y_1, %	y_2, %	y_3, %
Calculated	52,3	7,5	6,4
Actual	50,0	6,2	6,2

Analysis of the dependences of the output parameters on the values of the input factors shows (Figures 5-7) that with an increase in the values of the input factors all output parameters decrease. In this case, it is visually impossible to determine the optimal values of the input factors that ensure a high yield of technical cellulose from RS with a minimum content of mineral components in it. To find the optimal conditions, it is necessary to apply mathematical methods for solving optimization problems.

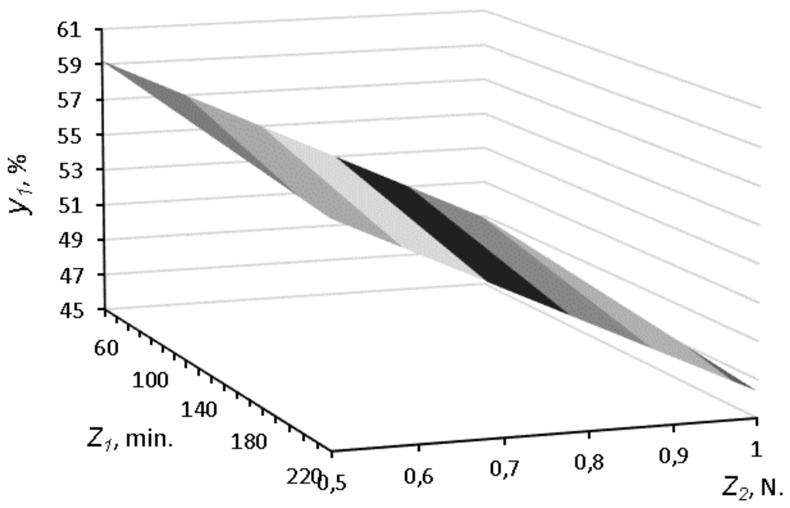

Figure 5: Surface of the dependence of the yield of technical pulp on the values of input factors

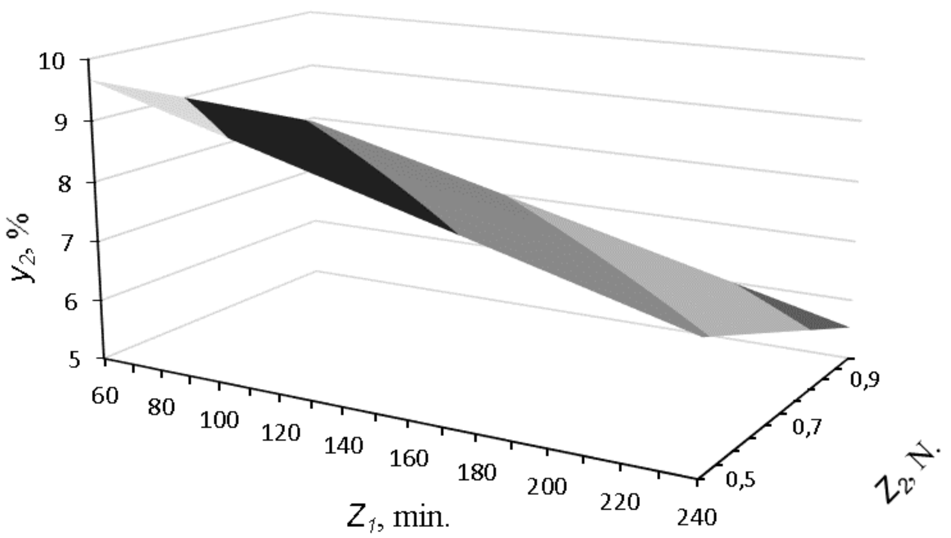

Figure 6: Surface of dependence of lignin content in technical pulp on the values of input factors

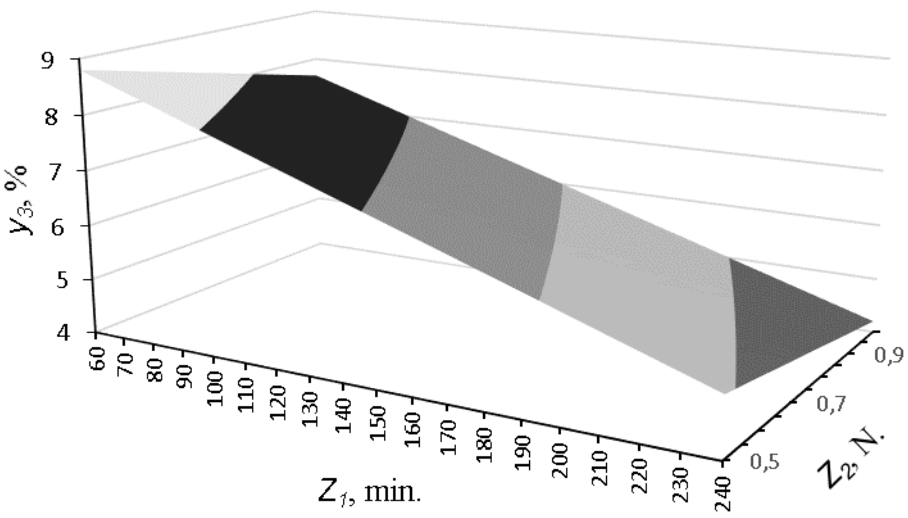

Figure 7: Surface of dependence of lignin content in technical pulp on the values of input factors

To solve the formulated optimization problem, the following mathematical model is proposed:

$$\begin{cases} y_3 = 11.3 - 0.023Z_1 - 2.5Z_2 + 0.003Z_1 \cdot Z_2 \rightarrow \min \text{ (objective function)} \\ y_1 = 70.3 - 0.0139Z_1 - 20.6Z_2 \geq 52 \text{ (limitation 1)} \\ y_3 = 11.3 - 0.023Z_1 - 2.5Z_2 + 0.003Z_1 \cdot Z_2 \geq 0 \text{ (limitation 2)} \\ y_2 = 7.05 - 1.4x_1 - 0.9x_2 + 0.05x_1 \cdot x_2 \geq 0 \text{ (limitation 3)} \\ 0 < Z_1 \leq 240 \text{ (boundary conditions)} \\ 0.5 < Z_2 \leq 1 \text{ (boundary conditions)} \end{cases}$$

The analysis of this mathematical model of the optimization problem shows that the problem pertains to single-criterion two-parameter nonlinear programming problems with deterministic continuous variables and has many solutions [18].

To solve this optimization problem, a numerical GRG (generalized reduced gradient) method was used through the procedure of "Finding solutions" of the Excel program.

The results show that the following input values are optimal:

duration of alkaline treatment of RS – 240 min.;

concentration of alkali – 0.69N.

With these values, the following output parameters can be expected:

yield of fibrous material – 52.0%;

lignin content in the fibrous material – 6.5%;

mineral substances content in the fibrous material – 4.7%.

Oxidation-organosolvent delignification of the fibrous material obtained under optimal conditions was performed to obtain commercial pulp with the following parameters: yield - 58.8%, residual lignin - 2.5%, residual mineral content - 0.05%.

Conclusion

The research has found out the following regularities of alkaline RS processing: maximum preservation of the high yield of commercial pulp - 58.8%, extraction of mineral part (residual content of mineral substances) - 0.05% and removal of lignin (residual lignin - 2.5%). The results show that the following values of input factors are optimal: duration of RS alkaline treatment is 240 min; the concentration of alkali is 0.69N.

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