Peroxide cellulose from hemp shives

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Abstract. Shives of hemp (Cannabis sativa) were delignified with the reaction mixture "acetic acid - hydrogen peroxide - sulfuric acid catalyst - water" at a sulfuric acid concentration of 0.45%, a liquid module of 6, and a temperature of 85°C. The influence of the concentration of hydrogen peroxide and the duration of the process on the yield, strength properties and whiteness of technical cellulose was studied. Due to its high strength characteristics, peroxide cellulose from hemp shives can be used in composition with other fibrous semi-finished products in the production of mass types of paper and cardboard products.

Keywords: hemp, shives, cellulose, delignification, hydrogen peroxide, peracetic acid, cellulose whiteness, cellulose strength

As a result of breeding work, varieties of industrial hemp (Cannabis sativa) were bred, in which the content of tetrahydrocannabinol and other psychoactive substances does not exceed 0.01%, and in 2011 industrial cultivation of this crop was allowed in Russia. It is expected that by 2025 the sown area will reach 20 thousand hectares, and the hemp yield will be 8.5 centners per hectare.

About 65% of the mass of hemp trusts is fibrous shives. One of the promising areas of industrial use of technical hemp is the production of pulp and paper products. From one hectare of cultivated area under hemp, you can get the same amount of cellulose as 4 - 7 hectares of forest. Also noteworthy is the high strength inherent in hemp cellulose paper.

Oxidative delignification of plant raw materials with peroxo compounds is considered as a "green" and resource-saving alternative to existing industrial methods of cellulose production. To date, the results of a large number of studies in this area have been published, including reviews [1-4]. The essence of the method lies in the processing of plant materials with an aqueous solution of hydrogen peroxide and acetic acid. In this reaction system, acetic acid undergoes catalyzed oxidation to peracetic acid, which, in its middle, oxidizes lignin, converting it into a soluble state.

Sulfuric acid is used as catalysts, as well as its combinations with tungstic acid, tungstate and sodium molybdate, titanium dioxide.

We have studied the effect of the conditions of one-stage delignification ("cooking") of hemp shives by the oxidative method on the yield and properties of technical cellulose.

The raw material for the research was shives from hemp brand "Surskaya". The chemical composition is determined by conventional methods [5]: mass fraction of cellulose (Kurschner-Hoffer method) 41.2%; lignin (sulfuric acid method modified by Komarov) 23.4%; extractives (extraction in a Soxhlet apparatus with an azeotropic ethanol-toluene mixture) 4.64%; ash 1.10%.

Shives were delignified with the reaction mixture "acetic acid - hydrogen peroxide - sulfuric acid catalyst - water". Constant delignification conditions: the initial concentration of acetic acid in the cooking solution is 6 g-mol/dm^3 (36%); sulfuric acid concentration 0.046 g-mol/dm^3 (0.45%); liquid module 6.0; isothermal cooking temperature 85°C.

Variable cooking factors:

X_1 – initial concentration of hydrogen peroxide in the cooking solution (variation interval 2 ... 4 g-mol/dm^3);

X_2 – cooking duration (interval of variation 135 ... 225 minutes).

The values of these factors varied according to a three-level design of the second-order experiment on the elements of a cube [6] (table 1).

At the end of cooking, a sample of the formed liquor was taken and analyzed for the content of hydrogen peroxide and peracetic acid. The pulp washed after cooking was ground in a CRA apparatus (Yokro mill) to a grinding degree of 34 ... 36°ShR. Paper casts of 75 g/m^2 were made on a Rapid-Keten sheet-molding machine. The experimental results were characterized by the following output parameters:

Y_1 – concentration of residual hydrogen peroxide in the liquor, %;

Y_2 – concentration of residual peracetic acid in the liquor, %;

Y_3 – solid residue yield (technical cellulose), %;

Y_4 – grinding time in CRA up to 35°SHR, min;

Y_5 – breaking length, m;

Y_6 – bursting resistance, kPa;

Y_7 – whiteness of castings, %;

Y_8 – density of castings, g/cm^3.

The results of the experiments are shown in table 1.

Table 1 - Conditions and results of the experiment

Mode number	Variable factors		Output parameters							
–	X_1	X_2	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	Y_7	Y_8
1	3	180	4.01	0.85	53.9	2	8500	198	57	0.651
2	2	135	4.08	0.66	88.2	21	2970	71	45	0.368
3	3	135	5.27	0.76	64.1	6	8120	171	56	0.534
4	4	135	6.51	1.33	54.9	2	9630	251	66	0.705
5	2	180	3.41	0.66	80.6	15	5050	110	48	0.405
6	3	180	4.25	0.89	54.4	2	8550	220	57	0.651
7	4	180	5.78	1.52	48.8	2	10240	272	70	0.783
8	2	225	2.81	0.57	67.7	6	6160	123	51	0.498
9	3	225	3.65	0.76	52.1	2	12000	238	60	0.594
10	4	225	4.42	1.33	47.8	2	12500	362	74	0.717
11	3	180	3.75	0.81	53.4	2	8450	180	53	0.651

Mathematical processing of the results was performed using the Statgraphics Centurion software package. The dependence of each of the output parameters on variable factors was approximated by polynomial second-order regression equations [8]:

$$\acute{Y} - b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2.$$

The terms with an estimate of the confidence probability of the regression coefficients of less than 95% were excluded from the equation with the recalculation of the remaining coefficients. Statistically significant coefficients (threshold significance level 0.05) are shown in table 2.

Regression equations were used to graphically represent the results in the form of three-dimensional response surfaces [7].

The dependences of the concentration of residual values of hydrogen peroxide Y_1 and peracetic acid Y_2 in the liquor on variable factors (fiigure 1) are almost identical and predictable, they are due to the nature of the above-mentioned sequentially occurring oxidative reactions.

Table 2 – Coefficients and statistical characteristics of regression equations

b_{ij} coefficients and statistical characteristics	Output parameters							
	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6	Y_7	Y_8
b_0	4.47	1.51	246.5	125.3	-7953	-244	12.91	0.129
b_1	1.07	-0.80	-82.1	-52.2	12551	96.8	11.0	0.156
b_2	-0.02	–	-0.37	-0.32	-110	0.852	0.067	–
b_{11}	–	–	9.08	5.20	-1586	–	–	–
b_{22}	–	0.198	0.074	–	0.409	–	–	–
b_{12}	–	–	–	0.083	–	–	–	–
Determination coefficient,%	92.5	95.9	98.2	97.5	97.4	96.0	95.5	84.3
Forecast standard error								

for Ý	0.332	0.076	2.30	1.32	586.4	18.4	2.14	0.0055

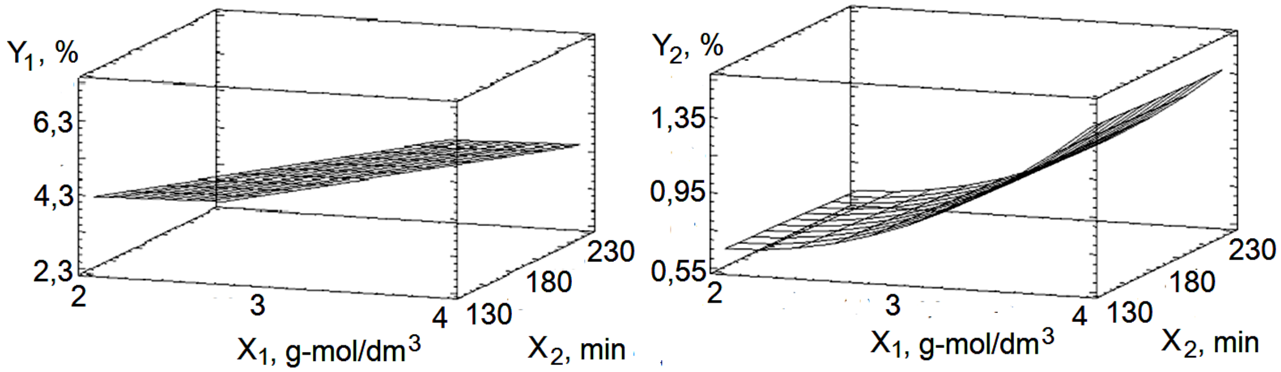

Figure 1 – Dependence of the concentration of hydrogen peroxide Y_1 and peracetic acid Y_2 in the liquor on the variable cooking factors

The yield of cellulose naturally decreases with an increase in the initial concentrations of active reagents in the cooking liquor and the duration of cooking (Y_3, figure 2). At the same time, the grinding time is significantly and almost symbatically reduced with the yield (Y_4, figure 2) - a consequence of the removal of cellulose incrustations as the shives are delignified.

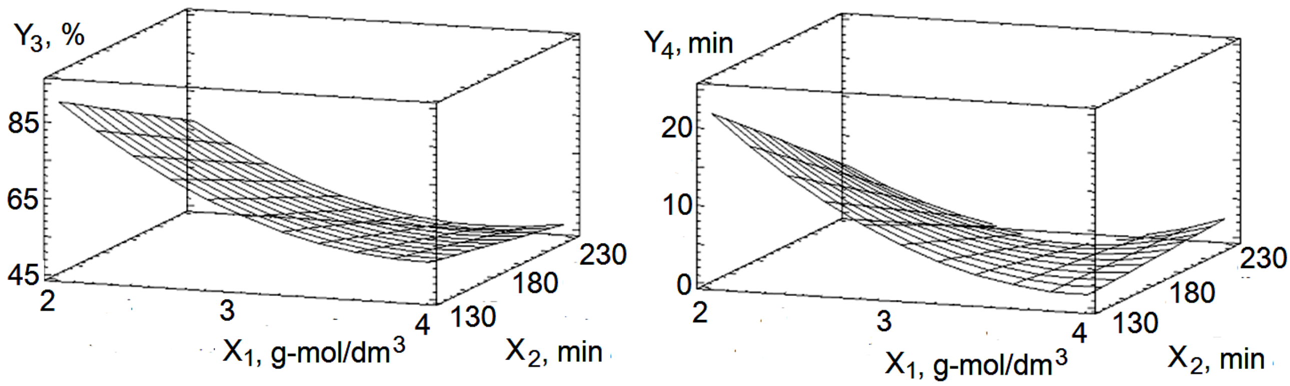

Figure 2 – Dependence of the yield of cellulose Y_3 and the duration of grinding Y_4 on the variable cooking factors

As a result of the deepening delignification, the strength characteristics of cellulose naturally increase - resistance to tearing and punching (Y_5 and Y_6, Figure 3), as well as its whiteness (Y_7, figure 4).

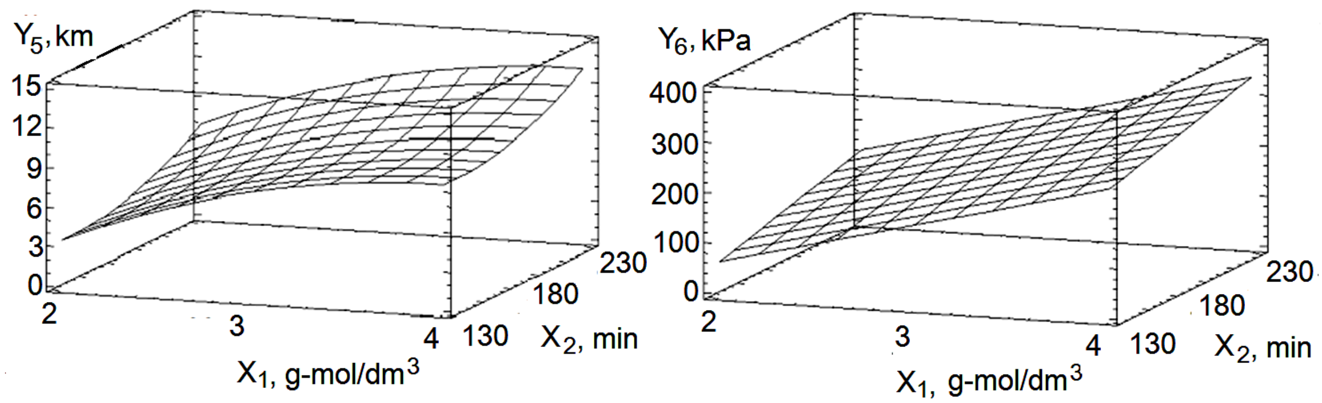

Figure 3 – Dependence of the resistance of cellulose to tearing Y_5 and bursting shear Y_6 on variable cooking factors

A characteristic feature of peroxide cellulose that has not yet received an explanation is the increased density of the paper sheet made from it [3]. In the experiment under discussion, this feature manifested itself most clearly (Y_8, Table 1 and figure 4): a decrease in the cellulose yield from 88 to 48% was accompanied by an increase in density from 0.37 to 0.72 g/cm^3.

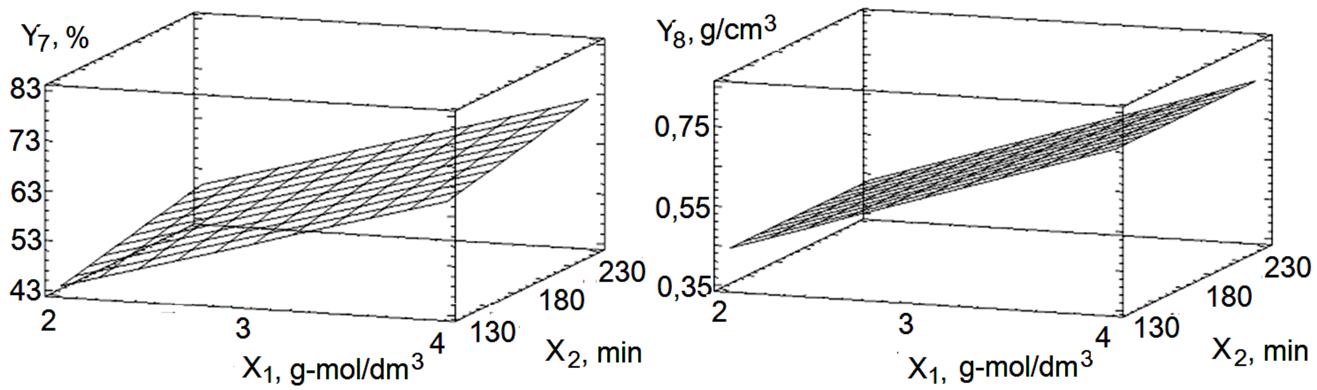

Figure 4 – Dependence of Y_7 whiteness and Y_8 dressing density on variable cooking factors

Due to its high strength characteristics, hemp shives peroxide cellulose can be used in combination with other fibrous semi-finished products in the production of many mass types of paper and cardboard products.

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