Delignification of hemp awn with peroxo compounds and characteristic of the cellulose

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Abstract. The hemp awn (Cannabis sativa) was 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. With a yield of about 45%, it is comparable to the properties of bleached sulphate cellulose from hardwood (OB-0 grade in accordance with GOST 14940-96) and without additional expensive bleaching can be used in the production of many high-quality mass types of paper.

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

In the XIX and early XX centuries in Russia, hemp (Cannabis sativa L - ordinary hemp) was one of the main crops. The area of its cultivation in 1928 reached 996 thousand hectares. But in 1961 the USSR joined the UN convention, which prohibited varieties with a narcotic content of more than 0.2%, and hemp sowing dropped sharply [1]. As a result of breeding work, varieties of industrial hemp were bred, in which the content of tetrahydrocannabinol (THC) and other psychoactive substances does not exceed 0.01%, and in 2011 industrial cultivation of this crop was allowed in Russia. For 2013, 23 varieties and hybrids of cannabis are included in the Russian state register of breeding achievements approved for use. The area under agricultural hemp in Russia is growing. 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 [2].

About 65% of the mass of hemp trusts is fibrous awn. One of the most promising areas of industrial use of technical hemp is the production of pulp and paper products. Currently, about 40% of all deforestation meets the needs of the paper industry. One hectare of hemp can produce the same amount of cellulose as 4-7 hectares of forest. A field planted with hemp bears fruit every year, while trees need at least 20 years to reach the condition necessary for production. 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 the existing industrial methods of cellulose production. To date, the results of a large number of studies in this area have been published, including reviews [3-6]. The essence of the method consists in processing plant materials with a solution of hydrogen peroxide and acetic acid. In this reaction system, acetic acid undergoes a 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 awn by the oxidative method on the yield and properties of technical cellulose.

The raw material for the research was awn from hemp brand "Surskaya". The chemical composition is determined by conventional methods [7]: 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%.

The prepared awn was delignified with the reaction mixture "acetic acid - hydrogen peroxide - sulfuric acid catalyst - water". Delignification conditions: initial concentration of acetic acid in the cooking solution 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 brewing factors:

X_1 – initial concentration of hydrogen peroxide in the cooking solution (variation range 3 ... 5 g-mol/dm^3);

X_2 – cooking duration (variation interval 180 ... 270 minutes).

These factors varied according to a three-level design of the second-order experiment on cube elements [8] (table 1).

The pulp washed after cooking was ground in a CRA apparatus (Yokro mill) for 2 minutes to a grinding degree of 34 ... 36 ^{o}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 – cellulose yield, %;

Y_4 – breaking length, m;

Y_5 – elongation to break, %;

Y_6 –bursting resistance, kPa;

Y_7 – tear resistance, mN;

Y_8 – whiteness of castings, %.

The results of the experiments are shown in table 1.

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Table 1. Conditions and results of the experiment

Mode number	Variable factors		Output parameters							
–	X1	X2	Y1	Y2	Y3	Y4	Y5	Y6	Y7	Y8
1	4	225	4.59	1.43	47.3	10032	2.41	249	196	74
2	3	180	3.99	0.85	53.9	8500	2.25	198	236	57
3	4	180	5.78	1.52	48.8	10236	2.42	272	210	67
4	5	180	6.20	1.71	45.6	11333	2.51	273	166	79
5	3	225	3.65	0.76	52.1	12000	2.40	238	166	60
6	4	225	4.59	1.23	48.1	11850	2.42	253	172	74
7	5	225	5.52	1.52	45.4	10777	2.47	253	166	84
8	3	270	2.80	0.95	50.8	10910	2.46	281	196	63
9	4	270	3.82	1.42	47.4	9906	2.42	245	220	81
10	5	270	3.57	0.95	44.3	10108	2.40	250	176	88
11	4	225	4.59	1.45	47.9	10090	2.45	249	190	72

Mathematical processing of the results was performed using the Statgraphics Centurion software package. The dependence of each of the output parameters Y 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.

Table 2. Coefficients and statistical characteristics of the 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	-1.153	-3.493	79.9	10523	0.556	-346.2	267.0	-7.42
b_1	2.608	1.345	-10.0	–	0.445	142.3	-15.0	22.6
b_2	0.019	0.016	-0.021	–	0.007	2.48	-0.074	-0.002
b_{11}	–	–	0.803	–	–	–	–	–
b_{22}	–	–	–	–	–	–	–	–
b_{12}	-0.008	-0.005	–	–	-0.002	-0.588	–	0.0167
Determination coefficient	0.928	0.694	0.980	–	0.919	0.731	0.247	0.983
Forecast standard error $\acute{Y}$	0.332	0.213	0.491	524	0.022	13.7	23.2	1.86

Regression equations were used to graphically represent the results in the form of three-dimensional response surfaces [9].

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

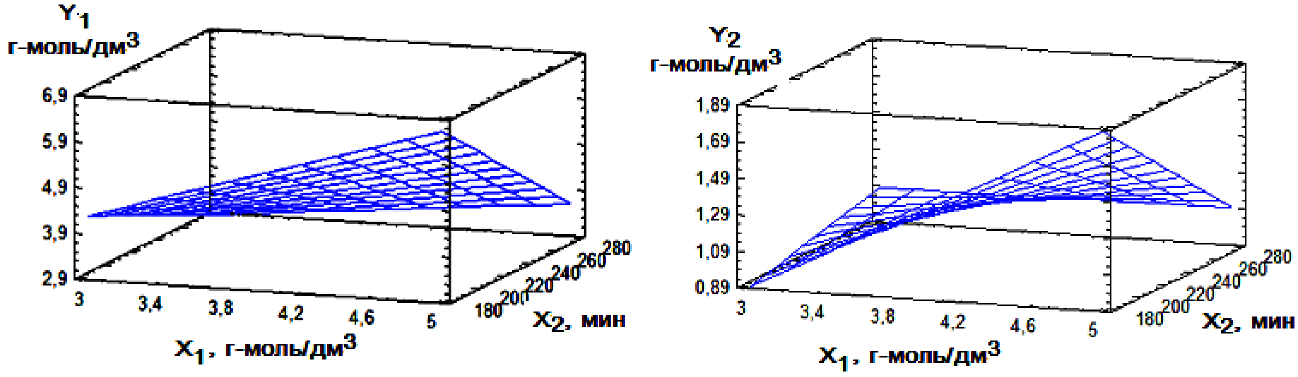

Figure 1. Dependence of the concentration of residual hydrogen peroxide in the liquor on the variables of cooking

The yield of technical cellulose decreases linearly with an increase in the initial concentration of hydrogen peroxide and the duration of cooking within the used range of their variation (Y_3, Figure 2).

The tensile strength of paper castings (breaking length Y_4) remained unchanged under the experimental conditions (did not go beyond the "noise background"; all regression coefficients are statistically insignificant, tab. 1). Since the breaking strength is highly dependent on the strength of the individual fibers, it can be argued that awn hemp fibers are resistant to the action of the cooking liquor components. The magnitude of the elongation of the paper samples under tension Y_5, on the contrary, is largely due to the strength of the interfiber bonds, the dependence of this parameter on the cooking conditions is ambiguous (Y_5, figure 2). These results are consistent with other strength properties - resistance to bursting and tearing, this is clearly seen when comparing figures 2 and 3.

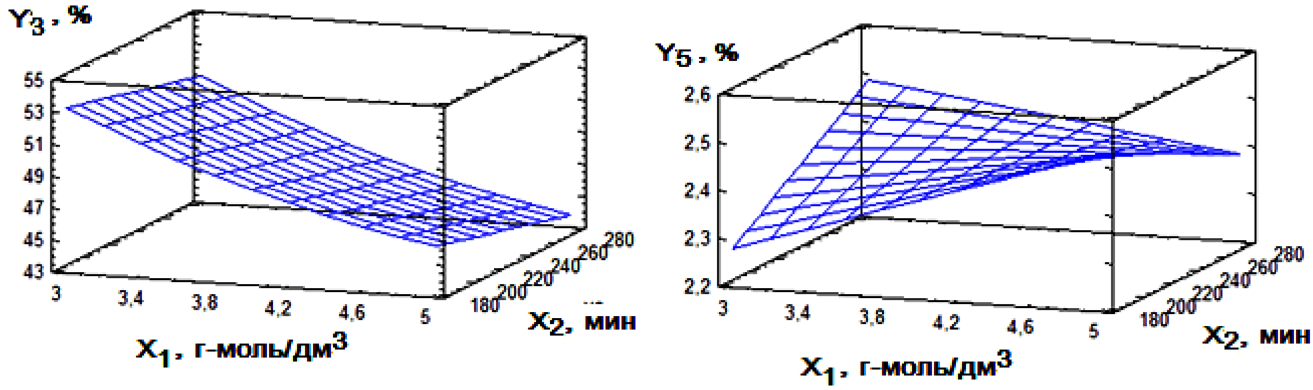

Figure 2. Dependence of pulp yield Y_3 and elongation at break Y_5 on variable cooking factors

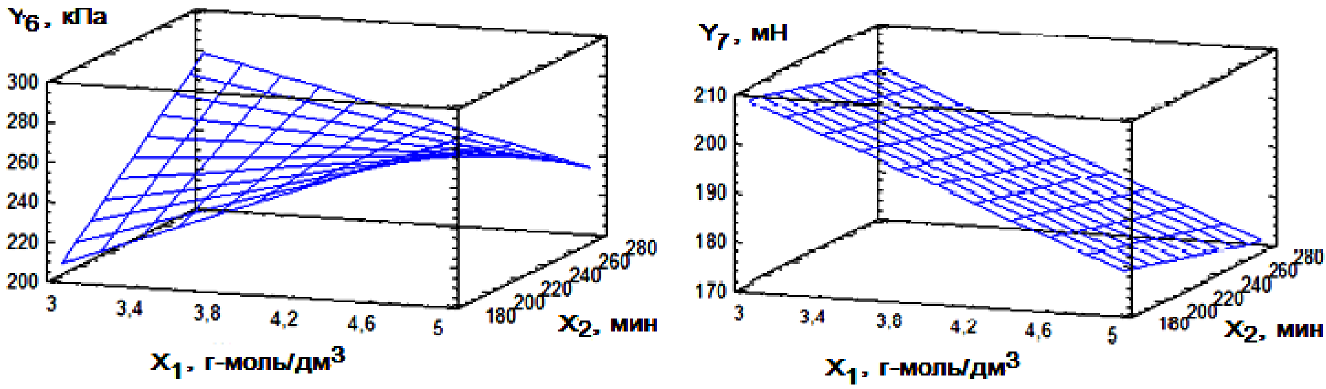

Figure 3. Dependence of the resistance of castings to punching shear Y_6 and tearing Y_7 on the variable factors of cooking

The whiteness of cellulose Y_8 grows from 58 to 89% in proportion to a decrease in the yield of Y_3 from 54 to 44% (the linear correlation coefficient is -0.966); therefore, we do not present the graph of the response surface of this parameter here. Note that according to GOST 14940-96, bleached sulfate cellulose from hardwood (aspen) of all grades, including OB-0, must have a whiteness of at least 86%. Consequently, the discussed awn hemp pulp without additional expensive bleaching can be used instead of bleached hardwood sulphate pulp in the production of many high-quality mass grades of paper.

The work was carried out within the framework of the state assignment of the Ministry of Education and Science of Russia for the implementation of the project "Technology and equipment for the chemical processing of plant raw materials biomass" by the team of the scientific laboratory "Deep processing of vegetable raw materials" (topic number FEFE-2020-0016).

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