Peroxide cellulose from hemp

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Abstract. Crushed hemp fibers (Cannabis sativa) was delignified with the reaction mixture "acetic acid - hydrogen peroxide - sulfuric acid catalyst - water" at a sulfuric acid concentration of 0.45% and a temperature of 85°C. with low fluid module 3.The influence of the initial concentration of hydrogen peroxide in the cooking solution (in the range 3 ... 5 g-mol/l) and the duration of the process (in the range 90 ... 180 min) on the yield and strength properties of technical cellulose has been studied. With a yield of 78 ... 90% and a degree of grinding of 36 ... 38°SR, the cellulose had a breaking length of up to 5.4 km, a fracture resistance of more than 140 double bends and a very high tear resistance - more than 1800 mN. Due to its high strength characteristics, peroxide cellulose from hemp fibers can be used in composition with other fibrous semi-finished products in the production of various types of paper and cardboard products.

Keywords: hemp, fibers, cellulose, delignification, hydrogen peroxide, peracetic acid, cellulose strength

During decortication (mechanical, chemical or biological treatment of hemp straw), two types of fibrous products are obtained - shives and fibers. Both types of fibers can serve as raw materials for the production of paper and cardboard products, but the technologies for their processing are different.

We reported earlier about the delignification of hemp shives with peroxo compounds and the properties of the resulting cellulose [1]. The chemical composition of fibers has a number of characteristics. Table 1 shows the results of a number of analyzes performed by conventional methods [2]: mass fraction of cellulose - by the Kurschner-Hoffer method, lignin - by the sulfuric acid method in Komarov's modification, extractives - by extraction in a Soxhlet apparatus with an azeotropic ethanol-toluene mixture. Unlike wheat straw and hemp shives, fibers contain significantly more cellulose and less lignin. This makes it possible to reduce the consumption of delignifying reagents - hydrogen peroxide and acetic acid - for cooking. Preliminary experiments have shown that in this case it is advisable to reduce not the concentration of reagents in the cooking solution, but the liquid module during cooking.

Table 1. Chemical composition of plant raw materials

Vegetable raw material	Mass fractions of components in raw materials,%			
	cellulose	lignin	extractive substances	ash
Wheat straw	46.6	22.0	1.22	5.37
Hemp shives	41.2	23.4	4.64	1.10
Hemp fibers	71.2	5.35	0.32	1.75

We have studied the influence of two variable factors of peroxide delignification, the initial concentration of hydrogen peroxide in the cooking liquor and the duration of the process, on the yield and properties of technical cellulose from fibers.

The raw material for the research was hemp fibers of the "Surskaya" brand, the chemical composition of fibers is shown in table 1.

Hemp fibers were crushed in a dry disc mill. For the experiments, a fraction passed through a sieve with a hole diameter of 8 mm was used.

The prepared fibers 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 3.0; 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 90 ... 180 minutes).

The values of these factors varied according to a three-level design of the second-order experiment on the elements of a cube [3] (table 2).

The pulp washed after cooking was ground in a CRA apparatus (Yokro mill) for 19 ... 22 minutes to a grinding degree of 36 ... 40 ^{o}SR. 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 –cellulose yield, %;

Y_2 – breaking length, m;

Y_3 – elongation before breaking, %;

Y_4 – bursting resistance, kPa;

Y_5 – tear resistance, mN;

Y_6 – break resistance, number of double kinks.;

The results of the experiments are shown in table 2.

Table 2 – Experimental conditions and results

Mode number	Variable factors		Output parameters					
–	X_1	X_2	Y_1	Y_2	Y_3	Y_4	Y_5	Y_6
1	4	135	80.7	3285	3.11	272	1373	45
2	3	90	84.5	4612	2.75	225	1144	132
3	4	90	89.7	5348	2.87	248	1216	118
4	5	90	81.0	46.71	2.99	241	1295	161
5	3	135	83.1	4687	2.66	225	1177	105
6	4	135	78.5	3244	2.79	262	1570	118
7	5	135	79.2	4249	2.74	226	1857	142
8	3	180	78.0	4036	3.36	226	1393	69
9	4	180	77.9	3790	3.01	228	1236	91
10	5	180	75.8	4389	2.69	209	1425	75
11	4	135	78.5	3455	2.25	190	1465	90

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 [3]:

$$\acute{Y} = b_0 + b_1X_1 + b_2X_2 + b_{12}X_1X_2.$$

Regression coefficients are shown in table 3.

Regression equations were used to graphically represent the results in the form of three-dimensional response surfaces [4].

The dependence of the yield of technical cellulose on the variable factors of cooking is shown in Figure 1. As expected, an increase in both factors, the initial concentration of hydrogen peroxide and the duration of the process, leads to an additive decrease in the yield. At the same time, contrary to expectations, the tear resistance of paper castings decreases almost symbatically (figure 2). This may be due to the removal of hemicelluloses from the fiber surface or partial destruction of the outer layers involved in the formation of interfiber bonds. The contribution of both of these processes to the formation of the paper-forming properties of the fibers is not excluded. An indirect indication of such a possibility can be the complex nature of the dependence of the elongation of paper castings at break on the conditions of delignification (in fact, on the yield of cellulose or the depth of delignification) (figure 3). Of course, these assumptions need more detailed study.

Table 3 – 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
b_0	192.39	7797	0.4033	158.9	227.3	98.57
b_1	-2.575	-224.8	0.6242	24.8	223.1	29.25
b_2	-0.111	-27.1	0.0188	0.480	4.210	-0.16
b_{12}	0.007	1.63	-0.0050	-0.183	-0.001	-0.13
Coefficient determination, %	72.8	28.2	28.1	18.9	38.1	13.6
Standard error of Ý forecast	2.43	1473	0.290	26.2	193.7	81.4

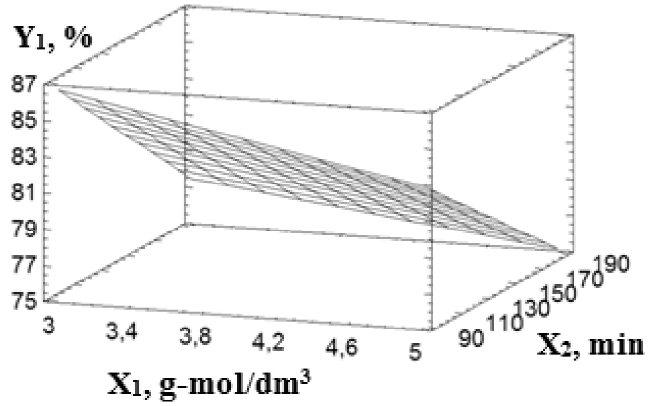

Figure 1. Dependence of technical cellulose yield on cooking conditions

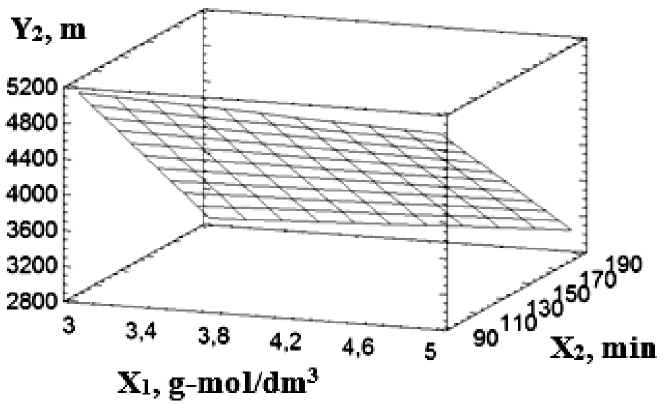

Figure 2. Dependence of tensile strength of paper castings on cooking conditions

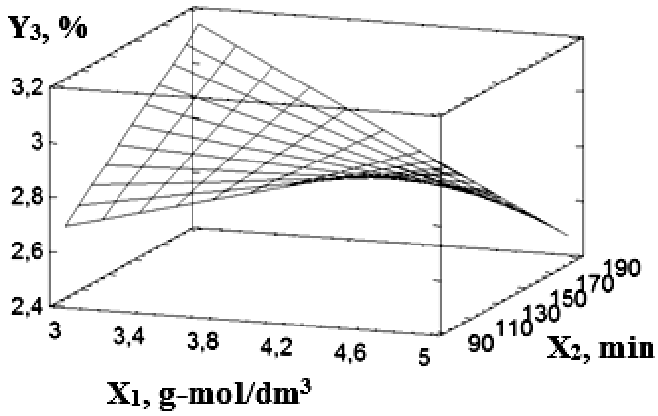

Figure 3. Dependence of elongation of castings at break on cooking conditions

A positive correlation is usually observed between the values of the resistance of a paper sheet to tearing and punching. In the experiment under discussion, this relationship manifested itself as a trend (the linear correlation coefficient is 0.64), which can be seen when comparing figures 1 and 4.

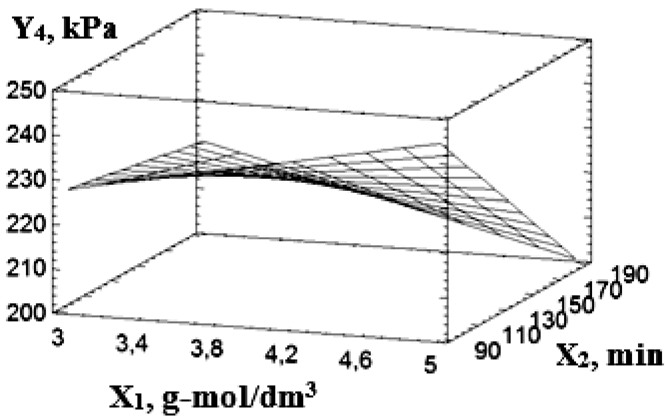

Figure 4. Dependence of resistance of castings to punching shear conditions

The dependence of the resistance of castings to tearing on the cooking conditions is consistent with a priori information on the delignification of the stems of other cereal crops: the value of the indicator increases with the deepening of delignification (figure 5). Note an essential feature of this property in hemp fibers - a very high value of tear resistance, which we have never observed in cellulose from other types of plant raw materials.

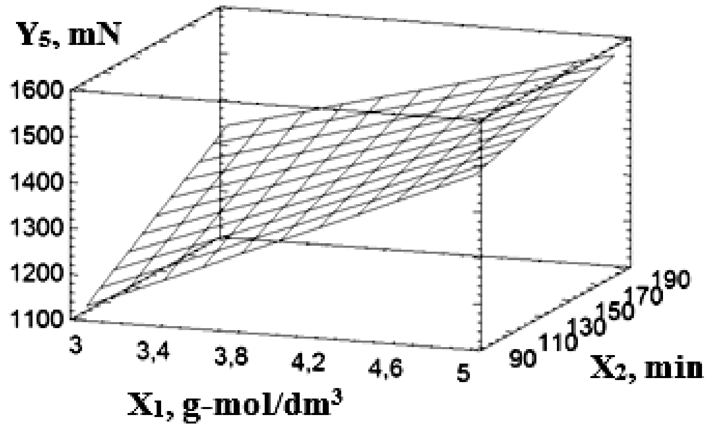

Figure 5. Dependence of the tear resistance of castings on the cooking conditions

There is a weakly expressed correlation between the indicators of resistance to rupture and fracture (figures 2 and 6; the correlation coefficient is 0.55), which is consistent with the available a priori information on the properties of cellulose from other types of plant materials.

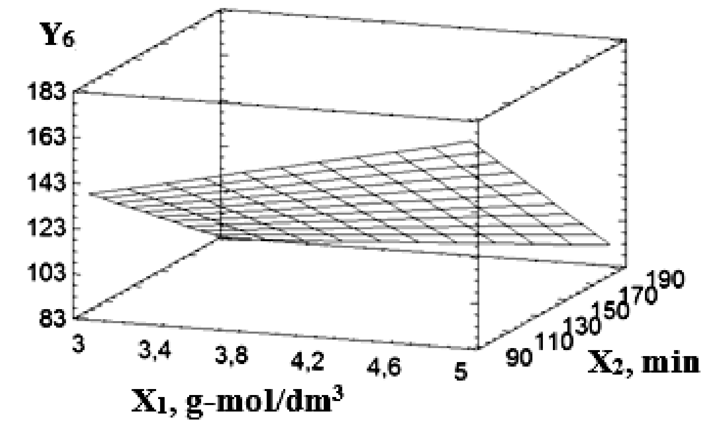

Figure 6. Dependence of the resistance of castings to fracture on the conditions of cooking

Summary. The peroxide delignification of hemp shives can be successfully performed at a low liquid modulus. Engineering design of alkaline delignification methods with modules 2.8 ... 3.2 are used in industrial installations for continuous cooking.

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