Morphological properties of peroxidic pulp from hemp bonfire

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Abstract. The bonfire (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 effect of cooking conditions (hydrogen peroxide concentration and process duration) and mass grinding up to 34 ... 36 °SR on the morphological properties of technical cellulose fibers - length, width, degree of inhomogeneity (polydispersity) - has been studied. Hemp fibers are inferior in length to those of spruce wood and wheat straw, but more uniform. The widths of hemp and wood fibers are almost the same. Due to its high strength characteristics, peroxide cellulose from bonfire is suitable for use in composition with other fibrous semi-finished products in the production of mass types of paper and cardboard products.

The use of non-woody plants for the production of cellulose has been mastered for a long time. With the development of new technologies, the emergence of modern concepts for the development of the pulp and paper industry, the need for rational use of resources and an increase in the volume of annual plants grown, straw processing takes on new importance.

The shortage of wood raw materials in many regions of the world has made it urgent to search for additional sources of technical cellulose. One of these sources is the straw of annual plants. Providing production with raw materials comparable to short-fiber deciduous wood in terms of quality, and at the same time solving the problem of agricultural waste processing, annual straw becomes a full-fledged source of cellulose and products based on it.

Hemp can become one of the resources of plant raw materials for the production of cellulose. Cannabis growing is the oldest branch of plant growing. Industrial hemp remained an important industrial raw material until the 1960s. In 1961, the UN adopted a new convention on narcotic drugs, which included cannabis. As a result of breeding work, varieties of industrial hemp (Cannabis sativa) have been developed, in which the content of narcotic substances does not exceed 0.1%, and industrial cultivation of this crop is allowed in many countries. About 65% of the mass of hemp trusts falls on the fibrous bonfire. One of the promising areas of industrial use of technical hemp is the production of pulp and paper products. From one hectare of sown area under hemp, you can get the same amount of cellulose as 4-7 hectares of forest.

In the production of cellulose fibrous semi-finished products from hemp bonfire, methods of oxidative delignification in aqueous-organic solvents, developed for the processing of wood and straw raw materials, can be used [1-6]. This opportunity opens up prospects for improving the technology in
terms of cooking liquor preparation and chemical recovery from spent liquor. At the same time, the positive aspects of the process remain: selectivity, low temperature and atmospheric pressure, the absence of harmful substances in wastewater and gas emissions.

Oxidative delignification of plant raw materials with peroxy 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. 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 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.

Continuing the studies begun earlier [7, 8], the authors studied the effect of the conditions of delignification ("cooking") of hemp bonfire by the oxidative method on the morphological and strength properties of technical cellulose.

The raw material for the research was a bonfire made of industrial hemp (Cannabis sativa) of the "Surskaya" brand. The chemical composition is determined by conventional methods:

- mass fraction of cellulose (Kurschner-Hoffer method) 41.2%;
- lignin (sulfuric acid method) 23.4%;
- extractives (extraction in a Soxhlet apparatus with an azeotropic ethanol-toluene mixture) 4.64%; ash 1.10%.

The bonfire was delignified with the reaction mixture "acetic acid - hydrogen peroxide - sulfuric acid catalyst - water". Delignification (cooking) 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. The pulp washed after cooking was ground in a CRA apparatus for 2 minutes to a grinding degree of 34...36 °SR. Paper casts of 75 g/m$^2$ were made on a Rapid-Keten sheet-molding machine.

Variable process factors:

- A - variable cooking conditions, two levels of variation (A1 - initial concentration of hydrogen peroxide in solution 5.0 g-mol/dm$^3$, cooking duration 270 minutes; A2 - 4.0 g-mol/dm$^3$ and 135 minutes, respectively);
- B - the degree of grinding of the pulp, two levels of variation (B1 - without grinding; B2 - ground up to 34-36 °SR).

Cooking conditions, yield, strength properties of cellulose (after grinding) are shown in Table 1.

The morphological characteristics of cellulose fibers (length, width, distribution histograms) were determined using a MorFi Neo analyzer (France). The sample size N (the number of measured fibers) in each measurement session was at least 5000.

| Cooking conditions (factor A levels), yield and pulp strength. |
|---------------------------------------------------------------|
| **Cooking conditions** | Concentration H$_2$O$_2$, g-mol/dm$^3$ | Duration, minutes | Output, % | Discontinuous length, km | Resistance tearing apart mN |
|------------------------|--------------------------------|-------------------|----------|------------------------|---------------------------|
| A1                     | 5.0                           | 270               | 44.3     | 8.79                   | 176                       |
| A2                     | 4.0                           | 135               | 54.9     | 8.35                   | 157                       |

To calculate the average length, all fibers are divided into n classes. Each class contains the number of Ni fibers of a certain length $L_i$ ($i = 1, 2, \ldots, n$). In the practice of analyzes, two types of average values are most often calculated: number average $L_\text{a} = \Sigma n_i L_i/\Sigma n_i$ (for microscopic analysis) and mass average $L_\text{m} = \Sigma n_i L_i^2/\Sigma n_i L_i$ (for sieve analysis). The degree of inhomogeneity of fibers along the length can be characterized by the polydispersity index $g = L_\text{m}/L_\text{a}$. (by analogy with the assessment of the
macromolecular heterogeneity of polymers [4]). If all fibers have approximately the same length, then $L_a \approx L_m$ and $g \approx 1$. Otherwise, $L_a < L_m$ and $g > 1$.

The measurement results were characterized by the following output parameters:

- $L_a$ - number average fiber length, μm;
- $W_a$ - number average fiber width, microns;
- $g$ - the degree of polydispersity of the fibers $g$ along the length.
- Particles with $L > 200$ μm and $L/W > 6$ were considered fibers.

The plan of two-factor analysis of variance, the measurement results and their statistical characteristics are shown in tables 2, 3, and 4. Mathematical processing of the results was performed using the Statgraphics Centurion software package [9]. The statistical significance of differences between the compared values of fiber properties was assessed using Fisher's dispersion ratios $F$ and significance levels $P$ (table 4). The influence of the factor on the analyzed property was recognized as significant with a confidence level of at least 95% if the corresponding value of $P$ did not exceed 0.05 and the value of $F$ was greater than the “threshold” value $F_{0.05}(1; 7) = 5.59$.

The dimensions of the fibers, their length $L$ and width $W$, are among the main parameters characterizing the paper-forming properties of technical cellulose. The histograms of the distribution of these characteristics of fibers are shown in figures 1 and 2, the results of analysis of variance are shown in figure 3.

As expected, as a result of grinding, the values of both properties decreased by about 18...24% (the influence of factor B), and the change in the delignification mode (factor A) practically did not affect them (figures 3a, 3b).

Table 2. Conditions and results of the experiment (two implementations).

| Factor levels (modes) | Output parameters |
|-----------------------|------------------|
|                       | $L_a$            | $W_a$ | $g$      |
| A1 B1                 | 581              | 24.1  | 1.181    |
| A1 B1                 | 585              | 22.8  | 1.165    |
| A1 B2                 | 468              | 19.9  | 1.128    |
| A1 B2                 | 452              | 19.1  | 1.134    |
| A2 B1                 | 512              | 23.8  | 1.178    |
| A2 B1                 | 530              | 22.2  | 1.184    |
| A2 B2                 | 475              | 20.1  | 1.178    |
| A2 B2                 | 435              | 18.9  | 1.158    |

Table 3. Statistical characteristics of measurement results.

| Characteristic names      | $L_a$ | $W_a$ | $g$  |
|---------------------------|-------|-------|------|
| The average               | 504.7 | 21.36 | 1.163|
| Standard deviation        | 57.10 | 2.108 | 0.02174|
| The coefficient of variation, % | 11.31 | 9.870 | 1.869|
| Minimum                   | 435.0 | 18.9  | 1.128|
| Maximum                   | 585.0 | 24.1  | 1.184|

Table 4. Criteria for the statistical significance of the influence of variables factors (F - Fisher’s variance ratio; P - significance level).

| Factors | $L_a$ | $W_a$ | $g$  |
|---------|-------|-------|------|
| A       | 5.18  | 0.0560| 1.78 | 0.2529 | 11.13 | 0.0980 |
| B       | 65.87 | 0.0013| 16.34| 0.0156 | 16.62 | 0.0980 |
| AB      | 5.32  | 0.0718| 1.78 | 0.2529 | 4.62  | 0.0980 |
Figure 1. Histograms of the distribution of cellulose fibers along the length.

Figure 2. Histograms of the distribution of cellulose fibers along the width.

Figure 3. Influence of variable factors on length (a), width (b) and length polydispersity (g) of fibers (mean values and 95% confidence intervals).

The influence of variable factors on fiber length polydispersity is shown in figure 3c. The value of the g index increased with an increase in the cellulose yield (influence of factor A) and decreased as a result of milling (influence of factor B). The influence of both factors is statistically significant (table 4), but relatively small in absolute values (coefficient of variation is about 1.9%, table 3), therefore, a reliable interpretation of this result at this stage of the study is hardly possible.

Table 5 shows the characteristics of fibers from hemp fire (before grinding) and fibrous semi-finished products obtained in a similar way from other types of plant raw materials - wheat straw and spruce wood [6]. Hemp fibers are inferior in length to straw and wood fibers, but more uniform. The widths of hemp and wood fibers are almost the same.
Table 5. Comparison of the morphological characteristics of cellulose fibers of different origins (peroxide delignification; before grinding).

| Fiber characteristics | hemp bonfire | wheat straw | spruce wood |
|-----------------------|--------------|-------------|-------------|
| Number average length, La, μm | 583 | 577 | 707 |
| Weight-average length, Lm, μm | 682 | 1340 | 1950 |
| Length polydispersity, g | 1.17 | 2.32 | 2.76 |
| Number average width, Wa, μm | 23.5 | 16.8 | 25.0 |

These characteristics make it possible to consider peroxide cellulose from hemp fire to be a fibrous semi-finished product, suitable for use in composition with other fibrous semi-finished products in the production of many mass types of paper and cardboard products.

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