The paper-forming properties of hemp fire peroxide cellulose in combination with wood sulphate cellulose

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Abstract. Hemp fire (Cannabis sativa) was delignified with the reaction mix "acetic acid - hydrogen peroxide - sulfuric acid catalyst - water" under sulfuric acid concentration of 0.45%, liquid module of 6, and temperature of 85 °C. The cellulose was ground to 34 ... 36°SHR and mixed in different ratios in compliance with the simplex-centroid experimental design with bleached sulfate softwood and hardwood pulp. The influence of the mixed composition formulations on the main strength properties of paper casts has been studied. It has been concluded that technical cellulose obtained from hemp fire applying this method, can be used for paper products manufacturing in combination with sulphate cellulose from coniferous and deciduous wood.

1. Introduction
It is known that wood fibers of a tubular structure contribute to the production of puffy types of paper with increased absorbency, while from the tape structure fibers - thick and durable paper is usually obtained. Hardwood cellulose typically provides paper with opacity, bulk, breathability and absorbency, while softwood cellulose gives paper a greater transparency, density, and tear resistance.

Due to its significant resistance to water loss, cellulose from culm is difficult to use on high-speed paper machines. Typically, such cellulose is utilized in combination with other semi-finished products. In particular, there are recommendations to employ a combination of straw and softwood sulphate cellulose in cases where a mixture of softwood sulphate and hardwood cellulose is usually used [1].

As already reported, hemp fire might be one of the raw materials of plant raw resources for cellulose production. It accounts for over 65% of the hemp straw mass. In terms of technological properties, cellulose from hemp fire is similar to the properties of fibrous semi-finished products from straw of other cereals and from deciduous wood. In the production of cellulose, fibrous semi-finished products from hemp fire, methods of oxidative delignification in aqueous-organic solvents, developed for the wood and straw raw materials processing can be applied [2-9]. This opportunity opens up prospects for improving the technology in terms of cooking liquor preparation and chemical recovery from waste liquor. At the same time, the positive aspects of the process remain as follows: selectivity, low temperature and atmospheric pressure, absence of harmful substances in wastewater and gas emissions ("green" technology).

2. Methods
The article presents the results of studying the properties of paper casts from wood sulphate cellulose, peroxide cellulose from hemp fire and from mixtures of these semi-finished products in different ratios.
Used in the experiments commercial sulfate bleached cellulose from coniferous wood grade HB-0 and deciduous wood grade LS-0 had been produced at JSC "ILIM Group" (Bratsk, RF).

Peroxide cellulose from the shive part of the industrial hemp stalks (Cannabis brand "Surskaya") was made in laboratory conditions. Straw (crust) crushed into lengths of 10 ... 20 mm was treated with a delignifying solution "acetic acid - hydrogen peroxide - sulfuric acid - water". Cooking conditions: concentration of acetic acid 6 g-mol/l; hydrogen peroxide concentration 4 g-mol/l; sulfuric acid concentration 0.45%; liquid module 6; isothermal cooking, temperature 85 ° C, duration 135 minutes. After washing, the pulp was dried in air at room temperature. The yield of technical cellulose amounted to 52.2%.

Prior to mass grinding, all cellulose samples were soaked in water for 30 minutes and dispersed in a disintegrator. Cellulose grinding of each type was carried out separately in a CGA mill to a fineness of 34 ... 36 SHR. The prepared fibrous semi-finished products were mixed in different ratios according to the simplex-centroid design of the experiment [10] (table 1). Paper casts with a mass of 75 g / m² were made on a Rapid-Kothen sheet former. The strength properties of the castings were determined by standard methods. The variable factors were the mass fractions \( X \) of semi-finished products of each type in castings:

- \( X_1 \) - softwood sulphate cellulose;
- \( X_2 \) - hardwood sulphate cellulose;
- \( X_3 \) - peroxide straw cellulose.

These variables were varied in accordance with the pattern of a simplex-centroid experiment design with duplication and randomization (table 1) [9]. The castings properties were characterized by the following indicators:

- \( Y_1 \) - density, g/cc;
- \( Y_2 \) - tensile strength, breaking length, m;
- \( Y_3 \) - elongation to the moment of failure, %;
- \( Y_4 \) - resistance to fracture, number of double kinks (d.f);
- \( Y_5 \) - punching shear resistance, kPa;
- \( Y_6 \) - tear resistance, mN.

All experiments were repeated twice. The experimental results (average values of two realizations) are shown in Table 1; the statistical characteristics of the observation area are given in Table 2.

3. Results

Mathematical processing of the results was performed using the Statgraphics Centurion software package. The dependence of each output parameter on variable factors was approximated by polynomial second-order regression equations [10]:

\[
\hat{Y} = b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3.
\]

Regression coefficients and statistical characteristics of the equations are shown in Table 3. Regression equations were used to graphically represent the results in the form of three-dimensional response surfaces [10].

**Table 1.** Mass fractions of fibrous semi-finished products \( X \) and properties of paper castings \( Y \).

| Mass fractions of components | Properties of paper castings |
|------------------------------|-----------------------------|
| \( X_1 \) | \( X_2 \) | \( X_3 \) | \( Y_1 \) (g/cc) | \( Y_2 \) (m) | \( Y_3 \) (%) | \( Y_4 \) (b.f.) | \( Y_5 \) (kPa) | \( Y_6 \) (mH) |
|------------------------------|-----------------------------|
|------------------------------|-----------------------------|
|------------------------------|-----------------------------|
The castings density practically does not depend on their composition as indicated by the observation results given in table 1 (column $Y_1$) and a very small value of the variation coefficient of 1.28% (table 2).

Table 2. Statistical characteristics of observation results.

| Index                  | $Y_1$ | $Y_2$ | $Y_3$ | $Y_4$ | $Y_5$ | $Y_6$ |
|------------------------|-------|-------|-------|-------|-------|-------|
| Sample volume          | 14    | 14    | 14    | 14    | 14    | 14    |
| Average value          | 0.640 | 7542  | 2.54  | 63.7  | 279.1 | 522.0 |
| Standard deviation     | 0.0022| 970   | 0.392 | 65.3  | 40.7  | 191.8 |
| Variation coefficient, % | 1.28 | 12.8  | 15.4  | 102.4 | 14.6  | 37.1  |
| Minimum                | 0.629 | 5758  | 2.00  | 1     | 228   | 182.0 |
| Maximum                | 0.653 | 8965  | 3.26  | 240   | 359   | 750.0 |

In contrast, the tensile strength of castings (breaking length) depends significantly on the ratio of fibrous components (Figure 1a). It is characteristic that the most durable casts are obtained from hemp cellulose; this property is well known and was used earlier in the production of the most durable and strong types of paper. The introduction of hardwood sulfate cellulose into the composition of castings is accompanied by a decrease in breaking length, which corresponds to a priori information. No noticeable phenomena of synergism and antagonism of properties were noted.

Table 3. Coefficients and statistical characteristics of the regression equations.

| Coefficients $b_{ij}$ and statistical characteristics | Output parameters |
|-------------------------------------------------------|-------------------|
| $Y_1$ | $Y_2$ | $Y_3$ | $Y_4$ | $Y_5$ | $Y_6$ |
|-------|-------|-------|-------|-------|-------|
| $b_1$ | 0.645 | 7257  | 3.24  | 189.7 | 355   | 735   |
| $b_2$ | 0.650 | 6340  | 2.43  | 25.7  | 232   | 636   |
| $b_3$ | 0.644 | 8679  | 2.03  | -0.33 | 253   | 184   |
| $b_{12}$ | -0.044 | -841  | -0.003 | -81.4 | -145  | 143   |
| $b_{13}$ | -0.015 | 839   | -1.12 | -107.4 | -17   | 164   |
| $b_{23}$ | -0.045 | 2267  | 0.54  | 34.6  | 140   | -246  |
| Determination coefficient, % | 32.2 | 72.5  | 91.6  | 86.2  | 89.4  | 99.6  |
| Standard error of prediction | 0.001 | 647   | 0.144 | 30.9  | 16.9  | 16.3  |
Figure 1. Dependence of tensile strength (breaking length) $Y_2$ and elongation to the moment of failure $Y_3$ of castings on the composition.

Elongation of specimens under tension to the breaking point (Figure 1b) is highly dependent on the fibers length. The highest elongation is demonstrated by softwood cellulose castings. With an increase in the proportion of short-fiber raw materials, the value of this indicator almost additively reduces. Likewise, the breaking resistance of paper castings depends on the length of cellulose fibers (Figure 2a). Comparison of the response surfaces in Figures 1b and 2a proves their symbasis. There is usually a linear correlation between the tear resistance and punching shear strength of the paper. In the case under discussion, an abnormal decrease in punching resistance with an increase in the proportion of hemp cellulose in the composition was unexpected (Figure 2b). Obviously, this phenomenon requires a more detailed study. The dependence of the castings resistance to tearing on the ratio of the mixture components (Figure 3) generally corresponds to the a priori information: the highest indicator was observed in softwood sulphate cellulose, close to it - hardwood sulphate cellulose. The inclusion of hemp peroxide cellulose in the composition markedly reduces the tear resistance of the castings.

Figure 2. Dependence of casting resistance to fracture $Y_4$ and punching shear $Y_5$ on the composition.
4. Conclusion
Technical cellulose obtained from hemp fire by the oxidative peroxide method can be used for paper products manufacturing in combination with sulphate cellulose from softwood and deciduous wood.

Acknowledgement
Studies were carried out in the laboratory “Deep processing of plant raw materials” of Reshetnev Siberian State University of science and technology. This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the framework of State Assignment of the “Technology and equipment for the chemical processing of biomass of plant raw materials” project (FEFE-2020-0016).

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Figure 3. Dependence of tensile strength of Y6 castings on the composition.
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