Resource potential and properties of cellulose obtained from tree willow wood

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Abstract. Willow trees occupy an important place in the dendroflora of the middle zone of the European part of Russia due to their extensive species diversity and large intrapopulation variability. In the Arkhangelsk Region and other regions in the North-East of Russia, abandoned agricultural land (post-agrogenic land) can serve as places for the creation of willow plantations. Currently, such lands are actively overgrown with various tree species, usually of low quality and not of significant commercial interest. The creation of plantations will allows by a short logging turnover to obtain stable wood yields and organize a highly profitable economy on unused land. There is no any information on the willow cultivation in Russia. Willows of the Salix genus grow everywhere and there are more than 130 species. About 30 of these species are found in the Arkhangelsk region. Based on the data of the State forest register of the North Taiga forest region, the tree willow occupies an area of 5.3 thousand hectares. Land with strong moisture is widespread in the Arkhangelsk region. Willow grows well in these areas. Due to this, as well as the good strength of the pulpwillow wood can be widely used in pulp and paper production.

1. Introduction

Since ancient times, willow has been widely used in various sectors of the national economy. Wood, leaves, bark and willow roots are excellent raw materials for processing. In many countries, including Russia, there is an interest in cultivation of fast-growing willow as a raw material for pulp and paper industry and for bioenergy. The experience in fast-growing tree species cultivation with a short growing period (cutting turnover) allows to get a current wood increment up to 25 m³ / ha per year. In the United States, there are about 23 thousand hectares of such plantations, which produce up to 20 tons / ha of dry matter per year, some of it is used in the pulp and paper industry and the rest as an energy resource. In Europe, the area of such plantings with a short cutting turnover exceeds 1 million hectares [1, 2]. The use of fast-growing willow plantations for bioenergy purposes is advisable with a wood yield of at least 9-10 tons /ha of dry biomass per year. It is established that such parameters can be obtained only with the use of specially introduced willow clones (varieties) and with the use of high-tech industrial technology [1, 2].
2. Methods and Materials
For the research, samples were taken from the tree trunks of the northern Willow (Salix borealis Fries.) and the Three-Stamen Willow (Salix triandra L.) and their hybrids without separation by species composition. The plantings were formed on former agricultural land.

In a laboratory scale the series of cookings of hand-prepared willow chips with industrial white spent liquor were carried out. The cookings were performed on an automated autoclave system CAS 420, designed to simulate in the laboratory the sulfite and sulfate processes of delignification of cellulose-containing raw materials. The weight of wood chips for one cooking was 70 g of raw materials. The degree of delignification of cellulose materials, i.e. the Kappa number, in the samples before and after the bleaching steps was determined according to GOST 10070-74 (ISO 302-81) “Cellulose and semi-cellulose” [3].

To determine the samples fractional composition of bleached and unbleached cellulose by fiber, the Fiber Tester device was used, which allows to perform an extended analysis of the properties of cellulose fibers. The measurement principle is based on scanning photos of a suspension of fibers pumped through a measuring cell. Images are processed using the program. The following parameters are included in the report by default:
- length, average value;
- width, average value;
- form, i.e. the quotient of the projection of the length by the actual length;
- triflcontent-expressed as the percentage of fibers shorter than 0.2 mm relative to the number of fibers longer than 0.2 mm;
- roughness, i.e. the weight of the fiber per unit length, for this purpose, the weight of the hitch on the dry fiber must be known.

To determine the standard parameters of mechanical strength in the laboratory, the samples weighing 75 g/m² were made. The pulp samples were ground in a “Jokro Mill” centrifugal milling machine (CRA). The production of laboratory samples was carried out on the “Rapid-Köthen” system sheet-draining machine in accordance with GOST 14363.4-89 (Cellulose. The method of preparing samples for physical and mechanical tests) [4], the grinding process was controlled by determining the degree of mass grinding. The quality indicators of laboratory samples were determined by standard methods: the sample thickness according to GOST 27015-86 (Paper and cardboard. Thickness determination, density and specific volume) [5] was done on the TMB-5-A device with a digital recording unit; tensile strength and elongation in accordance with GOST 13525.1–79 (Semi-finished fiber products, paper and cardboard). Determination of the tensile strength and elongation [6] was done on the device Test system 105; resistance to penetration according to GOST 13525.8-86 (Semi-finished fiber products, paper and cardboard). Determination of the pressure was done on the Lorentzen&Wettre Bursting device [7]. Determination of tear resistance was done in accordance with GOST 13525.3-97 (ISO 1974-90) [8]. All samples before testing were conditioned according to GOST 13523-78 (Semi-finished fiber products, paper and cardboard. Sample conditioning method) [9]. The determination of the deformability characteristics was carried out by testing the samples on a laboratory test complex, including a Test-system 101 bursting machine.

The "σ-ε" dependence curve was obtained by processing the "load-elongation" indicator diagram ("P-Δl") during static tensile tests on breaking machines equipped with a device for registering changes in the load and deformation of the sample during the test. When applying a tensile load in a capillary-porous material (samples of technical pulp, paper and cardboard), several stages of deformation development are observed, preceding the final destruction (figure 1): 0-1 – elastic zone; 1-2 – zone of viscoelastic deformations; 2-3 – zone of pre-destruction, deformation in it occurs under conditions of intensification of the destruction processes and completes with the separation of the sample into parts; Э-point, averagely characterizing the slow-elastic component of the viscoelastic zone.
Each test sample is characterized by a length (l), a width (b), and a thickness (d) averaged over measurements at several points. After testing each sample the information from the machine Test System 101 about the sample data and test results is transmitted via the RS-232 interface to the PC. One can see the curves for each of the tested parallel samples; all curves on a single graph; the elimination of drop-down points and repeated tests. At mathematical processing of experimental curves "load-elongation" obtained during parallel tests, the following procedures are performed: smoothing of the initial curves by the moving average method; construction of the average curve; automatic selection of the initial and final rectilinear sections; calculation of the elastic modulus of the initial (E1) and in the area of pre-fracture (E2); as well as determination of the characteristic points of the "stress-strain" relationship: the elastic limit (1); the effective point (E); the point of the beginning of plastic deformations (P); the point of the beginning of additional drawing (B); the point of destruction of the sample (P) (figure 2).

At each characteristic point the following characteristics are calculated:
1) force (P), N; elongation $\Delta l$, mm;
2) resistance ($s$), MPa
\[ \sigma = \frac{P}{b \delta} \] (1)
deformation \((\varepsilon), \%\)

\[ \varepsilon = \frac{\Delta l}{l} \] (2)
performance \((A), \text{MJ}\)

\[ A = \int_{0}^{\Delta} P \, dl \] (3)
current modulus of elasticity \((E_t), \text{MPa}\)

\[ E_t = \frac{d\sigma}{d\varepsilon} \] (4)
modulus of total deformation \((E_{od}), \text{MPa}\)

\[ E_{od} = \frac{\sigma}{\varepsilon} \] (5)
the stress relaxation time \((n), \text{sec}\), is calculated by solving the equation by numerical methods

\[ \sigma(n) = E_2 \varepsilon + v \cdot n \cdot (E_1 - E_2) \left(1 - e^{vn}\right) \] (6)
The results of estimations are presented as tables and charts and displayed on PC monitors with possibility of print output according user requirements.

Besides during the mathematical treatment the tensile stiffness index is calculated using the formula:

\[ S_t = E \delta = \frac{P}{b \varepsilon} \] (7)
where, \(S_t\) – tensile strength, \(N / m\); \(E\) – modulus of elasticity, \(N / m^2\); \(\delta\) – sample thickness, \(m\); \(P\) – power, \(N\); \(b\) – width, \(m\); \(\varepsilon\) – deformation, \(\%\).

3. Results and Discussion
For laboratory tests, willow wood was cooked. To reproduce the results of the experiment, the samples were placed in 4 parallel autoclaves. The selection of the cooking procedure was based on the deciduous wood procedures (aspen and birch), but with an increased time in the impregnation zones and lower cooking zone, taking into account the peculiarities of manual preparation of wood chips.

Figures in table 1 demonstrates the cooking process, which took place according to the following mode:

**Table 1.** Cooking process mode.

| Time of the mass presence in the zones, min |
|------------------------------------------|
| - impregnation zone                      | 50  |
| - upper cooking zone                     | 45  |
| - lower cooking zone                     | 75  |
| Consumption of active alkali, % of the weight of completely dry wood | 21  |
Cooking hydromodule

| Cooking zone temperature, ºC | 3.0 |
|-------------------------------|-----|
| -impregnation zone            | 115 |
| -upper brewing zone           | 154 |
| - lower brewing zone          | 160 |

Pulp indicators\(^a\)

| -output, %                  | 43  |
| -Kappa’s number             | 18.2|

\(^a\)averaged results for 4 parallel autoclaves

The resulting cellulose is characterized by a low level of sorted cellulose with a normal degree of delignification (Kappa’s numbers are 18 ... 20).

Then, the structural and dimensional characteristics of the fibers were determined on the L&W Fiber Tester. The results are given in table 2 and figure 3.

![Figure 3. The results of the mass analysis on the automatic fiber analyzer L&W Fiber Tester.](image)

This type of fiber is characterized by a lower length, compared to aspen and birch wood. To determine the mechanical strength indicators in the laboratory according to GOST, the samples weighing – 75 g (1 m\(^2\)) were made for the possibility of comparing their properties with the properties of deciduous bleached sulfate cellulose from aspen wood (GOST 14940-96 Bleached sulfate cellulose from deciduous wood (aspen). Specifications) [10] and deciduous bleached sulfate cellulose from a mixture of species (GOST 28172-89 Bleached sulfate cellulose from a mixture of deciduous wood. Technical specifications) [11]. It should be noted that the level of mechanical strength indicators of the willow pulp sample obtained corresponds to the level of cellulose indicators from a mixture of birch and aspen wood.

The mechanical strength indicators of the samples and the GOST data for comparison are presented in table 3.
Table 2. Structural and dimensional characteristics of the presented samples.

| Sample Name | Average length, mm | Average width, microns | Average Formfactor, % | Roughness | Average break angle | Deciduous Unbleached Sulphate Cellulose | Deciduous Bleached Sulphate Cellulose | Willow | | Number of large fractures per mm | Number of fractures per fiber | Number of large fractures per fiber | Average fracture index |
|-------------|-------------------|------------------------|-----------------------|----------|---------------------|----------------------------------------|---------------------------------|--------|---|----------------|---------------------|---------------------|---------------------|
| Birch/aspen | 0.960             | 23.4                   | 91.9                  | 93.1     | 45.2                | 0.074                                  | 0.342                          | 0.065  | 0.937        |                      |                      |                      |
| Birch/aspen | 0.926             | 22.8                   | 89.5                  | 76.1     | 49.1                | 0.165                                  | 0.530                          | 0.139  | 1.562        |                      |                      |                      |
| Willow      | 0.526             | 19.3                   | 92.6                  | 80.4     | 41.3                | 0.337                                  | 0.058                          | 0.178  | 0.031        |                      |                      |                      |

Table 3. Comparison of quality indicators of laboratory samples and characteristics of deciduous bleached sulfate cellulose (GOST).

| Sample | Structural and dimensional characteristics of paper | Strength indicators | Deformability characteristics |
|--------|----------------------------------------------------|----------------------|-------------------------------|
|        | White, % ISO | Average sample thickness, (δ) mm | Density, (d) g/cm³ | Breaking length, (L) m | Push-through resistance, (P), KPa | Fracture strength at multiple bends(N) | Tear resistance, (R), mJ | Tensile strength(S), kHm | Destructive Work (TEA), J/m2 | Destructive stress, (σ), MPa | Destructive deformation, (ε), % |
| GOST 14940-96 | 82 - 86 | - | - | 6200 - 7800 | - | - | - | - | - | - |
| GOST 28172-89 | 80 - 89 | - | - | 6000 and > | 300 (not standardized) | 300 (not standardized) | - | - | - | - |
| Willow | - | 91.2 | 0.763 | 8000 | 320 | - | 470 | 487.6 | 112.04 | 60.92 | 2.94 |

4. Conclusions
As a result, we can draw the following conclusions:
- willow tree cellulose is characterized by low output of sorted pulp with a normal degree of delignification (Kappa number 18...20).
- the element which identify the wood of a willow tree is the network structure on the fiber surface.
- the wood of the willow tree has revealed a large amount of surface resin. extractive substances.
- the structural and dimensional characteristics of the willow tree fibers are characterized by a lower length. compared to the aspen and birchwood.
the level of mechanical strength indicators of the obtained willow pulp sample corresponds to the level of pulp indicators from mixture of birch and aspen wood. that indicates the possibility of using the studied raw material – willow wood – for low-tonnage production of papers for various purposes.

- the resource potential of the tree willow cannot provide a stable supply of raw materials. at the same time. the creation of plantations from fast-growing willow clones. following the example of foreign enterprises. will ensure the stable operation of a small enterprise.

References
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[7] GOST 13525.8-86 (Semi-finished fiber products. paper and cardboard. Method for determining the pressure resistance (with Change No 1))
[8] GOST 13525.3-97 (ISO 1974-90)
[9] GOST 13523-78 (Semi-finished fiber products. paper and cardboard. Sample conditioning method (with Changes № 1. 2. 3))
[10] GOST 14940-96 Bleached sulfate cellulose from deciduous wood (aspen). Technical conditions
[11] GOST 28172-89 Bleached sulfate cellulose from a mixture of hardwoods. Technical conditions