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SOFTWOOD KRAFT PULPING WITH POLYACRYLONITRILE FIBERS

This article presents data on the polyacrylonitrile (PAN) effect upon the elastoplastic and mechanical properties of kraft pulp (unbleached softwood sulphate pulp). In the present research the possibility of obtaining in vitro sulphate pulp together with reinforcing agent of polyacrylonitrile was studied. PAN consumption was varied from 0.05 to 0.20 wt % based on the dry weight of the chips. Micrographs of cellulose samples showed that PAN was distributed on the surface of cellulose fibers in the form of fine spherical shape particles and made it possible to increase the strength of kraft pulp by 15−18% (breaking length was increased from 8,480 up to 9,990 m, breaking strength − from 93.8 up to 109.5 N, energy absorption at break − from 76.0 up to 92.6 J/m^2 and folding endurance − from 7 up to 13 double folds).

Introduction. In accordance with GOST 11208 there are four brands of sulfate unbleached pulp produced from softwoods: HC-1 – for making high-strength technical and packaging paper, wet-strength base paper for making abrasive cloth, telephone-cable paper, cartridge paper and waxed paper; HC-2 – for making bag paper, opaque paper, paper for textile spools and tapers, for gummed tape base paper, for top liner cardboard, boxboard, water-resistant board, waterproof upholstery covering board, gasket board, cardboard for footwear and other types of paper and cardboard; HC-3 – for making wet-strength paper, base paper for the inner layers of laminated decorative plastic, cardboard end caps of filter elements. It is known that all the above mentioned cellulose brands should have high strength indexes (breaking length should not be less than 7800 m, absolute bursting strength should not be less than 470 kPa and absolute tear resistance should not be less than 630 mN) [1]. However, the only production of high pulp brand mark HC-1 is difficult to reach. Pulp is assigned to a low quality grade if strength characteristics are lower than standard specifications.

Main part. In the process of kraft pulping wood chips are treated by cooking liquor, the components of which interact with lignin, extractives, hemicelluloses and cellulose itself partially destroying them. The main part of wood components (45–55 wt %) is transferred to the cooking liquor and cellulose fibers structure remains intact. Consequently the high-strength pulp consisting of cellulose, residual amount of lignin and other components of the original wood is produced.

Currently, there are several techniques of kraft pulping process and the two main are batch pulping and continuous pulping. Batch pulping may be prolonged (8 h), accelerated (5 h) and rapid – "quick cook" process (4 h). The main factors of the pulping process, which affect the yield and the pulp quality, are temperature and pressure in a digester, cooking time, *H*-factor, the concentration of active reagents in the cooking liquor (pulping liquor) and pulpchips parameters. As is known, alkaline medium (due to the presence of NaOH and Na_2S) and high temperature created in a digester during kraft process can lead to alkali hydrolysis of polymer materials. Sulphate pulping technique together with polyacrylonitrile (PAN) fibers (Fig. 1) and the possibility of getting strengthening agent from PAN in the pulp structure was of scientific interest. Study of the effect of this component on the pulp and black liquor properties are also of scientific interest.

Fig. 1. Staple fibers from PAN

The purpose of the research was to study the effect of polyacrylonitrile fibers on the yield and quality of softwood pulp received during kraft pulping process.

The objectives of the study were as follows:

– to carry out the softwood kraft pulping in vitro with PAN-fibers;

– to keep accurate control of pulping profiles ($T = f(\tau)$ and $P = f(\tau)$);

– to compare the properties of cellulose received in the softwood kraft pulping process with PAN-fibers to the properties of kraft cellulose received also in vitro without PAN-fibers and to the data of GOST 11208 "Softwood sulphate unbleached pulp".

Pulpchips and all the necessary reagents were prepared at the beginning of research in the laboratory of the Department of chemical processing of wood. Raw material and reagent's characteristics are shown in Table 1.

Table 1

Pulp-making materials and pulping reagents charge

Parameter	Value
Wood species	Pine
Felling period	09.2012
Wet chips charge, g	300.0
Chip moisture, wt %	31.2
Oven-dry chips charge, g	206.0
Chips dryness coefficient	0.687
Chips moisture content, g	94.0
Pulping liquor charge at a given liquor-to-wood ratio, cm^3:	
– white	1000
– black	0
Liquor-to-wood ratio, cm^3/g	5.3
Total active alkali charge for pulping, wt %	50.4
Degree of liquor sulfidity, wt %	19.0
Active alkali (AA), g Na_2O/l	145.7
Effective alkali (EA), g Na_2O/l	103.8
Sulfidity, g Na_2O/l	19.8
H-factor in cooking stage	3250
Time of start cooking, h	8^{00}
Time of end cooking, h	12^{00}
Cooking period at 175°C, h	2^{10}
Total cooking time, h	4^{00}

Chips' processing by white pulping liquor was performed in a laboratory autoclave (Fig. 2) in accordance with temperature profile of a quick kraft pulping. The amount of the polyacrylonitrile fibers input was changed from 0.05 to 0.2 wt % of oven-dry wood in increments of 0.05 wt %.

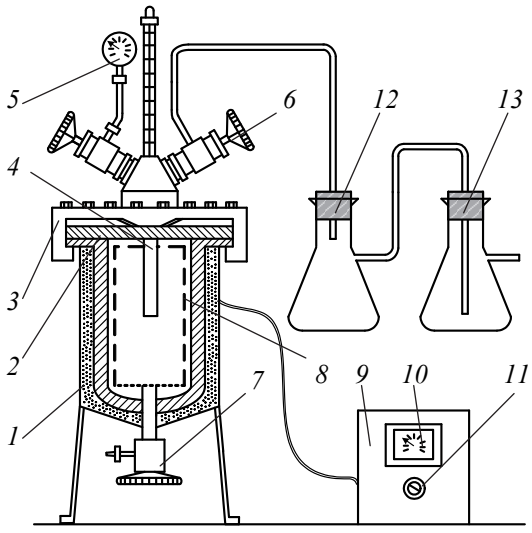


Fig. 2. Laboratory autoclave (digester) for chips cooking:
1 – cylindrical unit case; *2* – cover device; *3* – locking clamp; *4* – hopper; *5* – manometer; *6* – blow vent; *7* – liquor sampling valve; *8* – mesh sleeve; *9* – transformer; *10* – voltmeter; *11* – voltage regulator; *12* – wash tank; *13* – absorber

To compare the PAN-fibers influence on the kraft pulp properties the check softwood kraft pulping without PAN-fibers was performed. Thus, the total number of kraft cooks was five.

Reliefs out of the autoclave were performed during the pulping process using blow vent *6* in the time interval 60–120 min, in this case pressure rise inside the laboratory digester slowed down as is seen from the pulping profile (Fig. 3). Manometer *5* was used for pressure control. The temperature in the digester was regulated using a voltage regulator *11* and controlled by a mercury thermometer.

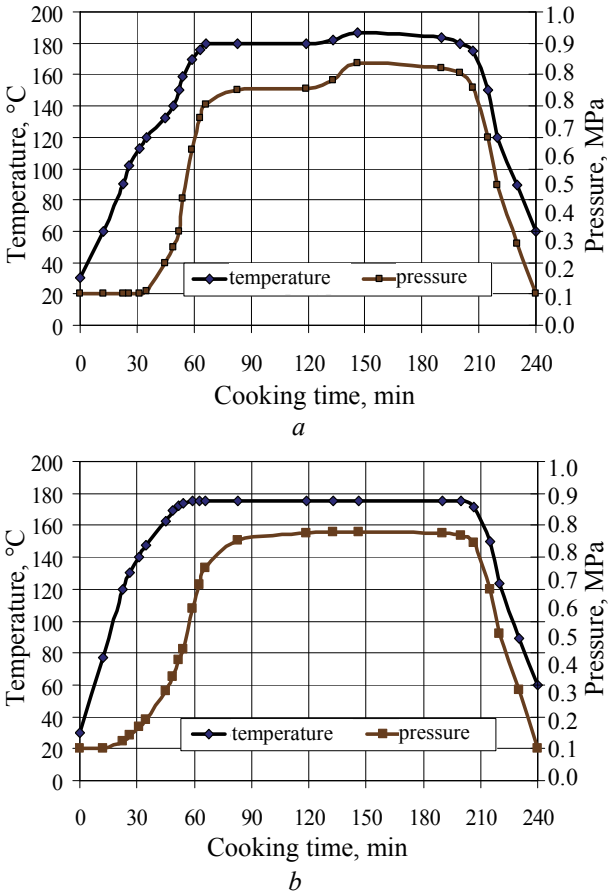


Fig. 3. Temperature profiles of quick kraft pulping: *a* – practical; *b* – theoretical

For ensuring the equal pulping conditions in the autoclave temperature and pressure were regulated in accordance with the pulping profile (Fig. 3, *a*). Naturally, it's impossible to attain an exact compliance of temperature and pressure of five kraft pulping processes with theoretical pulping temperature and pressure profile (Fig. 3, *b*). Therefore, it is necessary to adjust the *H*-factor, which equals to the surface area under the pulping temperature curve and is characterized by the chemical reaction constant (eq. 1).

$$H = \int_0^{\tau} K \cdot d\tau, \qquad (1)$$

where K – reaction constant; τ – time of kraft pulp cooking, h [2, 3].

After cooling the contents of the digester the remainder was separated into kraft pulp, concentrated kraft liquor (black liquor) and undercooked pulp (solid bits of wood chips that didn't separate into fibers during the washing process). Consequently it was obtained weak kraft liquor while pulp washing with water.

Thereupon in accordance with conventional methods the kraft pulp was tested for the degree of delignification (Kappa or permanganate number), the pulp yield and amount of the undercooked pulp depending on the polyacrylonitrile charges [4]. Also density and residual content of active components were determined in black liquor (Table 2).

It has been found that the degree of delignification (permanganate number) is in the range of specifications for unbleached softwood kraft pulp (22–32). Pulp yield was almost at the same level (about 25 wt %) for all cooking processes, indicating of sufficiently close regulation of pulping parameters, particularly of the *H*-factor.

It also disclosed that the higher the residual lignin content of the pulp (kappa number), the lower black liquor density.

At the next stage of research in vitro there were carried out the testing of the unbleached softwood kraft pulp quality according to the GOST 14363.4 "Pulp. Preparation of samples for physical and mechanical tests". Therein pulp sample with 6.5 wt % moisture content was slushed with 1500 cm^3 of water (dispersed into an aqueous suspension) in a laboratory disintegrator BM-3 for 8 min. Two portions of pulp slurry were obtained and transferred into the beater tank (Valley beater). Slurry density during pulp beating was 0.75 wt %. To achieve pulp slurry freeness equal to 60°ShR it was necessary to regulate the time of refining (23 min) as well as pressing of beating roll with a matching grooved stainless steel bedplate. Freeness was controlled by using Schopper-Reigler unit – SR-2 (ISO 5267-1, GOST 14363.4).

Pulp handsheets samples were manufactured from the refined pulp slurry, the samples being 75 ± 2 g/m^2 and 0.2 m in diameter. Pulp handsheets making was performed on a Rapid-Ketten sheet former (Ernst Haage Company, Germany) in accordance with the requirements of ISO 5269-2. For reproducibility of results the pulp handsheets samples were subjected to acclimatization for 24 h at temperature (20 ± 2)°C and relative air humidity (65 ± 5)%.

We studied the effect of PAN-consumption (from 0.05 up to 0.20 wt % of oven-dry wood) on different samples properties. Thus, strength properties were tested using for tension testing machine SE 062/064 L&W (GOST ISO 1924-1-96), folding endurance for Schopper double fold tester (ISO 5626), tear strength for Elmendorf tear strength tester (GOST 11208, ISO 1974), compressibility for Bendtsen tester SE 114 L&W (ISO 8791-2, GOST 30022.2) and whiteness for tester Kolir (ISO 2470, GOST 30113). All applied research techniques were consistent with the standards adopted in the pulp and paper industry. At least five samples were manufactured and tested at each experimental point. Fig. 4 shows graphs of depending strength properties and whiteness on polyacrylonitrile charge into the autoclave.

Table 2

Pulp and black liquor properties

Properties of pulp produced during softwood kraft pulping					
Parameter	PAN-consumption, wt % of oven-dry wood				
	0	0.05	0.10	0.15	0.20
Permanganate number (Kappa number), ml $KMnO_4$/g	18.8	19.9	31.4	21.2	26.9
Oven-dry undercooked pulp weight, g	4.79	1.27	0.25	2.59	3.19
Pulp yield, wt %	24.7	25.3	25.2	25.0	24.2
Tear resistance, kN/m	6.26	6.05	6.87	6.93	7.30
Compressibility, %	62.8	60.7	59.8	60.3	55.6
Properties of black liquor from softwood kraft pulping					
Density, kg/m^3	1175	1122	1106	1135	1118
Solids content, wt %	27,0	22.9	23.5	25.3	24.1
Active alkali (AA), g Na_2O/l	41.8	36.4	45.2	42.3	34.5
Effective alkali (EA), g Na_2O/l	15.2	18.2	8.2	15.3	12.5
Sulfidity, g Na_2O/l	5.1	6.2	5.1	6.3	5.5

As is seen from the graph curves (Fig. 4), the increase of PAN-consumption from 0.05 to 0.20 wt % of oven-dry wood results in the increase of tensile strength of pulp samples. Thus, tensile strength in the dry state increases from 93.8 up to 109.5 H, breaking length – from 8480 up to 9990 m, energy absorption at break – from 76.0 up to 92.6 J/m^2, folding endurance – from 7 up to 13 double folds. This may be due to the probable formation of a hydrolized polyacrylonitrile reinforcing agent during the kraft pulping process which contributes to rised elastoplastic properties. However, tear strength of pulp samples decreased from 1706 to 1270 mN and whiteness – from 31.5 to 21.8%.

The first one, i.e. tear strength decrease, may be due to a possible reduction in the quantity of free microfibrils on the cellulose fibers surface because of their binding to polyacrylonitrile particles and the reduction in the number of contacts between microfibrils in the *z*-direction of the sheet material. The second one, i.e. whiteness decrese, can occur as a result of interaction of ammonia released during the polyacrylonitrile fibers hydrolysis (Fig. 5) with lignin. Chromophore compounds absorbing light waves will form in this case [5–7].

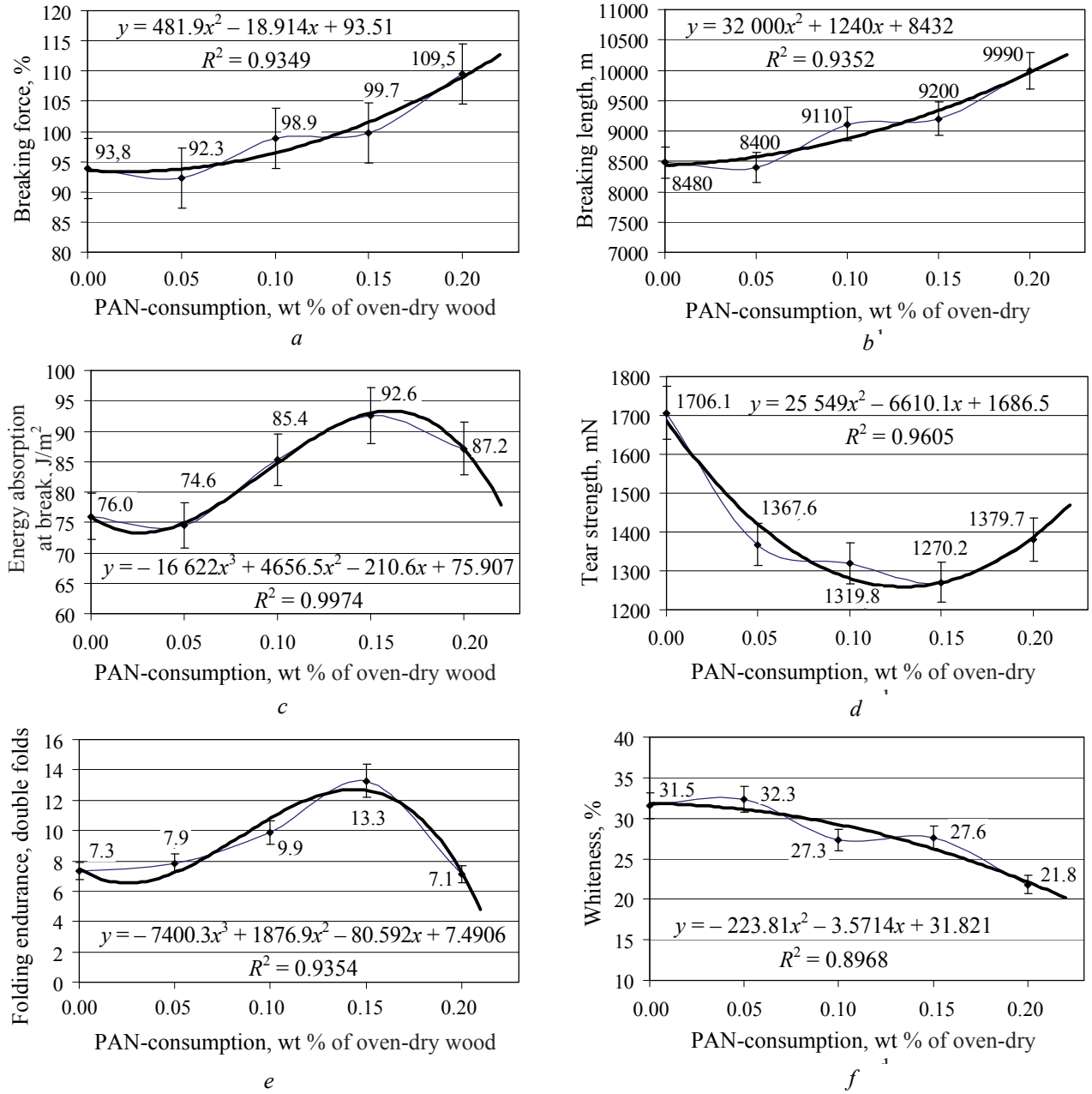


Fig. 4. PAN-consumption influence on the properties of unbleached softwood kraft pulp:
a – breaking force; *b* – breaking length; *c* – energy absorption at break;
d – tear strength; *e* – folding endurance; *f* – whiteness

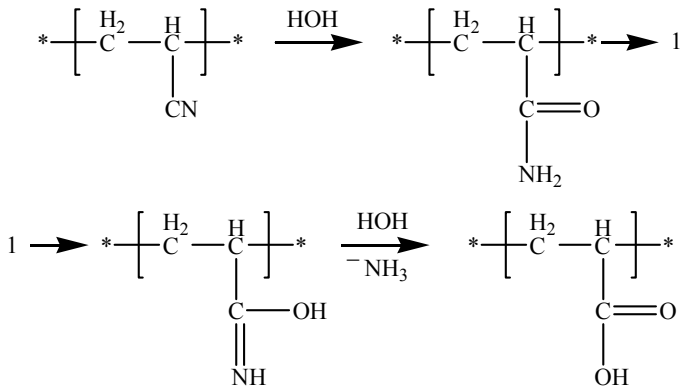
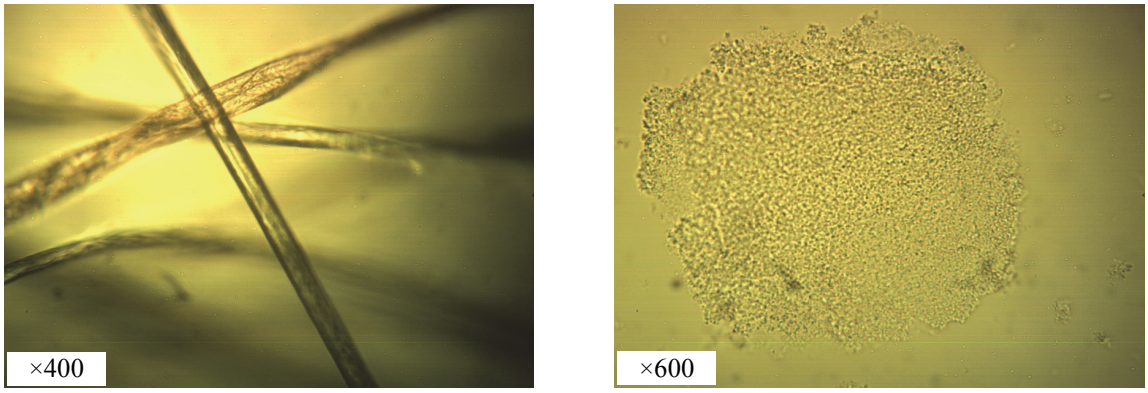


Fig. 5. Chemical reaction of polyacrylonitrile hydrolysis under alkali action

Literature data [8] indicate that in conditions of sulphate (kraft) pulping (high temperature and alkaline pH) polyacrylonitrile fibers are subjected to the following chemical changes: amidine groups are formed at temperature above 150°C and ammonia is released. Thus, the higher the proportion of carbo–xyl groups in the polymer macromolecule, the more intensive is the fibers staining in a yellow color.

By means of an optical microscope with a photographic attachment and installed software Optica Vision Pro 4.1 it has been ascertained that most part of original polyacrylonitrile fibers have a cylindrical shape and fiber diameter being 14–18 μm (Fig. 6, *a*).

Polyacrylonitrile fibers processed with white liquor in 60 min became partially destroyed and yellow, and in 120 min are completely converted into spherical PAN-particles (Fig. 6, *b*). These particles can coagulate to form coarse aggregates with a cross dimension of about 150 μm. The pulp having been washed off the black liquor, the micrograph (Fig. 7) revealed single fine particles 0.5–2.0 μm in diameter which are not linked to the cellulose fibers.



a *b*

Fig. 6. Micrographs of original polyacrylonitrile fibers (*a*) and fibers processed by cooking liquor at 160°C (*b*)

Fig. 7. Cellulose fibers and PAN-particles

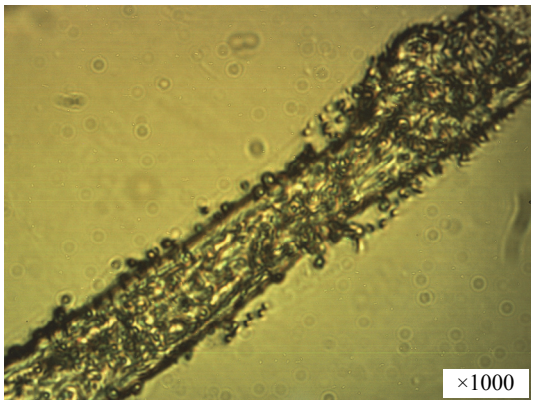


Fig. 8. Fine PAN-particles distributed on the surface of cellulose fibers

Table 3

Comparison of pulps quality parameters

Pulp property	Unbleached softwood sulphate pulp				
	Check sample (without PAN)	PAN-containing sample with consumption, wt % of oven-dry wood		GOST 11208	
		0,15	0,20	brand mark HC-1	brand mark HC-2
Permanganate number, ml $KMnO_4$/g	18,8	21,2	26,9	24,0–32,0	26,0–36,0
Breaking length, m	8480	9110	9990	9100	8700
Tear strength, mN, not more	1700	1270	1380	no less 830	no less 810

Interesting thing was that the pulp having been beaten in a laboratory beater was covered by the fine particles which were evenly distributed and held on the surface of cellulose fibers. Their retention may be due to the presence of microfibrils on the cellulose fibers surface that impart strength to the pulp fibers bound in a sheet (Fig. 8).

Comparing the properties of the kraft pulp (Table 3) obtained in the laboratory autoclave with the pulp obtained by the check softwood kraft pulping without PAN-fibers and the kraft pulp properties of the GOST standard specifications, it is obvious that PAN-fibers consumption even by 0.15 wt % of oven-dry wood imparts the pulp higher strength properties than those of the best kraft pulp (brand mark HC-1). The most prominent is the tear strength value reaching 1270 mN.

Conclusion. The results of the research have ascertained that:

– increase of the PAN-fibers consumption from 0.05 to 0.20 wt % of oven-dry wood results in the increase of pulp strength by 15–18% (breaking length raised from 8480 up to 9990 m, breaking force when dry – from 93.8 up to 109.5 N);

– whiteness of the pulp is reduced by 10%, which may be due to the formation of chromophoric compounds of residual lignin and ammonia released by polyacrylonitrile hydrolysis;

– influence of the PAN consumption on the cellulose yield and the amount of undercooked pulp is not revealed. These amounts depend largely on the *H*-factor, temperature and pressure in an autoclave, and the content of effective alkali in the white liquor;

– kraft pulp obtained by the cooking process with PAN-fibers is comparable by its properties to the best brand mark of kraft pulp HC-1 (up-to-date GOST 11208) and can be used in the composition of high-strength packaging paper and cardboard.

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