

# Processes of Wood Delignification and Cellulose Mercerization under Conditions of Shear Deformations

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## SYNOPSIS

The development of high-yielding and environmentally safe procedures of processing wood and cellulose constitutes a topical problem at present. To facilitate delignification of wood and mercerization of cellulose, a method was proposed, its principle of action based on the use of shear deformations combined with pressure. It is shown that under the conditions of plastic flow the fibrous high-yield semifinished product produced from birch wood features, due to its specific structure, shows better physicochemical properties. It is established that under the conditions of high pressure and shear deformations, when cellulose interacts with hard alkali, alkaline cellulose is produced, which is proved by X-ray analysis data. The depth of wood delignification and cellulose mercerization processes under the conditions of plastic flow does not depend on temperature, i.e., these processes are inactive.

## INTRODUCTION

Numerous works have been devoted to the study of chemical transformations that occur under the conditions of a joint effect of high pressure and shear deformations (e.g., see Refs. 1–4). Basic findings of these investigations are summed up in Ref. 5.

The specific features of these processes are the following: (1) When reactions take place in solid substances at high-pressure values (up to 50 kbar) in combination with shear deformations, certain phenomena occur. To explain these, an assumption must be made that the "diffusion coefficient" under these conditions will be  $10^5$  to  $10^{10}$  times the value usually observed in solid bodies. (2) Various chemical processes under such conditions are characterized by extremely low values of activation energy (roughly, 1.5 kcal/ppm).

We studied chemical transformations of natural solid-chain cellulose polymer and of a complex polymer complex (wood) that occur under the conditions of shear deformations. Here, two processes of high practical value were conducted: (1) inter-

action of wood with alkali for the purpose of partial elimination of lignin (delignification of wood) and of obtaining a high-yield fibrous semifinished product; and (2) treatment of cellulose with alkali to produce alkaline cellulose (cellulose mercerization).

Modern methods of obtaining high-yield fibrous semifinished products are based, mainly, on the properties of the wood lignin-carbohydrate complex to become mellow and to be transformed into a viscous-flowing state at temperatures beyond 100°C. The process of obtaining these semifinished products comprises two independent stages: The first stage is a preliminary chemical-thermohydrolytical treatment of chips to loosen the interfiber bonds, to destroy part of the bonds between lignin and the carbohydrate complex, and to soften lignin. It is noteworthy that while thermohydrolytical treatment of chips helps to preserve the length of natural fibers, reducing the content of fines and awn, the use of chemical reagents (sodium bisulfate, etc.) is aimed, above all, at transforming lignin into a state of high elasticity, which is prompted by a reduced temperature of vitrification under these conditions, and at loosening and partial destruction of interfiber bonds, while the length of fibers remains the same and their flexibility and plasticity are considerably enhanced.<sup>6</sup> The second stage of the process consists of the mill-

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ing of the chemically treated chips in disk mills, where the chips are mechanically separated into fibers.

Because of the continuous production of paper and board, the consumption of fibrous semifinished products constantly increases. Considering the present deficit of coniferous species, much attention must be paid to expanding the production of semifinished products from the processing of the wood of leaf-bearing species with a view to obtaining new types of mechanical mass of a different purpose with an improved combination of physicochemical properties.

The search for new environmentally sound reactions of cellulose modification represents a serious technological problem. Among the numerous cellulose derivatives, alkaline cellulose is one of the most common and widely used in the manufacture of viscose and of simple cellulose ethers.

In industry, alkaline cellulose is mercerized by treating sheet cellulose with 18% aqueous alkali having a hydraulic modulus of around 20 in view of the necessity to have a complete and uniform cellulose swell.<sup>7</sup>

For improving the production of fibrous semifinished products from leaf-bearing tree species and for improving cellulose mercerization, these processes were arranged in twin-screw continuous-action mixers, whose principle of action is based on the combination of pressure and shear deformation. The principle of combined effect on a solid material of pressure and shear deformation consists of the "pumping" of elastic energy into a solid body, accumulation of this energy with prior compression of the material, and deforming the body by shear.<sup>8</sup> To achieve this, it is sufficient to produce an insignificant shear effort so as to allow the formation of a new surface, in which case the process will develop at a low specific consumption of energy and at high speed. The obtained samples were studied, using different physicochemical methods.

## EXPERIMENTAL

### Study of Sample Structure by Raster Electronic Microscopy (REM) Method

The samples of a fibrous semifinished product for study were prepared by drying at a critical point.<sup>9</sup> This avoids distortions produced when the fibers are dried in the open air.

The fibers were dried at a critical point, using an HCP-2 instrument (Hitachi Critical Point Dryer).

The samples of fibers under study, subjected to prior dehydration in acetone, were placed in the instrument's chamber, where acetone was replaced by liquid carbon dioxide. After that, the temperature in the chamber was gradually increased to the critical value (for CO<sub>2</sub>  $t_{cr} = 31^{\circ}\text{C}$ ,  $P_{cr} = 7.14\text{ MPa}$ ), whereupon the sample was kept for 30 min at a pressure of 9.8 MPa. This done, the gas was gradually released from the chamber at 45°C. As soon as atmospheric pressure was achieved, the sample was cooled to 20°C and removed from the chamber. The cellulose fibers dried by this method were then slightly jilted and closely examined under a REM Hitachi S-405A.

### Identification of Physical and Mechanical Properties of Fibrous Semifinished Products

Physical and mechanical properties of obtained fibrous semifinished items were identified, using standard procedures.<sup>10</sup> The tests allowed us to determine the breaking length, elongation by tension, punching, fracture, and tear strength.

### Establishing Degree of Delignification of Fibrous Semifinished Products

To determine the content of residual lignin (Klasson's lignin), a sample of analyzed material ( $\sim 1\text{ g}$ ), its pitch extracted by a mixture of spirit with benzene or sulfuric ether, was first treated by 15 mL of 72% H<sub>2</sub>SO<sub>4</sub> for 2.5 h at 25°C. Then, the mixture of lignin and sulfuric acid was thinned by 200 mL of distilled water, boiled for 1 h, and filtered, using a Shott filter. Lignin was leached up to a neutral reaction and then was dried until its weight was constant. The obtained quantity of lignin was computed as a percentage of absolutely dry wood, with the aid of the following formula:

$$L = \frac{m}{G(100 - w)} \%$$

where  $m$  is the weight of residue on the filter;  $G$ , the weight of the air-dry sample, its pitch extracted; and  $w$ , the moisture of wood, its pitch extracted, %.

The content of lignin was computed on the basis of its acid-soluble fraction (ASF). The ASF value was determined spectrophotometrically, following the published procedure<sup>11</sup> and using the filtrate obtained after the treatment of the studied sample by 72% H<sub>2</sub>SO<sub>4</sub> with subsequent computation of the concentration in accordance with the Lambert-Buger-Bear's law.

The degree of delignification, which is the ratio of the mass of lignin, removed by delignification, to the absolutely dry mass of the original lignin, expressed in percent, was computed using the following formula:

$$D = \frac{L_0 - L}{L_0} \%$$

where  $L_0$  is the content of lignin in the original wood.

### Determining Degree of Substitution of Cellulose Hydroxyl Groups ( $\gamma$ )

A weight of alkaline cellulose ( $\sim 0.1$  g) was poured over with 30 mL of absolute isoamyl spirit. After some time, the alkaline cellulose was filtered using a Shott filter, then was replaced in a flask and was poured over with isoamyl spirit. The analysis was continued in a similar fashion until leaching water showed neutral reaction. After that, alkaline cellulose was leached with water and titrated by 0.1N  $H_2SO_4$ , first for phenolphthalein to the extent of decolorization, and then for Methyl Orange, and was dried at 105°C to constant weight.

On the basis of the quantity of  $H_2SO_4$  used for the titration of a particular cellulose weight, the degree of hydroxyl group substitution ( $\gamma$ ) was computed:

$$\gamma = \frac{162 \cdot 0.004 \cdot 100 \cdot [a - (c - a)]}{40 \cdot B}$$

where  $a$  is the quantity of mL 0.1N  $H_2SO_4$  used in titration for phenolphthaleine;  $c$ , the quantity of mL 0.1N  $H_2SO_4$  used in titration for phenolphthalein and Methyl Orange; and  $b$ , the absolutely dry weight.

### Degree of Cellulose Polymerization Determined

The degree of polymerization ( $DP$ ) of alkaline cellulose was determined by measuring the characteristic viscosity of cellulose solutions in the iron-vinicsodium complex (IVSC).

The IVSC solution was prepared by mixing gradually 500 mL of water with 209 g of  $Na_2(C_4H_4O_6) \cdot 2H_2O$  and 121 g of  $Fe(NO_3)_3$ . After that, the vessel was placed on ice and a solution of NaOH was added by portions (96 g of NaOH per 200 mL of water). Concentration of the pulp solution in IVSC was chosen, depending on the desired  $DP$ . Mean viscosity  $DP$  was computed by the following formula:

$$DP = \frac{[\eta]}{8 \cdot 14 \cdot 10^{-4}}$$

where  $[\eta]$  is the intrinsic viscosity.

### X-Ray Analysis of Cellulose Samples

Diffractiongrams of samples were obtained on a DPOH-3 diffractometer with a copper anticathode at 30 kV and 20 mA (Ni filter).

## RESULTS AND DISCUSSION

Birch wood chips were chosen to be the source material for the fibrous semifinished product. Prior to milling, the chips were treated for 30 min at 90–95°C with a sodium hydroxide solution amounting to 5–10% of absolutely dry wood or by a mixture of solutions of hydroxide and sodium sulfate at a hydromodulus of 5. This done, the treated chips were subjected to defibrination in a twin-screw mixer at 50°C. The choice of temperature was determined by the need to conduct the defibrination process at a temperature somewhat lower than lignin plasticization but beyond 20°C, because defibrination at 20°C causes destruction of fibers in a crosswise direction, whereas at temperatures over 120°C, lignin is transformed to a flowing state and is solidified when the mass is cooled afterward. As a result, a solid film is formed on the fibers, which reduces their flexibility and impairs the physicochemical parameters of the obtained fibrous mass.<sup>12</sup>

We studied the ultrastructure, physicochemical properties of the produced fibrous semifinished products; we also established the degree of delignification and yield.

When studying the structure of the fibers of the wood mass with the aid of a light microscope, it was found that under conditions of plastic flow the wood is separated not into bunches but into individual fibers, where their initial length remains unchanged. The structure of the fibers is highly peculiar, the fibers themselves having quite a different look compared with wood mass fibers produced by disk mills (refiners). Intensive exterior fibrillation of fiber surface was observed in the samples, especially when the timber was pretreated by a mixture of hydroxide and sodium sulfate. However, the nature of fibrillation is in sharp contrast with the commonly observed bandlike shape. Fibrils look like pointed burdock-shaped formations sitting on fiber surface.

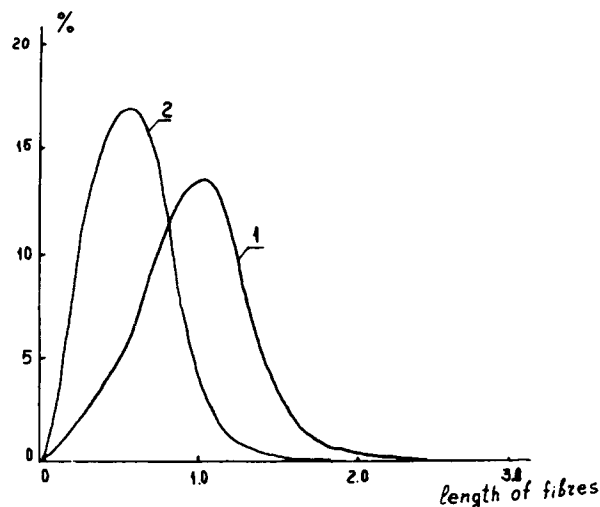
The obtained fibers have also been studied by the REM method. It was discovered that under the con-

ditions of plastic flow a folding structure is formed, which indicates that softening and deformations occur not just in the exterior part of the fiber but throughout its entire volume. As the outer layers get peeled off, internal layers are exposed and swell up in an alkaline medium, accompanied by nonuniform swelling of the fiber lengthwise. In REM, like in a light microscope, a burdock-shaped outer surface of the fiber was observed. A more intensive peeling off of outer layers occurs, when pretreatment is done by a mixture of sodium sulfite and sodium hydroxide. In this case, external fibrillation is far more pronounced, while internal fibrillation remains as strong as ever. The obtained data on the size and structure of fibers were confirmed by the results of research into fraction composition of the fibrous semifinished product.

We studied fractional composition of the obtained mass and established the mean length of the fiber. Figure 1 shows the mean-mass function of fiber-length distribution for two samples of a fibrous semifinished product derived from birch wood. It appears from Figure 1 that in the course of chemical treatment of the chips, using alkaline solution only, prior to milling, a mass with a shorter length of fiber (0.86 mm) is produced, unlike treatment by hydroxide and sodium sulfate (0.93 mm). The latter is due to the fact that sulfonation of lignin makes the fibers more flexible and elastic and less prone to destruction, when subjected to milling.

As it turned out, these facts are important for lignin strength characteristics, which was demonstrated in the study of its physical and mechanical properties.

Physical and mechanical properties of a fibrous semifinished product from birch wood are presented in Table I. It follows from the table that treatment of the chips by a sodium hydroxide solution produces a mass with a yield of 91.5% and notably low-strength characteristics. When thermohydrolytical treatment is done by a mixture of hydroxide and sodium sulfate, the yield of the mass goes down by 6.5%, which is associated with a more profound process of wood delignification (up to 35–40%). Paper-forming properties of the fibrous mass in this case are improved considerably. Although following the milling of the chips in a twin-screw mixer the mass had a low milling degree, it assumed the shape of a fairly hard sheet with good strength parameters. Particularly high was the value of separation resistance: around 700 mH. This also proves that in the process of milling in a twin-screw mixer the length of the fibers becomes slightly shorter. When using sodium sulfite in concentrations beyond 5% of ab-



**Figure 1** Mean-mass function of birch sample fiber-length distribution. (1) Thermohydrolytical treatment of chips by alkaline solution; initial concentration of NaOH, 10 wt % to absolutely dry wood. (2) Thermohydrolytical treatment of chips by a mixture of NaOH and  $\text{Na}_2\text{SO}_3$  solutions in 1 : 1 ratio; initial concentration, 10 wt % to absolutely dry wood.

solutely dry wood, the physical and mechanical properties of the fibrous semifinished product remain practically unchanged.

The formation of alkaline cellulose as a result of interaction between cellulose and solid alkali under the conditions of a combined effect of high pressure and shear deformations is of great scientific and practical interest.

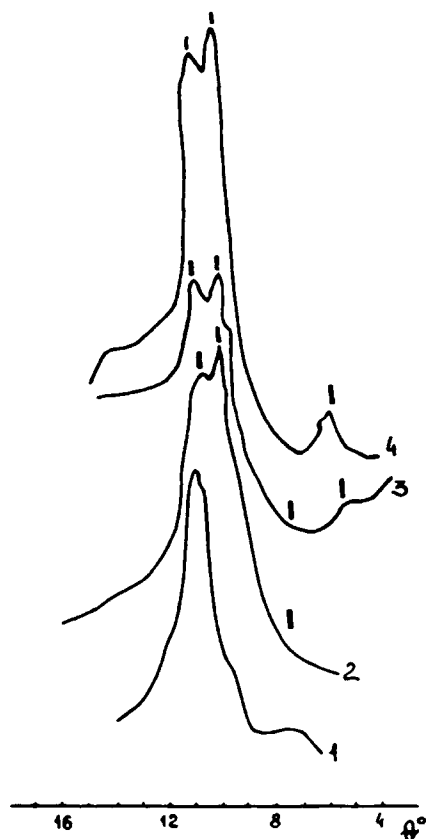
This reaction was studied in an apparatus of Bridgeman's anvil type, where the mixture of powdered cellulose and alkali was subjected to the pressure of 1 and 2 GPa and in twin-screw mixers of continuous action under plastic flow conditions.

It is a fact<sup>13</sup> that in the course of treatment of cellulose, having structural modifications of cellulose I (CI), by alkaline solutions and during subsequent regeneration of alkaline cellulose, there occurs a structural modification of the cellulose (CII) due to transformation of the cellulose lattice. The role of aqueous alkali boils down to alkali molecules getting in between cellulose fibers, which results in cellulose swelling and its structure being modified. Obviously, no such mechanism will be at work in the case of cellulose treatment by solid alkali.

However, X-ray analysis of the reaction mixture subjected to the effect of pressure and shear deformations [after leaching unreacted adsorbed alkali by isoamyl spirit and washing alkaline cellulose by water (regeneration)] revealed a substantial change

Table I Physicomechanical Properties of Chemicommechanical Mass (CMM) Produced from Birch Wood

Concentration of Reagents in Solution (% of Absolutely Dry Wood)	Yield of CMM from Wood (%)	Parameters after Twin-Screw Miller						Parameters after Final Milling of Mass to 130 mL Distillation					
		Distillation (mL)	Density (g/cm <sup>3</sup> )	Breaking Length (m)	Fracture Strength (No. Bends)	Resistance to Forcing Through (kPa)	Resistance to Shredding (mH)	Density (g/cm <sup>3</sup> )	Break Length (m)	Resistance to Fracture (number of double inflections)	Resistance to Forcing Through (kPa)	Resistance to Shredding (mH)	
10 NaOH	91.5	680	0.48	1850	2	40	340	0.58	4800	36	160	540	
10 NaOH													
5 Na <sub>2</sub> SO <sub>3</sub>	85.0	580	0.53	4450	57	166	700	0.71	8000	390	364	480	
10 NaOH													
10 Na <sub>2</sub> SO <sub>3</sub>	85.6	630	0.52	4200	49	168	740	0.71	8500	430	411	480	
10 NaOH													
15 Na <sub>2</sub> SO <sub>3</sub>	85.2	600	0.56	4400	54	164	620	0.77	8800	490	408	450	
Technical mass from leaf-bearing species of trees		130		3800	—	120	425	—	3800	—	120	425	



**Figure 2** X-ray photograph of regenerated alkaline cellulose obtained with varying initial content of alkali in mixture: (1) 10% of NaOH; (2) 20% of NaOH; (3) 32% of NaOH; (4) 60% of NaOH;  $P = 1$  GPa.

in diffraction. Here, the crystalline structure CI with characteristic peaks at  $\theta = 11^\circ$  and  $8^\circ$  is destroyed and crystalline structure CII is formed with specific reflexes at  $\theta = 10^\circ$  and  $6^\circ$ . Figure 2 shows X-ray pictures of regenerated alkaline cellulose obtained at different values of initial content of alkali in the mixture. The data in Figure 2 clearly show the transition from CI structure at 10% initial content of alkali to the well-defined structure of CII at 60% of alkali content. This fact agrees with the results of studying structural transitions of alkaline cellulose subjected to the treatment by alkaline solutions of different concentrations.<sup>13</sup>

Along with structural studies of alkaline cellulose, investigations were conducted to evaluate the degree of substitution of the cellulose hydroxyl groups ( $\gamma$ ). The  $\gamma$  value was found to depend on the initial content of alkali in the mixture and to grow in proportion with its increase, the maximum value reaching 60–70 at an initial concentration of alkali between 25 and 45%. A further increase of NaOH initial concentration leads to a certain drop of  $\gamma$ , which, ap-

parently, is due to cellulose hydroxyl groups being blocked by alkali. Variation of the pressure from 1 to 2 GPa practically has no effect on the values.

The varying degree of polymerization of regenerated alkaline cellulose showed that  $DP$  grows in proportion with the increase of NaOH concentration in the mixture. Obviously, the increase of initial content of alkali results in reduced destruction of cellulose chains under the conditions of shear deformations.

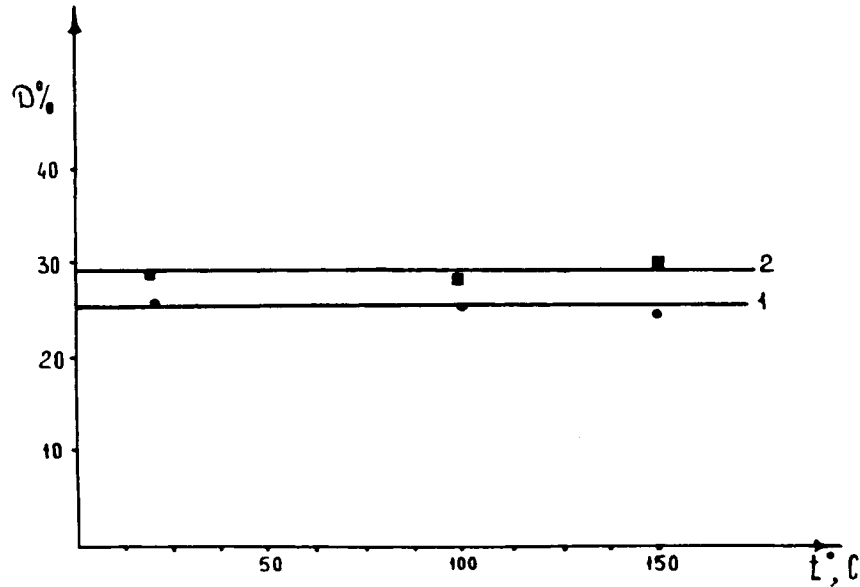
Reaction of mercerization was also conducted in twin-screw mixers of continuous action. In the course of mercerization, precrushed sheet cellulose was treated by alkaline solutions at a hydromodulus of 2–3.5. Depending on the initial alkali concentration and hydromodulus value, the produced alkaline cellulose can be different from the standpoint of hydroxyl groups substitution degree ( $\gamma$ ), extent of polymerization, and some other characteristics.

Thus, under the conditions of a shear deformation effect, alkaline cellulose with desired parameters can be produced with a hydromodulus several times lower compared with the traditional method.

We studied the effect of temperature on the processes of wood delignification and cellulose mercerization. It was demonstrated previously<sup>14</sup> that the effect of temperature on the process of wood delignification was adequately described in Arrhenius's general theory of chemical activation; thus, the values of activation energy were computed for alkaline cooking: 32 kcal/ppm and for sulfite cooking: 16 to 22 kcal/ppm. It was also shown that raising the temperature of the process by 10 doubles the rate of the delignification reaction.<sup>14</sup>

Figure 3 shows the temperature correlation between the degree of wood delignification under the conditions of shear deformation and at initial concentration of caustic soda, expressed in weight percent of absolutely dry wood within the temperature range of 20–150°C. As we can see from the data in Figure 3, the depth of the process does not depend on the temperature of reaction and is constant for the particular alkali concentration, i.e., the process of delignification under these conditions proceeds without the activation energy. The dependence of wood delignification degree on temperature in the case of a prior chemothermohydrolytical treatment, undertaken for maximum removal of lignin, is also shown in Figure 3.

Figure 4 shows the effect of temperature on the degree of cellulose hydroxyl group substitution, when cellulose is mercerized within the temperature range of 20–150°C. It appears from these data that the nature of temperature correlation throughout the

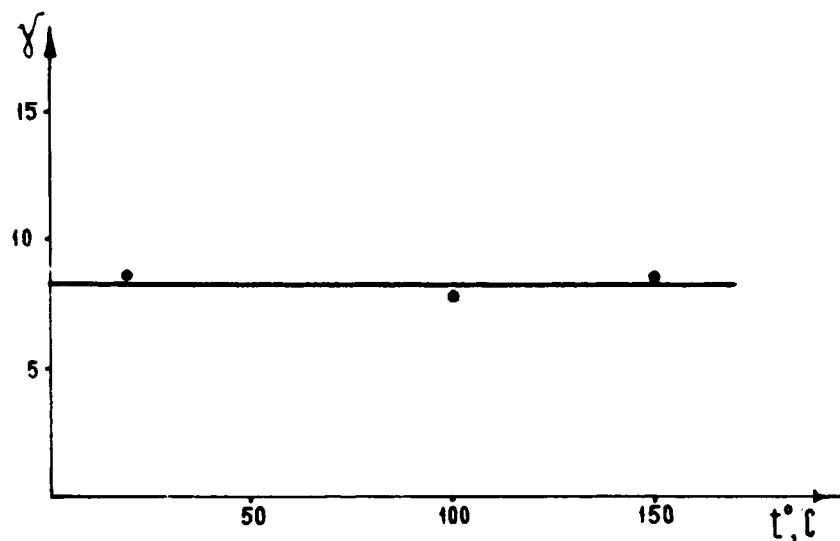


**Figure 3** Wood-delignification degree vs. temperature dependence. Initial concentration of NaOH: (1) 5 wt % to absolutely dry wood; (2) 10 wt % to absolutely dry wood.

cellulose mercerization process proved to be similar to that observed in the study of wood delignification. This means that this reaction under the conditions of plastic flow also requires practically no activation energy.

Thus, as a result of investigations undertaken, we demonstrated the possibility of obtaining a fibrous semifinished product and alkaline cellulose with the aid of a twin-screw mixer. Its principle of action is based on a combination of pressure and

shear deformations. The produced fibrous semifinished product is characterized by good paper-forming properties. Apparently, this is due to better external and internal fibrillation of the fibers. The fibers, owing to their intrinsic structure, possess improved physicomechanical parameters, similar to fibrous semifinished products from coniferous species and having mechanical strength 2.5–3 times that of fibrous semifinished products from leaf-bearing tree species produced on traditional equipment.



**Figure 4** Cellulose hydroxyl group substitution degree vs. temperature dependence (initial concentration of NaOH, 5 wt % to absolutely dry cellulose).

Applying shear stresses and pressure to cellulose within specific limits makes it possible to produce alkaline cellulose with desired characteristics and improved properties by enhancing its uniformity. Besides, the use of a minimum bath module allows the elimination of the stage of removal of excess alkaline solution and, hence, the reduction of water and alkali consumption 10-fold and threefold, respectively. This contributes in large measure to improvement of the environment.

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