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THE INFLUENCE OF TENSO-PULSE MODULATION ON CONVERTING LIGNOCELLULOSIC MATERIALS IN ALKALINE SOLUTIONS

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The article examines the influence of acoustic (tenso-pulse) effects on the processing of birch and spruce wood in a solution of sodium hydroxide and sodium sulfide in order to intensify the pulping process. The vibration was created using the ability of a steel conductor to compress and elongate when an intermittent short circuit occurs. Since the conductor-antenna is rigidly fixed to the reaction vessel, vibrations are transmitted to the contents. At a certain frequency and amplitude set on the generator, a low-energy effect on wood processing occurs, leading to a decrease in wood residues, an increase in cellulose yield and an increase in the optical density of the solution at wavelengths corresponding to the absorption of lignin. Optimal exposure frequencies are 170 kHz for birch wood and 180 kHz for spruce wood in solutions of sodium hydroxide and sodium sulfide. The optimal amplitudes generated on the oscillator are in all cases around 3 V. The effect is maintained when increasing the autoclave capacity from 150 ml to 1500 ml and stirring. The lignin content in cellulose obtained in a 1500 ml autoclave is reduced as a result of mixing and vibration generated by a generator with a selected frequency and amplitude. The experimental results were analyzed using traditional forest chemical methods. It is assumed that the effect occurs due to the formation of rotating liquid clusters during vibration.

Keywords: alkaline pulping, birch chips, spruce chips, sodium hydroxide, sodium sulfide, acoustic effect.

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Introduction

Research to improve the kraft process continues in the direction of reducing the degradation of polysaccharides, despite the proven process for producing cellulose using sodium hydroxide and sodium sulfide [1, 2]. Reducing energy consumption during pulping is also under close attention [3].

Acoustic impacts in the pulp and paper industry are known. Sound exposure is used to prevent the formation of flocculated fibers and dispersion of already formed flocculated fibers, better distribution of chemical additives, increased fibrillation, prevention of the formation of microbiological and other types of growths on machine parts and other parts of circulating water circulation systems [4], to reduce foaming [5], increasing the dispersion of cellulose [6, 7]. Completely unknown in the field of cellulose production, tenso-pulse modulation (TIM) can increase the rate of heterogeneous processes, as well as increase heat transfer and mass transfer [8–10] with prolonged exposure. The TIM modulation is a change in the parameters of impulse signals in time or in space. Usually this process is a kind of modulated oscillations, where a sequence of pulses is used as a "bearer" of information. There is an optimal frequency of influence on the speed of the process and the properties of the materials obtained [8–11]. For the chemical processes, the theoretical basis of the tensile-pulse modulation is proposed, based on modern physical and physicochemical concepts, fundamental laws, mathematical analysis, and the computer simulation apparatus. The existence of upper amplitude thresholds indicates natural self-organization and distinguishes the method from directive, powerful ultrasonic influences [8, 9]. Long-term heterogeneous processes in the pulp and paper industry

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are the processes of pulping and bleaching. Lowering the pulping temperature by vibration can reduce energy costs. The aim of the work was to establish the tenso-pulse signal, frequency and amplitude, leading to an increase in the degree of delignification.

Experimental

Air-dried wood chips from the sapwood part of *Betula pubescenes* and *Pícea ábies* were used as a raw material for pulping. Birch chip sizes: length – 20 mm, width – 20 mm, thickness – 2–3 mm. Spruce chip sizes: length – 15 mm, width – 15 mm, thickness – 3 mm.

The moisture content of plant materials is 6%. Sodium hydroxide solutions and solutions containing sodium hydroxide and sodium sulfide were used for cooking.

Delignification of spruce wood was carried out in an autoclave with a capacity of 150 mL. 24 g of air-dried wood chips were poured into a 150 mL autoclave and 115 mL of cooking solution was added. Module – 1 : 5. Sodium hydroxide solution with a concentration of 11.5% was used when cooking in an alkali solution. Processing time – 4 hours. 1000 mL of a solution with sodium sulfide for treating spruce wood was prepared by mixing 620 mL of an aqueous solution of Na_2S (54 g/L), 322 ml of a solution of NaOH (313 g/L) and 97 mL of H_2O. The active alkalinity of the solution was 51.1 g per 1000 mL. The sulfidity of the solution was 48 g per 1000 mL. Processing time – 3 hours. The autoclave was heated to 120 °C for one hour, then stood for 30 min, rising to operating temperature lasted for 30 minutes.

Delignification of birch wood was carried out in autoclaves with a volume of 150 and 1500 mL. 24 g of air-dried wood chips were poured into a 150 mL autoclave and 90 mL of cooking solution was added. Module – 1 : 4. 594 mL of an aqueous solution of Na_2S (59 g/L), 309 ml of a NaOH solution (313 g/L) and 97 mL of H_2O were mixed to prepare 1000 mL of liquor. The active alkalinity of the solution was 51.6 g per 1000 mL. The sulfidity of the solution was 46 g per 1000 mL.

The autoclave was placed in a thermostat. To connect the electromagnetic oscillation generator, a steel wire was wound around the lid, the end of which was brought out to the top of the drying cabinet. The generator terminals were connected to this end (Fig. 1). The vibration was created due to the periodic contraction of the antenna wire during an electrical short circuit.

The power of the generated signal when obtaining the best results did not exceed 1.5 mW. JDS-6600 signal generator with the following characteristics: upper limit: 15 MHz; waveform: sinusoidal, rectangular, triangular, pulsed, sawtooth; frequency: 0.01 Hz – 15 MHz. Accuracy ±20 ppm. Resolution 0.01 μHz. Amplitude: range (no load) from 2 mVpp to 20 Vpp. Accuracy ±5%. Resolution 1 mV. Output Power 2 W. Output Impendance 50Ω±10%. Attenuator 20 dB + 40 dB. The signal was generated in the form of a meander. Previously [11] it was shown that the effect is observed only if a rectangular signal is used.

Birch chips weighing 255 g were loaded into a 1500 mL rocking autoclave for pulping and 1 L of white liquor solution (770 mL liquor and 230 mL water) was added. The swing frequency is 32 times per minute. The autoclave was heated to 120 °C for an hour, then held for 30 minutes, rising to operating temperature lasted 30 minutes. Cooking time was 90 minutes. The diagram of the laboratory setup is shown in Fig. 2.

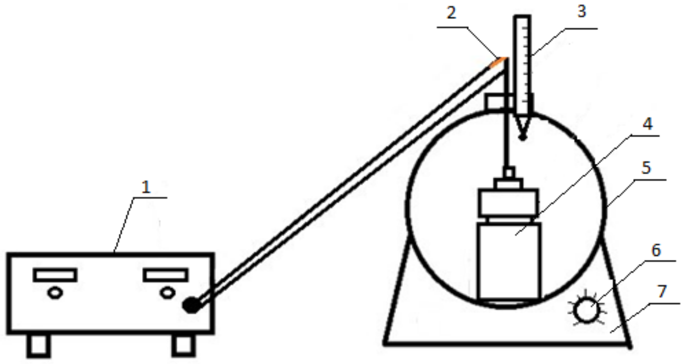

Fig. 1. Laboratory setup diagram: 1 – Signal generator; 2 – Antenna (steel wire 2 mm thick); 3 – Thermometer; 4 – Autoclave 150 mL; 5 – Thermostat (±2 °C); 6 – Temperature regulator

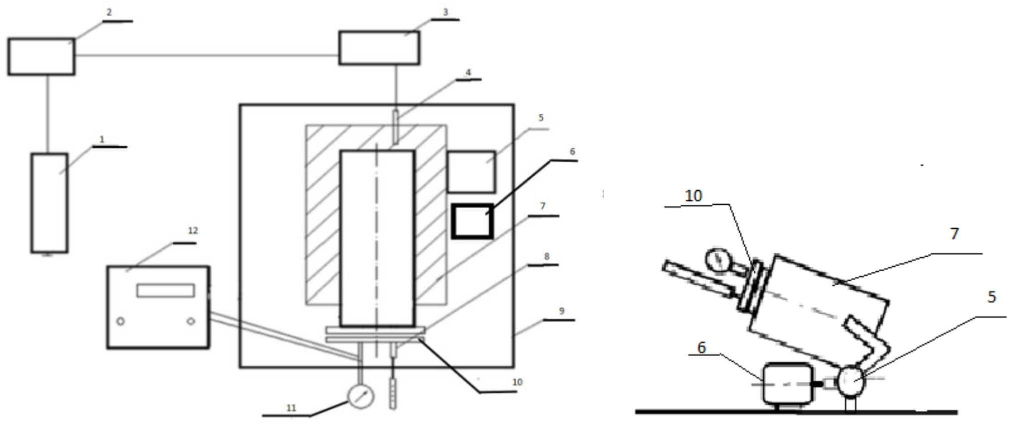

Fig. 2. Diagram of a laboratory setup with a 1.5 liter rocking autoclave: 1 – Transformer; 2 – Ammeter; 3 – Heating regulator; 4 – Thermocouple; 5 – Gearbox; 6 – Electric motor; 7 – Heating body; 8 – Autoclave thermometer; 9 – Autoclave stand; 10 – Autoclave; 11 – Pressure gauge; 12 – JDS-6600 signal generator

The pulping results were assessed according to the following parameters:

1. Amount of solid residue after pulping in a 150 mL autoclave. The weight of the residue was determined after repeated settling, washing until the wash water was neutral and drying at 103±2 °C.

2. The amount of solid residue that passed through standard sieves. The solid residue was washed through a three-stage sieve with pore sizes: No. 1 – 1.25 mm, No. 2 – 0.42 mm, No. 3 – 0.177 mm after cooking and cooling the autoclave.

The cellulose fiber located on the 2nd and 3rd sieves was washed with water. The resulting cellulose fiber (sieves No. 2, No. 3) was squeezed out, dried and weighed, and the moisture content was determined [12]. Lignin in the product was determined according to Komarov [12].

3. The optical density of the solution after dilution was assessed immediately after alkaline treatment of the wood chips and cooling of the autoclave. For dilution, 1 ml of the filtrate was taken and diluted with distilled water in a 1000 ml volumetric flask (solution No. 1). The optical density of the resulting solution was assessed at wavelengths of 270 and 286–350 nm on an SF-26 spectrophotometer (USSR).

The solution after cooking in a shaking autoclave (Fig. 2) was first diluted 4 times, taking 25 ml of samples into a 100 ml volumetric flask, and then 1 ml of the resulting solution in a 1000 ml flask.The experiments were repeated 3 times without the use of vibration and were repeated 3 times experiments in which the maximum optical density was observed of the solution. In all cases, the differences in the results of analysis of did not exceed 0.4% (solid residue) and 1.5% (optical density).

Results and discussion

Both spruce and birch wood were treated with alkaline solutions at elevated temperatures with different frequencies and amplitudes.

1. Processing of coniferous chips. The optimal frequency-amplitude intervals for processing spruce wood were established in an autoclave with a capacity of 150 mL (Fig. 1). The concentration of the aqueous solution of sodium hydroxide was 11.5%, Module – 5, Temperature -180±3 °C. The optimal frequency with an amplitude of 3.00 V turned out to be 170 kHz (Table 1).

The optimal amplitude set by the generator is 3 V (Table 2) in the amplitude range indicated on the generator. A signal of this amplitude is fed to the autoclave antenna.

More precise intervals of optimal frequencies were determined after adding sodium sulfide to the cooking solution. The experiments were carried out in an autoclave with a capacity of 150 mL, at modulus 5, solution alkalinity – 51.1, sulfidity – 48 g/L Na_2O, temperature 180±3 °C. Processing time – 3 hours. Under these conditions, the optimal frequency turned out to be 180 kHz, with an amplitude of 3.00 V (Table 3).

An amplitude of 3 V is optimal in the range of 2.8–3.2 V (Table 4).

Table 1. Experiments with spruce chips and sodium hydroxide solution, amplitude on the generator – 3.00V

№	Frequency (kHz)	Optical density at wavelength 270 nm	Solid residue (% of a.d.m.)	Fibrous product (%)
1	–	0.264	84.6	7.7
2	3	0.561	86.0	7.0
3	150	0.559	85.4	7.3
4	160	0.564	81.0	9.5
5	170	0.973	65.0	17.5
6	180	0.593	86.7	6.6
7	250	0.528	84.8	7.6
8	500	0.538	85.8	7.1

Table 2. Experiments with spruce chips with different amplitudes and frequency 170 kHz

№	Amplitude (V)	Optical density at wavelength 270 nm	Solid residue (% of a.d.m.)	Fibrous product (%)
1	1.00	0.561	84,8	7.6
2	3.00	0.973	65.0	17.5
3	5.00	0.661	83.8	8.1
4	10.00	0.560	85.2	7.4

Table 3. Effect of acoustic exposure on the processing of spruce chips in an alkaline solution with the addition of sodium sulfide. Amplitude 3.00 V

№	Frequency (kHz)	Optical density at wavelength 286 nm	Solid residue (% of a.d.m.)	Fibrous product (% of a.d.m.)
1	–	0.423	65.0	0.2
2	170	0.412	60.7	1.2
3	180	0.728	55.8	1.6
4	160	0.669	57.4	1.0
5	175	0.284	59.4	0.4
6	185	0.445	59.9	1.2
7	177	0.452	57.3	0.8
8	183	0.496	60.8	0.6

Table 4. Effect of amplitude on acoustic impact when processing spruce chips in a solution of sodium hydroxide and sodium sulfide with a frequency of 180 kHz

№	Amplitude (V)	Optical density at wavelength 286 nm	Solid residue (% of a.d.m.)	Fibrous product(% of a.d.m.)
1	2.80	0.579	62.0	0.9
2	3.00	0.929	55.8	1.6
3	3.20	0.532	61.5	0.9

2. Processing of birch chips. The optimal frequency-amplitude intervals for processing birch wood were established in autoclaves with a capacity of 150 and 1500 mL (Fig. 2).

Experiment 7 showed the best results (Table 5) at the selected amplitude. The optical density of the liquor increased due to the intensification of the delignification process and the mass of wood residue decreased. The signal amplitude also affects delignification (Table 6).

We believe that the conditions of experiment No 10 (Table 6) are the best, since when the solid residue is preserved, the maximum optical density of the solution is observed, which indirectly indicates the transition of lignin into solution. The study of the influence of amplitude was also carried out in a shaking autoclave with a capacity of 1500 mL (Table 7). The use of a large autoclave with mechanical stirring made it possible to test whether the deformation-pulse effect affects the process during stirring. Increasing the size of the autoclave could lead to a weakening of the vibration effect, which needed to be checked.

Since pulping was carried out with stirring, the formation of cellulose fibers from wood was observed. After pulping, the lignin content in cellulose fibers was assessed.

According to the results of the studies, it is clear that the effect of the tenso-pulse effect is observed when scaling the pulping volumes, but at a larger amplitude – 3.10 V, which may be due to vibration damping by a more massive vessel or the influence of stirring.

3. Explanation of the results obtained. Thus, under a certain very weak external, sound, non-energy-consuming influence, the process of delignification of birch and spruce wood in a solution of sodium hydroxide and sulfide is intensified. The process changes as a result of weak directive influences. It is known that vibrations improve the movement of fluid through pipes, reducing the degree of turbulence that slows down the movement [13]. It is possible that the impact of vibration (vibration is formed due to the electromagnetic conversion of current in a short-circuited conductor) causes the clots of liquid to rotate inside the vessels of plants. The optimal frequency required for cluster rotation depends on the mass and radius of the particles [14]. Probably, an increase in the frequency above the optimal one and a change in the vibration amplitude leads to a mismatch of the system and the regime of fluid movement inside the vessels becomes chaotic. It is possible that the effect of vibration (vibration is formed due to the electromagnetic transformation of current in a short-circuited conductor) leads to the rotation of liquid clots inside the vessels of plants. Water and its solutions consist of clusters [15, 16]. Perhaps the yield of substances dissolved in alkali improves as a result of the organized rotation of clusters of solution molecules. Differences in optimal frequencies and amplitudes may be associated with differences in the compositions of solutions [17] and, accordingly, with differences in the sizes of clusters, as well as with differences in the sizes of plant vessels. Perelman proposed that the diameter, length of cavities, and cell wall thickness influence the frequency of acoustic resonance [18, 19].

Table 5. Effect of frequency of tenzo-pulse action at an amplitude of 3.00 V on the processing birch wood. Pulping time 2.5 hours. Temperature – 160 °C. Autoclave volume – 150 mL

№	Frequency (kHz)	Optical density, at wavelength 270 nm	Solid residue (% of a.d.m.)
1	–	0.305±0.005	63.7±0.2
2	119	0.300	63.0
3	121	0.320	62.1
4	160	0.310	63.0
5	165	0.305	63.6
6	168	0.330	60.5
7	170	0.380±0.005	60.1±0.2
8	173	0.320	62.0
9	175	0.315	63.3
10	180	0.310	63.4

Table 6. Effect of tenzo-pulse action at a frequency of 170.0 kHz. Time – 2.5 hours

№	Amplitude(V)	Optical density, at wavelength 270nm	Solid residue (% of a.d.m.)
1	–	0.305±0.005	63.7±0.2
2	2.70	0.390±0.005	59.4±0.2
3	2.73	0.330	64.5
4	2.75	0.400	64.0
5	2.78	0.300	64.7
6	2.80	0.440	60.3
7	2.81	0.400	59.9
8	2.83	0.380	63. 5
9	2.84	0.350	60.9
10	2.85	0.440±0.005	61.2±0.2
11	2.90	0.390	61.3
12	2.95	0.320	66.0
13	3.10	0.350	60.2

Table 7. Effect of the amplitude of tenso-pulse action in an autoclave at 1500 mL. Frequency – 170.0 kHz. Temperature 138±2 °C

№	Amplitude (V)	Optical density, at wavelength 270 nm	Yield of dry fibrous product, %	Lignin in cellulose, %
1	–	0.240±0.005	47.9±0.2	7.1±0.1
2	2.85	0.240	47.0	6.3±0.1
3	3.00	0.230	46.5	6.5±0.1
4	3.10	0.266±0.005	46.1±0.2	3.9±0.1
5	3.30	0.230	47.3	4.8±0.1
6	3.50	0.210	50.3	6.1±0.1
7	3.70	0.235	36.8	7.4±0.1

Conclusions

The conditions of sound, deformation-pulse influence on the heterogeneous process of cooking birch and spruce wood in a solution of sodium hydroxide and sulfide, under which acceleration of delignification is observed, have been determined. It has been established that at certain frequencies (170±1 kHz) and amplitudes (2.85–3.1 V) the amount of solid residue decreases from 64 to 60% when treating birch wood with a solution of sodium hydroxide and sodium sulfide. Scaling the process in a 1500 ml autoclave and mechanical stirring did not interfere with the observed phenomenon. When processing spruce wood in a sodium hydroxide solution, the optimal frequency was also 170 kHz. The use of a solution of sodium hydroxide and sulfide required an increase in frequency to 180 kHz. The frequency we used for the experiments is ultrasonic, but the impact power does not exceed 1 mW, in contrast to the known methods of using ultrasound to extract plant materials, where the impact power ranges from 20 W to 1 kW [20–23].

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Conflict of Interest
The authors of this work declare that they have no conflicts of interest.

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