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IDENTIFICATION OF CHEMICAL AND MECHANICAL CHANGES IN THERMOMECHANICALLY COMPRESSED ALDER WOOD

The article presents the results of thermogravimetric analysis, IR spectroscopy, and microscopic examination of the densified alder wood. Purpose of the research was the identification of chemical and mechanical changes resulting from its piezothermal treatment. The results of thermogravimetric analysis were used to execute substantiation changes in wood properties during compaction. The obtained results allowed to choose the criterion for assessing the degree of wood plastification.

Introduction. At the present time one of the tasks of the timber and woodworking industry of the Republic of Belarus is sustainable and multiple use of forest raw material resources. One solution to this task is to reduce consumption of hardwood by replacing it with compressed softwood, including the parquet production [1]. In earlier works, authors propose a number of ways to improve physical and mechanical properties of softwood using various methods [2, 3, 4]. Their main disadvantage is energy intensity of processes, and the use of toxic chemical compounds. In the proposed wood compression method chemical compositions are not used, physical and mechanical properties are improved only under the influence of high temperature and high pressure, which makes the technology harmless to humans and the environment.

Main part. The objective of this work is to determine chemical and mechanical changes in alder wood due to piezothermal treatment. To evaluate chemical changes occurring in the wood when compressed, differentially-thermo-gravimetric (DTG) and thermo-gravimetric (TG) analyses using thermo-analytical system METTLER TOLEDO were applied. Thermogravimetry (TG) is a method of thermal analysis, wherein the sample mass variation is recorded depending on temperature. Experimentally obtained weight change temperature curve an idea of the thermal stability and composition of a sample in the initial state, of the thermal stability and composition of substances formed at

intermediate stages of the process, and of the residue composition, if any [5].

DTG is a mathematical differential weight change curve. It is a temperature (time) derivative of the test substance weight change function $dP/dT = f(T)$, i. e. a derivative of $P = f(T)$ [6]. Using the DTG curve can help to determine temperatures of the start and end points of a reaction more accurately, and using the DTG curve peak we can determine temperature of the maximum reaction rate. Samples were heated in a programed mode using thermoscales to a temperature of 500°C, and the weight change of the test substance P was graphically recorded depending on temperature and heat time in the form of a typical thermogram (TG curve).

An earlier thermogravimetric study of natural and compressed wood samples allowed determining the difference between them at the chemical level and assuming a mechanism of wood plasticization in the compression process [7]. The main difference is a change of quantitative ratio of bonds with different thermal stability due to changes in the spatial structure of lignin macromolecules: under high temperature (110°C) in the presence of moisture (8%) an initial condensation reaction takes place with the participation of benzyl alcohol hydroxyl groups and free radicals. A cross-linking reaction with benzyl-alcohol hydroxyl and aromatic nucleus to form a relatively thermally stable intra- and intermolecular alkylaryl C-C-bonds is best known (Fig. 1).

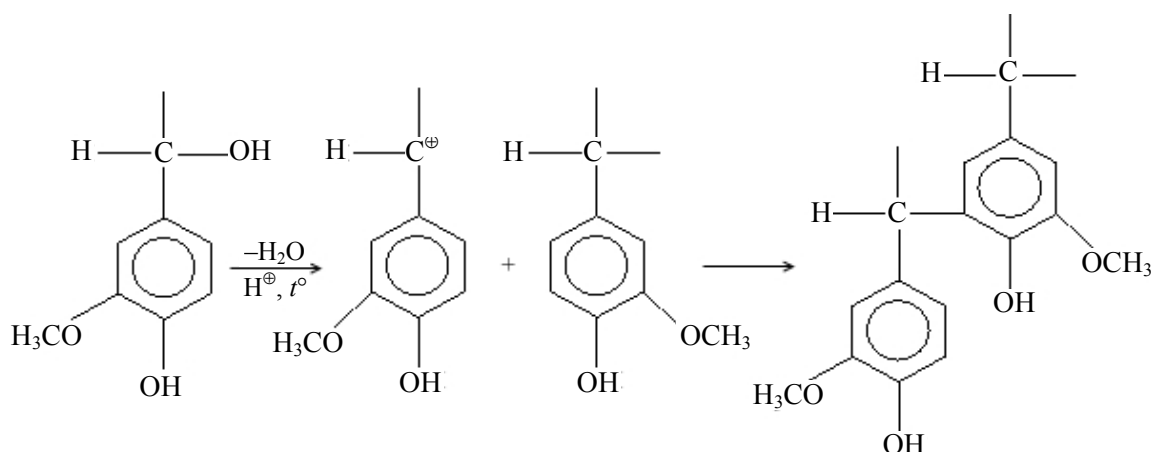


Fig. 1. Mechanism of a cross-linking reaction with benzyl alcohol hydroxyl and aromatic nucleus

This reaction is considered to be the most representative in the process of condensation formation of a three-dimensional network in full volume of lignin substance. Due to condensation reactions lignin thermal stability increases [8]. In this way, the dimensional stability of compressed wood depends on the amount of new bonds generated in lignin macromolecule following the condensation reaction. Activation energy of thermal-oxidative degradation can be taken as a criterion for assessing the degree of wood plasticization. Activation energy of thermal-oxidative degradation is an excess of energy required to break chemical bonds forming a polymer chain under the influence of heat and air environment oxygen.

TG curves allow determining activation energy of thermal-oxidative degradation (E_D), which was calculated using the Broido method applied to cellulose pyrolysis and based on double logarithmation [6, 9]. This calculation method was improved in work [10] and is currently widely used to study the dependence of mechanical properties of polymers on their chemical composition and structure.

A hinge of natural and compressed wood was made in order to conduct a research. Wood was compressed at 110°C under a pressure of 20 N/mm² for 1 minute. The hinge of a compressed wood was 10.3–10.5 mg, the heating rate was 5°C/min. TG curves were recorded in the temperature range of 25–500°C. The temperature for calculating E_D was determined by extremum on the DTG curve. The results of the thermogravimetric analysis of compressed wood are shown in Fig. 2.

It is shown that effective activation energy of thermal-oxidative degradation (E_D) of thermo-plastic polymers in both liquid (in a molten form) and solid (film, fiber, etc.) phases is a universal and highly sensitive parameter. The parameter E_D increases in partial crosslinking of polymer macromolecules. All other conditions being equal, the parameter E_D is a measure of polymer resistance to thermal-oxidative degradation. Therefore, the greater is the cross-linking degree, the higher is the E_D value. The calculation of E_D based on mathematical treatment of the TG curve using the Broido double logarithmation method, which is accurate enough for polymers, is performed by the formula 1 [9]

$$\ln\left(\ln\frac{100}{100-\Delta m}\right) = -\frac{E_D}{R} \cdot \frac{1}{T} + \text{const}, \quad (1)$$

where Δm — sample weight loss, % at each of temperatures within the range of substance decomposition; R — a universal gas constant equal to $8.31 \cdot 10^3$ kJ/mol·K.

The condition of Broido method adaptability is the first-order decomposition reaction, which is true for many polymers [6]. The substance weight loss is a process of the first order ($n = 1$), if the linear dependence $\ln^{100}/_{100-\Delta m}$ on T , K is observed. Knowing the sample weight loss (Δm) at a temperature of T , a line, in which E_D was expressed by slope ratio of logarithmic dependence Δm on T [9, 10], was graphed. Then, we find a value of degradation activation energy in kJ/mol by the following formula (2)

$$E_D = \text{tg}\varphi \cdot R. \quad (2)$$

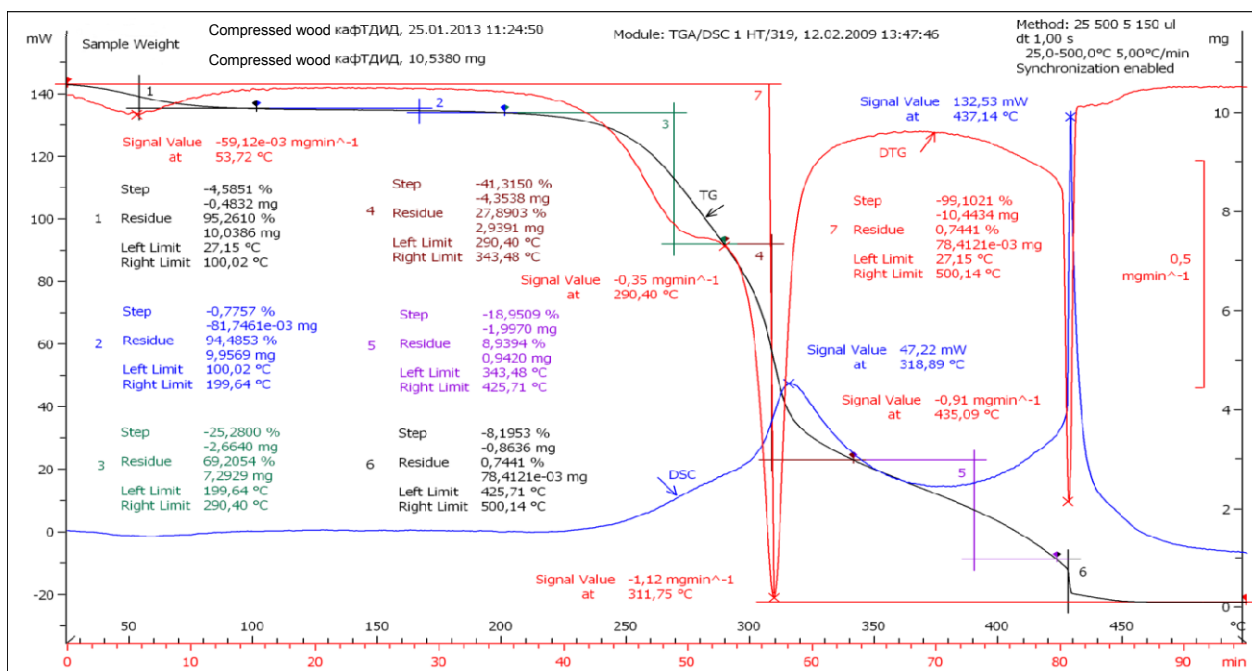


Fig. 2. Sample thermogram from compressed alder wood

Experimental results processing, i.e. mathematical transformation of the TG (DTG) weight loss curve was performed in Excel. Below are Δm - T logarithmic dependence diagrams (Fig. 3, 4).

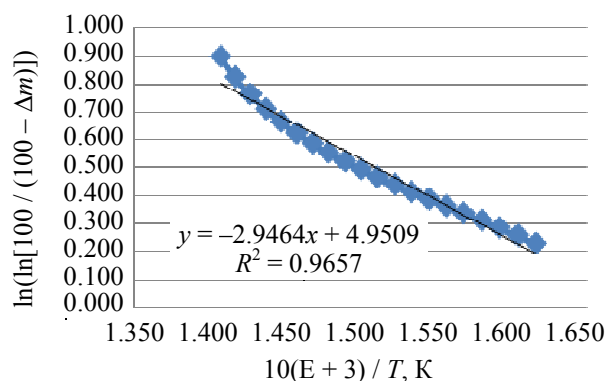


Fig. 3. Δm - T logarithmic dependence under thermal degradation of natural alder wood

Therefore, activation energy of thermal-oxidative degradation of compressed wood exceeds activation energy of natural wood by 12.5%, which shows an increase in lignin stability following wood compression.

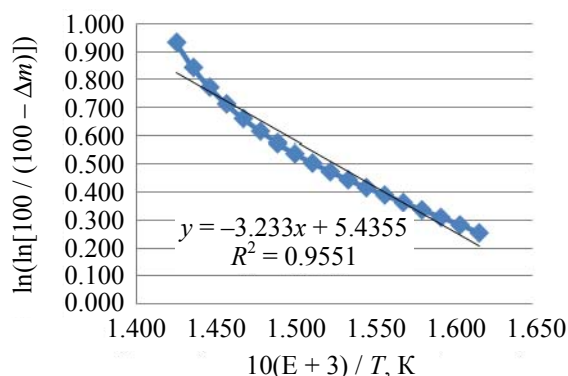


Fig. 4. Δm - T logarithmic dependence under thermal degradation of compressed alder wood

Compressing softwood can be carried out using positional equipment or rolling machines. When compressing wood on rolling machines, time of thermal treatment of wood, which stimulates wood plasticization process, is reduced (depending on equipment design).

Therefore, it is necessary to conduct additional researches of the effect of thermal treatment duration on wood to substantiate softwood rolling technology.

To conduct research on wood compression using the method of rolling to determine the optimal duration of thermal treatment we took alder wood 2.0 mm thick.

Variable factors are wood warm-up time and compression time. Wood compression was carried

out at a temperature of 110°C and under a pressure of 20 N/mm².

Controlled parameters are a degree of compression and activation energy of thermal-oxidative degradation, as a criterion for assessing a degree of wood plasticization. An experiment planning matrix in physical terms and mean values of compression degree and activation energy are presented in the table.

An arithmetic mean of triplicate definitions with an absolute value of differences between them not exceeding the total error of measurement results ($\pm 1,0\%$) at confidence probability = 0.95 was taken as an analysis result.

Experiment planning matrix in physical terms

Experiment number	Warm-up time, T , s	Compression time, t , s	Compression degree mean value ε , %	Activation energy mean value E_D , kJ/mol
1	30	12	59.59	26.98
2	15	12	35.91	25.77
3	30	6	53.54	26.54
4	15	6	32.28	24.54
5	30	9	55.23	26.76
6	15	9	33.12	24.94
7	22	12	43.92	26.26
8	22	6	35.77	25.79

All other conditions being equal, the parameter E_D is a measure of polymer resistance to thermal-oxidative degradation. The calculation of lignin activation energy confirms the nature of change of thermal effects and argues for reducing thermal degradation of plasticized wood. As is seen from the table, the value E_D depends on the time of high thermal exposure on the samples. The greater the total temperature of exposure during heating and compression, the more extensive the primary lignin condensation reaction.

The second-order regression equations in code designations considering the effect of each factor on the value of the compression degree and activation energy of thermal-oxidative degradation are obtained in the result of calculations. The significance of regression coefficients was assessed by Student t-test. After removing insignificant coefficients the equations acquired the following form:

1. The value of the alder wood compression degree in a coded form:

$$Y_1^C = 38.690 + 11.175x_1 + 2.972x_2 + 0.605x_1x_2 + 5.485x_1^2 + 1.155x_2^2.$$

2. The value of the activation energy of lignin thermal-oxidative degradation of compressed alder wood in a coded form:

$$Y_2^C = 25.918 + 0.838x_1 + 0.357x_2 - 0.198x_1x_2 + 0.107x_2^2.$$

In physical terms, the regression equations are as follows:

1. The value of the compression degree:

$$Y_1^H = 61.454 - 3.14T - 1.924t + 0.027Tt + 0.097T^2 + 0.128t^2.$$

2. The value of the activation energy of thermal-oxidative degradation:

$$Y_2^H = 21.514 + 0.191T + 0.103t - 0.009Tt + 0.012t^2.$$

Based on the obtained regression equations, compression degree and activation energy of thermal-oxidative degradation dependences on warm-up and compression time were calculated and shown. The dependences are shown in Fig. 5 and 6.

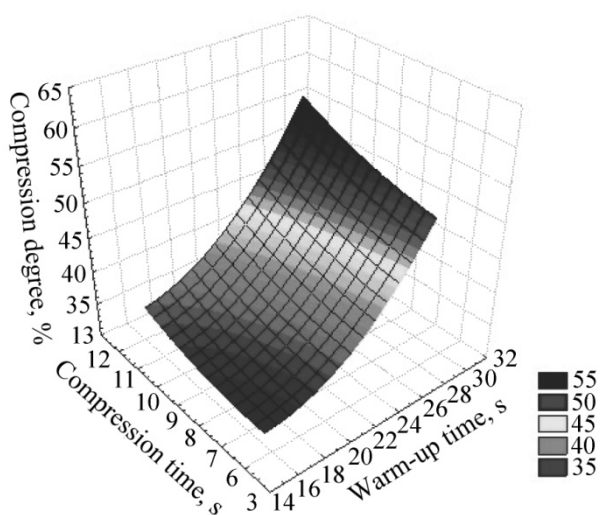


Fig. 5. Compression degree dependence of alder wood on warm-up and compression time

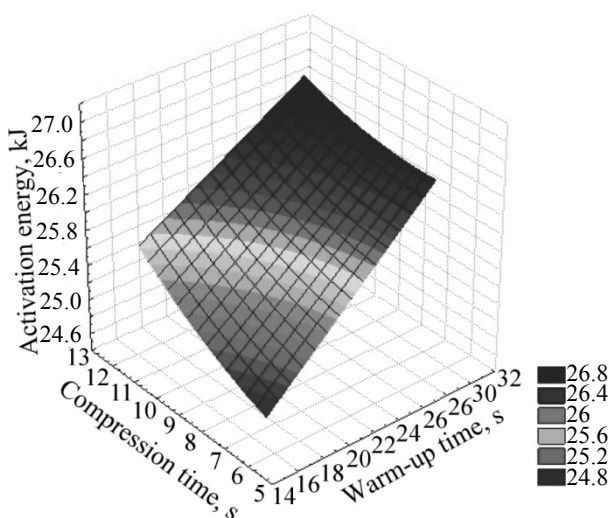


Fig. 6. Dependence of energy activation value on warm-up and compression time

As can be seen from the above dependences, the compression degree and activation energy increase with an increase of the total time of exposure to wood. It should be noted that the activation energy is significantly increased (9.5%) with an increase of the total thermal exposure time, when the warm-up time is 22 s and the compression time is 12 s. It may be concluded that sample warm-up and compression time equally affect the increase of activation energy.

The compression degree is also equally dependent on the warm-up and compression time but reaches the minimum desired value of 30% when the warm-up time is 30 s and compression time is 6 to 12 s. As was shown by the above experiments, the improvement of physical and mechanical properties of wood depends on an increase in wood compression degree; covariance coefficient of compressed wood hardness and compression degree is 0.97.

Analyzing the results, we conclude that the total time of thermal exposure on alder wood should be at least 30 s and is distributed in the ratio of 3/1, the sample warm-up time to the time of its compression, the compressed wood being as thick as 2.0 mm.

Softwood is, therefore, advisable to be compressed using rolling machines equipped with heating chambers. The processing time should be 30 s or more. In this case, the modes with warm-up time of 20 seconds or more, and compression time of 10 seconds or more are rational.

An infrared spectroscopic study was used to identify the interaction products of the wood components being compressed.

The spectra were obtained using IR-Fourier spectrometer NEXUSTM E.S.P. (Thermo Nicolet, USA) with a diamond cuvette and an MFTIR-attachment (multiply frustrated total internal reflectance) to analyze solid and liquid samples. The spectrometer is widely used in a laboratory routine. The recorder scale for all spectra was 100 cm^{-1} per 1.00 cm of a diagram. Resolution power and accuracy of wave numbers, signal-to-noise ratio, and spectrum recording time are interrelated and fully determine the quality of recorded spectra. The following modes of operation were selected: resolution power of wave numbers – 16 cm^{-1} , their accuracy – $\pm 0.25 \text{ cm}^{-1}$, signal-to-noise ratio of 8000 : 1 with the spectrum recording time of 1 min. These modes are optimal for recording panoramic spectra on the devices being used at high resolution and high signal-to-noise ratio. The attained accuracy of wave numbers was due to performance specifications of the device, in particular, with the use of a helium-neon laser to get a sampling interferogram scale. The spectrophotometer scale was calibrated by using polystyrene absorption bands (area of

400-4000 cm^{-1}). The deviation of instrument readings from the true value of a wave number by a spectrum ranged from 0 to 1 cm^{-1} . The amplification coefficient of a recording device in each case was automatically selected depending on the nature of a spectrum being recorded.

When analyzing IR absorption spectra of samples under investigation, according to the standard practice of IR spectroscopic studies, the number of absorption bands related to fluctuations of this ion or a molecule, and the frequency range of their manifestation were considered. The number of bands in the infrared absorption spectrum was determined by using sample procedures for the point symmetry group, which depends on the spatial arrangement of atoms in this ion or molecule [11].

When comparing the obtained IR spectra of alder wood before compression and after compression, significant differences were not found. The results of this study confirm that the change in wood properties takes place under the influence of external factors and suggest that chemical reactions of the primary lignin condensation, which proceed without chemicals release and changes in the chemical composition of wood form the basis for interaction between wood components.

Microphotography of the surface of preset wood samples with a scanning electron microscope JSM-5610LV was used to identify mechanical changes in the wood structure.

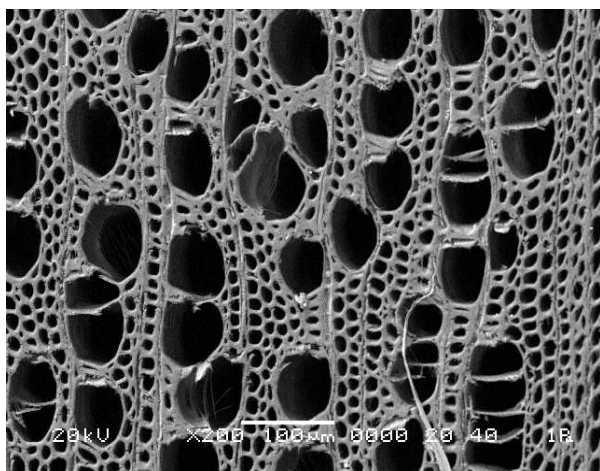


Fig. 7. Natural wood sample (200 times magnification)

The samples were placed into a pressure-tight chamber of the working part of the microscope, after which air was evacuated automatically from the space, thereby increasing measurement accuracy and image quality. Using a graphical interface, performed under MS Windows, and automatic control system of the microscope movable table (by two coordinates) as well as lens zoom in/out it is possible to obtain 8-bit (shades of grey) images of the

sample surface at different zoom. Pictures of wood were obtained using 200 zoom. The picture resolution is 640×480 pixels (127 pixels per inch).

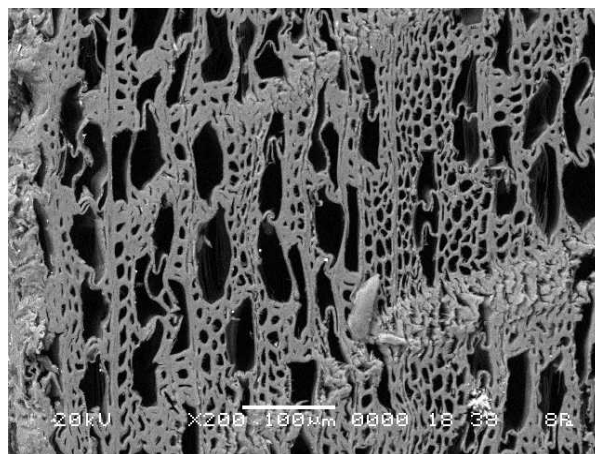


Fig. 8. Compressed wood sample (200 times magnification)

By comparing pictures of natural and compressed wood, it is possible to see a significant reduction in vessel cavities and tracheids, as well as the crushing of their walls, due to mechanical impact. The destruction of wood elements was not observed.

Conclusion. The following conclusions can be drawn from these data. When compressing wood, the primary condensation of lignin is observed, which results in the increase in thermal stability and wood plasticization. Effective criterion for assessing the degree of plasticization can be regarded as activation energy of thermal-oxidative degradation. The results of IR-spectroscopy and microscopic examination show no chemical changes and destruction of wood anatomy.

Dependence research data of wood plasticization degree on thermal exposure time during thermal rolling allow recommending the rolling as an energy-efficient and high-performance way to compress wood.

As can be seen from the above, the obtained data permit the development of rational modes of softwood compression: press table temperature - 110°C , compression pressure - 20 N/mm^2 , warm-up time - 20–30 s, compression time - 10–15 s.

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