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ESTABLISHING REGULARITIES IN THE APPLICATION OF DRY PINE WOOD

Yuriy Tsapko**
Corresponding author
Doctor of Technical Sciences, Professor*
E-mail: juriyts@ukr.net
Nataliia Buiskykh
PhD*
Ruslan Likhnyovskyi
PhD
Research and Testing Center
Institute of Public Administration and Research in Civil Protection
Vyshhorodska str., 21, Kyiv, Ukraine, 04074
Oleksandra Horbachova
PhD, Associate Professor*
Aleksii Tsapko**
PhD, Senior Research Fellow
Department of Research of Quality and Conditions of Storage of Oil Products and Industrial Group of Goods
Ukrainian State Research Institute "Resource"
Kasimir Malevich str., 84, Kyiv, Ukraine, 03150
Serhii Mazurchuk
PhD, Associate Professor*
Andrii Matviichuk
PhD
V. I. Vernadsky National Library of Ukraine
Holosiivskyi ave., 3, Kyiv, Ukraine, 03039
Maryna Sukhanevych
Doctor of Technical Sciences, Senior Researcher
Department of Building Materials**
*Department of Technology and Design of Wood Products
National University of Life and Environmental Sciences of Ukraine
Heroiv Oborony str., 15, Kyiv, Ukraine, 03041
V. D. Glukhovsky Scientific Research Institute for Binders and Materials
**Kyiv National University of Construction and Architecture
Povitroflotsky ave., 31, Kyiv, Ukraine, 03037

The issue related to using dry wood products for building structures is to ensure their stability and durability during operation while it is necessary to take into consideration changes in their properties and structure. Therefore, the object of this study was pine wood struck by drying out. It is proved that in the process of drying, wood porosity decreases, and, accordingly, the tensile strength, depending on the degree of damage by the fungus. Specifically, with the area of damage in the range of 30–50 %, the strength limit decreases by more than 1.3 times, and if the fungus affects the area within 80÷100 %, the wood becomes softer, more ductile while the strength limit is reduced by 1.1 times. Based on the results of physicochemical studies, discrepancies in the IR spectra were identified, indicating structural changes in the constituent components of wood. There is a decrease or absence of intensities of absorption bands of some functional groups and the appearance or intensification of others. Wood samples, in determining the highest calorific value, show a difference in values, which is explained by structural changes in wood components caused by biological processes. Thermogravimetric analysis data indicate complete burnout of dry pine wood. However, for wood with tree stands not weakened by drying, the coke residue burns out at a higher temperature. Wood with blue pigmentation affected by microorganisms has significant differences in the heating area of 400÷700 °C. The nature of coke burnout allows us to make assumptions about the different qualitative and quantitative composition of the coke residue, which is formed due to structural changes. The practical significance is the fact that the results of determining the properties and structure of dry wood make it possible to establish the operating conditions for articles and building structures

Keywords: pine wood, dry wood, tensile strength, change in wood structure, damage by microorganisms

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1. Introduction

Interest in wood as a restorative material is growing rapidly since wood elements belong to the class of light building structures, the use of which is one of the important areas for improving the efficiency of construction production. However, the active consumption of wood in the world has led to the fact that deforestation is 10 times higher than forest plantations while in the last decade, the volume of drying out of coniferous stands has become alarming. One of the main causes of drying out is climate change, which has caused changes in water balance and, in turn, has affected the spread of pests, diseases, and other negative factors. One of the ways to prevent the mass reproduction of pests is to carry out sanitary felling, as a result of which a large volume of dry wood is formed. Most often, dry wood is considered in terms of its impact on the environment and as a source of high carbon content [1]. At the same time, the question arises of the rational use of large volumes of dry wood formed as a result of sanitary felling.

Most often, dry wood is used as a material for the manufacture of containers, limited – the production of board

materials and cellulose. It is noted that the use of dry wood as a starting material to produce cellulose is less profitable since the difference between the yield of cellulose from standard wood and dry wood is about 12 %.

Since wood is a natural restorative material, interest in the use of all its types is growing. One of the possible ways to use dry wood is to use it in construction as a structural material and as a heater. In addition, dry wood has a lower coefficient of volumetric drying, which reduces cracking, warping, and shrinkage during its use.

Therefore, studies aimed at determining the properties of wood and changing its structure during drying, which are necessary to establish the scope of its use, are relevant.

2. Literature review and problem statement

Paper [2] points out that an increase in the frequency, duration and/or severity of drought and heat stress associated with climate change can fundamentally change the composition, structure, and biogeography of forests in many regions. Of particular concern is the potential increase in tree drying associated with climatic physiological stress and interaction with other climatic processes, and especially forest fires. Despite this risk, forests may become increasingly vulnerable to tree drying out and dying off, which also indicates risks to ecosystem services. Therefore, it is necessary to include the loss of sequestered forest carbon and the associated atmospheric feedback. The review also identifies key information gaps and scientific uncertainties that currently interfere with the ability to predict tree deaths in response to climate change and highlights the need for a globally coordinated surveillance system. In general, the review shows the potential for increased tree drying due to drought and heat in forests around the world. However, it does not say what to do with dry wood.

In [3], it is said that the total biomass reserves of dry wood, standing dead and living trees, increased (18.3 %, 14.7 %, and 3.9 %, respectively) with the accumulation of biomass in large living trees. This, combined with an increase in the biomass of smaller dead trees, can lead to changes in the components of forest biomass, which includes downed dead wood (DDW), standing dead trees (SDs), and living trees. Wood illustrating the impact of tree stand development in U. S. forests on the scale of individual forest ecosystems was mainly due to the appropriate amount of living aboveground biomass and the cumulative impact of decomposer communities and climate (that is, self-degenerating). Overall, amid expected future global changes and growing interest in maintaining carbon reserves in land forests, interconnection with broader efforts to monitor carbon/forest biomass is important. This requires the inclusion of analytics focused on dead wood, an assessment of the microbial/fungal community, or dead/living biomass is essential to interconnect with broader efforts to monitor carbon/biomass forests.

In [4], it is noted that lumber from dry trees is characterized by such features as mycological and insecticidal lesions, cracks, etc., the effect of which on the strength and performance of timber has not yet been studied. Traditionally, there is a growing interest in the use of wood in construction as material from renewable environmentally friendly raw materials. One of the possible uses of pine dry trees may be the production of building lumber. The lack of characteristics of such wood makes it impossible to predict its behavior during processing and operation and, accordingly, makes it difficult to determine the directions of its rational use, especially in structures. An attractive feature of such raw materials from the economic aspect is the much lower cost of wood from dry pine trees, compared to wood from non-dried pines. However, the areas of application of such wood are not indicated.

The studies reported in [5] established the possibility of using dry wood as heat-insulating products made of wood wool. The coefficient of thermal conductivity for products made of dry pine wood was calculated, which reaches 0.132 W/(m·K). In the case of processing wood products with an adhesive composition, it is reduced to 0.121 W/(m·K), and when creating heat-insulating plates made of wood wool, it is reduced to 0.079 W/(m·K), respectively. The thermal conductivity of a homogeneous material depends on the volumetric mass. Thus, with a decrease in the volumetric mass of the material to 183 kg/m^3, the thermal conductivity decreases by 1.67 times, and vice versa, when using boards, the thermal conductivity decreases only by 1.1 times. This makes it possible to assert the compliance of the detected real mechanism of thermal insulation and the identified conditions for the formation of material properties based on wood wool and binder. And the attractiveness of the proposed technological solutions for the use of low-quality wood.

In [6], genetic and ecological variations and correlation models are given, which are characterized by the modulus of elasticity (MOE), the break module (MOR), and the associated features of wood. Specifically: the proportion of late wood, the density of wood, spiral fiber, the angle of microfibrils, and the lignin content in five families of full-breed trees Norwegian spruce. The assessment was carried out on the basis of samples of pure wood from the transition zone of young-ripe wood of 93 selected trees at the age of 30 from the seeds. The average samples differed significantly (p<0.05) for all the wood features studied, except for the lignin content. The MOE ranged between 7.9 and 14.1 GPa among trees, and between 9.4 and 11.0 GPa among families. MOR ranged between 47–87 MPa among trees and 61–71 MPa among families. Tree families remained significantly different in the analysis of specific MOE (MOE/density) and MOR (MOR/density). Hence, relying only on wood density as a sign of wood quality when cultivating trees will not provide a complete potential genetic advantage for MOE and MOR.

The study reported in [7] was carried out to assess the density of wood and the mechanical properties of Pinus kesiya Royle ex Gordon grown in Malawi. Wood samples from six P. kesiya families at the age of 30 were used for the study. The estimated average density of wood, modulus of elasticity (MoE), break modulus (MoR), and humidity were 0.593±0.001 g/cm^3, 13.46±0.07 GPa, 113.67±0.57 MPa, and 12.0 %±0.0 %, respectively. There were statistically significant (p<0.001) differences in wood density and mechanical properties along the radial direction and stem height. The density and mechanical properties of wood increased from the core to the bark and decreased from the joint upwards. There were no reliable (p>0.05) differences in wood density and mechanical properties between families. This suggests that any tree in the family can be selected for tree improvement programs if the density is treated as a variable. The density of wood had a strong positive significant linear relationship at both MoE (r=0.790; p<0.001) and MoR (r=0.793; p<0.001). This indicates that it has the potential to simultaneously improve the density of wood and the mechanical properties of this breed. However, it is not said about its natural destruction.

In [8], it was found that the stress of drying wood causes a variety of drying defects, which are the result of the microstructure of the wood and the transfer of heat and mass during drying. This is a fundamental way to solve the issue of defects to clarify the law and mechanism for the development of stress and deformation of wood during drying. In the cited paper, based on the analysis of wood drying defects, theoretical and experimental methods for testing the stress and deformation of drying were summarized. At the same time, artificial neural networks (ANNs) and their applications in the field of wood drying were investigated. Traditional cutting and slicing methods have been used practically in research and the wood drying industry, but stress changes were not captured in the process. Image analysis and near-infrared spectroscopy technologies provide a new opportunity for detecting stress and drying deformation. Thus, of interest is the combination of the theory of heat and mass transfer during drying with the theory of microscopic mechanics of the cell wall and macroscopic drying. It is necessary to develop a more complete system for obtaining and analyzing images in order to practically implement monitoring of drying deformation and cracking in real time. However, to achieve predictability accuracy, a more acceptable and reasonable model of stress and deformation during wood drying should be built.

In [9], it was noted that the raw materials have different quality requirements depending on the material or wood product. However, the physical and mechanical properties of wood are heterogeneous in radius and height of the trunk and depend on the breed, location in the trunk, and growing conditions. The purpose of the cited study was to examine the variability of porosity and density of pine wood (*Pinus sylvestris L.*) in the trunk of a tree growing in dry forests of the forest-steppe zone of eastern Europe. The studies were conducted on sections of wood sawn at different heights of the trunk. A change in the density of pine wood in terms of trunk height by 1.43 % per meter was established. The porosity of wood increases from the end to the top by an average of 5.5 %. New information about the variability of wood properties makes it possible to rationally and reasonably approach the choice of raw materials to produce materials with specified performance characteristics. However, it is not specified how those processes occur for dry wood.

The large-scale death of pine forests in the region requires solving the issue of the use of dry forests [10]. Evaluation of the qualitative and durable characteristics of the wood of dying forests will determine how to use such wood. The main qualitative characteristics of wood in dying forests can be reduced to determining the strength characteristics of wood samples and the degree of their biodegradation. The cited article reports the results of determining the mechanical properties of dry wood samples using the sample compression technique along the fibers. Experimental studies were carried out according to standard procedures on the AG-50kNX SHIMADZU test machine. The tests have shown high homogeneity of strength properties and density of pine wood samples in each experiment. At the same time, a comparative analysis of the compressive strength of wood from dry plantations and freshly cut wood confirmed that the mechanical properties of such wood are within the normal range. The test results make it possible to develop a further method for studying dried wood, depending on the degree of their biological damage. However, the scope of application of such wood has not been determined.

A study reported in [11] has shown that dry wood is also a major component of the nutrient cycle, it regulates water flows, prevents soil erosion, and promotes carbon accumulation in the forest. Taking into consideration the latter aspect, a method of selection and analysis of the density of wood in dry wood (standing and lying) with different rates of decay is proposed. The density of wood provides valuable information necessary to calculate the carbon content in dry wood. The method was applied to seven species of alpine species (fir, spruce, European pine, European black pine, pine, European larch, and beech) localized in several valleys of the province of Trentino in northeastern Italy. Laboratory analysis of a sample of dry wood determined the humidity, and density of fresh and dry wood. Humidity in logs was much higher than in snags; moreover, this value decreased from the first to the third class of decay, and then increased from the third to the fifth grade. Dry density decreased at a constant rate from lower to higher decay classes. For all species, the maximum percentage of reduction in dry density is between the fourth and fifth classes of decay. The cited study provides a preliminary set of data on the density of dry wood, above all, taking into consideration the increasing importance of the carbon content closely related to that attribute.

Thus, our review of scientific literature [4, 6, 8–10] has established that the drying of the wood changes the structure and properties of wood, including physicochemical ones. All this gives grounds for conducting a study into determining the parameters that ensure the use of such wood.

3. The aim and objectives of the study

The aim of this work is to identify patterns of reduction in the mechanical performance of pine wood during drying and changing its structure. That will make it possible to justify the possibilities of expanding the scope of application of dry wood products.

To achieve the set aim, the following tasks have been solved:

– to study the mechanical properties of pine wood under the influence of changes in its structure during drying;

– to examine the structure of pine wood during its drying and dry pine wood affected by the fungus of the family *Ceratostomaceae*.

4. The study materials and methods

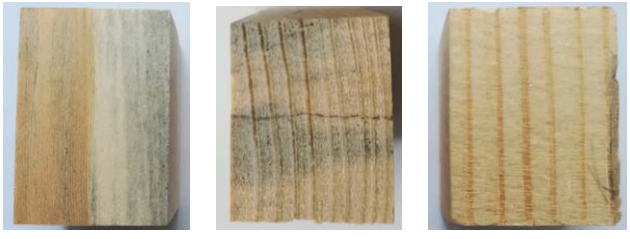
4. 1. The study's object and hypothesis

The object of this study is a change in the properties and structure of pine wood during drying. The scientific hypothesis implies a comprehensive study of changes in the mechanical properties and structure of pine wood affected by drying out to justify the conditions for its use.

4. 2. The examined materials used in the experiment

Samples of dry pine wood, dry pine wood affected by a fungus of the *Ceratostomaceae* family, and samples from undisturbed drying pine stands (ordinary) were used for our research. The sample size was 20×20×30 mm (Fig. 1).

The samples were dried to a moisture content of 5 %. The density of the samples from dry pine wood at a humidity of 12 % was about 385 kg/m^3, that of the samples of ordinary pine wood was 443 kg/m^3, respectively.



a *b* *c*

Fig. 1. Model samples: *a* — dry pine wood; *b* — wood from dry pine trees affected by a fungus of the family *Ceratostomaceae*; *c* — wood from undisturbed drying stands

To determine the possibility of using wood as building structures, mechanical tests were carried out on samples of ordinary pine wood and dry pine wood with varying degrees of damage by the fungus of the *Ceratostomaceae* family. Specifically, damage volume up to 10 %, within 30÷50 %, and 80÷100 %.

4. 3. Methods to study wood properties and its structure

To determine the regularities of changes in the structure of dry wood and from undisturbed drying of wood stands, physical and mechanical properties were determined, in particular, bending strength. And we also determined changes in its structure by a Fourier transform infrared spectroscopy (FTIR) and identified them through thermogravimetric analysis and heat of combustion.

Determining the bending strength of wood was carried out according to ISO 13061-3:2014 [12].

The Fourier transform infrared spectroscopy (FTIR) was performed taking into consideration [13]. Research method: 0.5 mg sample crushed with 70 mg potassium bromide (chipped from a single crystal). From the resulting mixture, the tablet was compressed under a pressure of 10 MPa, achieving maximum optical transparency (to reduce scattering). The spectrum is recorded in the range of 4000–400 cm^{-1}, with an optical slit width of 4 cm^{-1}, the spectrum was averaged over 12 scans. The analysis was performed on the Spectrum One (Perkin Elmer) spectrometer (USA).

Thermogravimetric analysis was carried out in accordance with [14]. In order to determine the region of temperatures at which thermal destruction of wood occurs most intensively, a thermogravimetric study of destruction processes under a dynamic mode was carried out. For this purpose, equipment was used involving the TA (thermal analysis) Instruments (USA) research station with the TGA module (thermogravimetric analysis) – TGA Q50.

Determining the heat of combustion was carried out in accordance with [15]. The studies were conducted on the automatic calorimeter ICA C6000 isoperibol (Germany). Samples of pine wood had the shape of a cube with a side of 10 mm. The mass of the wood sample in each study was 0.3 g, weighted to an accuracy of the fourth sign. The combustion of the sample took place in a tank for decomposition in the atmosphere of pure oxygen, which was supplied to the calorimeter under a pressure of 4 MPa. The test mode was isoperibolic at a constant temperature of 22 °C. Ignition of a wood sample took place using a cotton twist. The resulting values of higher calorific values are the arithmetic mean of three parallel experiments with a relative standard deviation RSD not exceeding 0.03 %.

5. The results of studies of the properties of wood and its structure

5. 1. The results of studies of the mechanical properties of dry pine wood

The results of determining the bending strength of wood are shown in Fig. 2.

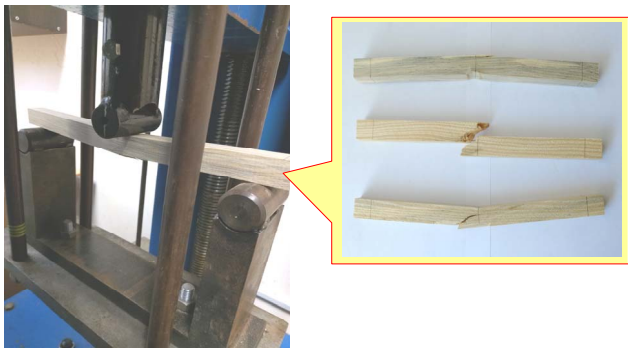


Fig. 2. Determining wood bending strength

Samples of regular pine and dry pine wood are characterized by crushing of fibers at the loading point with slight chipping (Fig. 2). In samples, the surface of which is 50 % damaged by blue, complete destruction is observed under the action of the load.

The results of determining the resistance of pine wood to bending depending on the level of fungal damage by the family *Ceratostomaceae* are given in Table 1.

Table 1

The strength of wood samples for static bending

Sample material	Dimensions of the sample, mm			Maximal load, N	Tensile strength, MPa
	width	thickness	length		
Pine	19.92	19.96	300.00	1951.05	89
Dry pine (up to 10 %)	19.92	20.12	300.00	1640.18	73
Dry pine (30÷50 %)	20.18	20.35	300.00	1568.88	68
Dry pine (80÷100 %)	19.97	20.22	300.00	1838.25	81

Note: up to 10 %, 30÷50 %, and 80÷100 % – the level of damage to the surface by bluish wood

As a result of our research, it was found that with a slight level of fungal damage, pine wood becomes brittle, so the tensile strength decreases by more than 1.2 times. With an increase in the fungal damage to the area within 30÷50 %, the tensile strength decreases by more than 1.3 times, and if the fungus affects the area within 80÷100 %, the wood becomes softer, more plastic while the tensile strength decreases by 1.1 times.

5. 2. Results of studying changes in the structure of pine wood during drying

Fig. 3 shows the IR spectra of the studied wood samples.

Further description of the obtained IR spectra is given taking into consideration the absorption bands of wood components: cellulose, lignin, and the representative of hemicellulose – 4-O-methylglucouronoxylane [25, 26].

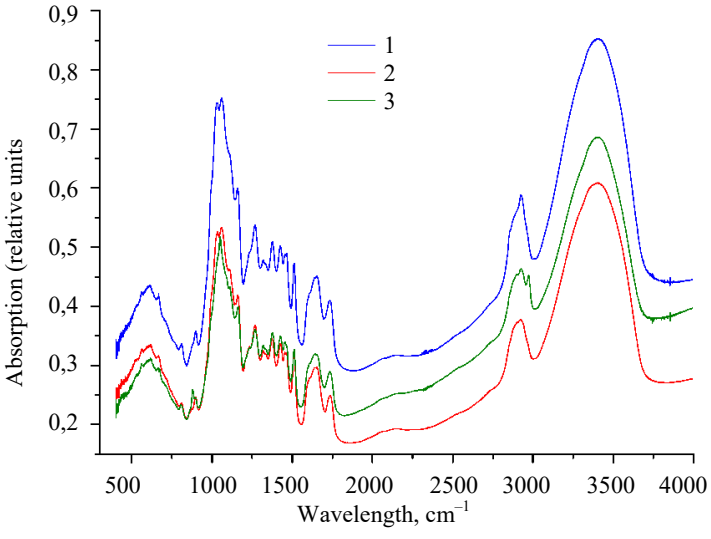


Fig. 3. Spectra of absorption of wood samples: 1 — dry pine wood affected by a fungus of the family *Ceratostomaceae*; 2 — dry pine wood; 3 — wood from undisturbed drying stands

The region of the IR spectrum of lignin, 3700–3100 cm^{-1}, is characteristic of valence oscillations of various types of hydroxyl groups. The frequencies of valence oscillations of aliphatic hydroxyl groups are somewhat higher than those of phenolic ones.

In the same region of the IR spectrum of cellulose, valence oscillations of hydroxyl groups are detected.

All hydroxyl groups of lignin and cellulose in the region of 3700–3100 cm^{-1} are involved in hydrogen bonds.

The xylene spectrum in the region of 3700–3100 cm^{-1} contains several types of hydrogen bonds. Hydroxyl groups that are included in the intramolecular H-bond have a characteristic absorption band in the range of 3570–3450 cm^{-1}, in the intermolecular – in the region of 3460–3100 cm^{-1}. The free OH group is manifested in the frequency range of 3700–3500 cm^{-1}.

In the region of 3000–2800 cm^{-1} of lignin, there are bands of valence oscillations of C–H bonds. It should be noted that the valence oscillations of aromatic C–H bonds have absorption bands in the region of 3100–3000 cm^{-1}. However, in the lignin spectrum, a wide band of valence oscillations of OH groups involved in hydrogen bonds is superimposed on this region. The region of 3000–2800 cm^{-1} characterizes the symmetric and asymmetric valence oscillations of C–H in methyl and methylene groups.

In the same region of 3000–2800 cm^{-1}, valence bond fluctuations in the methylene and methylene groups of cellulose are manifested.

In xylene, in the region of 3000–2800 cm^{-1}, valence oscillations of C–H bonds are manifested in the groups CH_3, CH_2 and CH with a maximum of 2930 cm^{-1}.

Bands in the region of 1800–1400 cm^{-1} of lignin characterize various valence oscillations of groups with multiple bonds (C=O, C=C, Car–CAr). In addition, in this region there are bands that are caused by deformation oscillations of the C–H bonds and other groups.

The region of 1500–900 cm^{-1} of cellulose spectra is partially superimposed on the region of 1800–1400 cm^{-1} of lignin and characterizes various fluctuations of C–H-, C–O-, and O–H bonds, fluctuations in the glycosidic bond and glucopyranose ring of cellulose.

Xylene in the region of 1800–1400 cm^{-1} is characterized by oscillations of groups C=O in acetyl groups (1740–1730). Deformation oscillations H–O–H of crystallization water (1650–1630), COO – asymmetric valence (1600), CH_2-scissor asymmetric deformation (1465), CH^2-symmetric deformation (1425), and COO – symmetric valence (less intense than asymmetric).

The region of 1400–1000 cm^{-1} of the lignin spectrum characterizes various valence oscillations of C–C- and C–O bonds, deformation oscillations of the C–H bonds, and OH groups. Absorption bands of 1376–1325 and 1220–1170 cm^{-1} refer to the deformation oscillations of O–H bonds in phenols and valence oscillations of C–O bonds. The bands of 1270, 1230, and 1130 cm^{-1} in guaiacol compounds and 1335 and 1235 cm^{-1} in syringic derivatives are caused by valence oscillations of the ring and C–O bonds. The bands of 1160 and 1040 cm^{-1} in guaiacol and syringic derivatives are referred to as deformation oscillations of the C–H bonds of the aromatic ring. In the region of 1150–1000 cm^{-1}, bands of absorption of valence oscillations of C–O bonds characteristic of primary, secondary, and tertiary OH groups are manifested.

In the region of 988–960 cm^{-1} of lignin, deformation oscillations of the C–H bond are manifested during a double bond in the trans position. In the region of 900–750 cm^{-1}, extraplanar deformation oscillations of the C–H bonds of the aromatic ring are manifested. Two bands are manifested in guaiacol compounds that characterize the oscillations of one or two hydrogen atoms – 880–850 cm^{-1} and 855–800 cm^{-1}. Syringic compounds have a band of 860–830 cm^{-1}, which refers to the deformation oscillations of one hydrogen atom. All these bands have very low intensity.

In the spectrum of cellulose in the region of 860–400 cm^{-1}, a wide blurred absorption is observed, against the background of which a number of fuzzy absorption bands are recorded, characterizing various oscillations of the pyranose ring and deformation oscillations of hydroxyl groups.

In the xylene spectrum, deformation symmetrical oscillations of CH_2 appear at 1465 cm^{-1}. Deformation oscillations of OH groups appear at frequencies of 1440, 1365, 1350, and 1245 cm^{-1}. The presence of a C–O–C bond between acyl groups and carbohydrates is manifested at 1260 cm^{-1}. The band of 1160 cm^{-1} is attributed to the asymmetric valence oscillation of the bridge between xylo-pyranose units. The band of 1115 cm^{-1} characterizes the valence oscillations of the C–O bond of the secondary alcohol group CH–OH. The band of 1085 cm^{-1} is referred to as the valence oscillation of the C–O-bond in the C_3H–OH group. A band of ~900 cm^{-1} in the xylene spectrum characterizes the configuration at the first carbon atom of the pyranose ring. Extra-plane deformation oscillations of hydroxyl groups lie between 770–650 cm^{-1}.

Discrepancies in the IR spectra of the studied wood samples. On the IR spectrum (3), a region of 2980–2970 cm^{-1} is manifested with a maximum absorption band at 2975 cm^{-1}, which is absent on spectra (1, 2). The analysis of the groups showed that this absorption region is caused by asymmetric valence oscillations of C–H bonds in methyl lignin groups.

Also, on the IR spectrum (3) there is a region of 890–850 cm^{-1} with a maximum absorption band at 880 cm^{-1}, which manifests itself on spectra (1, 2) in the form of an arm. This region is characterized by oscillations of one hydrogen atom in the guaiacol compounds of lignin.

The band of ~900 cm^{-1} in spectra 1,2 (spectrum 3 is of very low intensity) of cellulose characterizes the asymmetric oscillation of the ring and the oscillation of the C^1 atom and the four surrounding atoms in the spectra of β-glycosidic structures.

On the IR spectra (1, 2) in the region of 1150–1000 cm^{-1}, there are not clearly separated two bands with absorption maximums at 1025 cm^{-1} and 1065 cm^{-1}, which are absent on the IR spectrum (3) or their intensity is very low. Instead, on the 3rd spectrum, an absorption band appears with a maximum at 1045 cm^{-1}.

Absorption bands at 1065 cm^{-1}, 1025 cm^{-1} of lignin characterize asymmetric and symmetric valence oscillations of C–O–C bonds in aliphatic ethers.

A band of 1045 cm^{-1} characterizes the C–O valence oscillations of 4-O-methyl-glucuronoxylane.

In addition, in the cellulose spectrum, the band at 1060 cm^{-1}, which is referred to as the valence oscillation of the C–O bond in the C_3H–OH group, bands 1035 cm^{-1}, 1015 cm^{-1}, and 1000 cm^{-1}, is characteristic of the valence oscillations of the C–O bond in the primary alcohol group in various conformations. These bands are superimposed on the absorption bands of lignin and 4-O-methylglucouronoxylane.

The infrared spectrum of wood is not just the sum of the absorption bands of its individual components but also contains bands that characterize the bonds that exist between the macromolecules of cellulose, lignin, and hemicellulose. To determine the individual characteristics of the reduced wood, it was identified by thermogravimetric analysis.

Graphic images of thermogravimetric analysis of wood samples are shown in Fig. 4.

Analysis of the obtained TGA results for wood samples shows that from the beginning of heating (20 °C) to 100 °C, the TG curves reflect the loss of unbound water samples, the main volume of which is released in the range of 40–50 °C (DTG curves). Further, on the TG and DTG curves from 100 °C to 200 °C, there is a slow decomposition of the components of wood, in particular, less stable hemicelluloses. After 200 °C and up to about 400 °C on the TG curves, there is a sharp increase in destructive processes in lignin, cellulose, hemicellulose residues, with a maximum loss of sample mass of about 340 °C. As well as the formation of a coke residue that burns out at temperatures above 400 °C. Burnout of the coke residue is characterized by highs of different temperature values and the shape of peaks on the DTG curve. These features indicate a different qualitative (H/C ratio) and quantitative chemical composition of the coke residue, namely polyaromatic hydrocarbons. Upon reaching 700 °C, dry wood burns out completely, and samples 1 and 3 have unburnt inorganic residues.

To obtain complete information on the combustion of wood, its heat of combustion was determined. The results from determining the highest calorific value are given in Table 2.

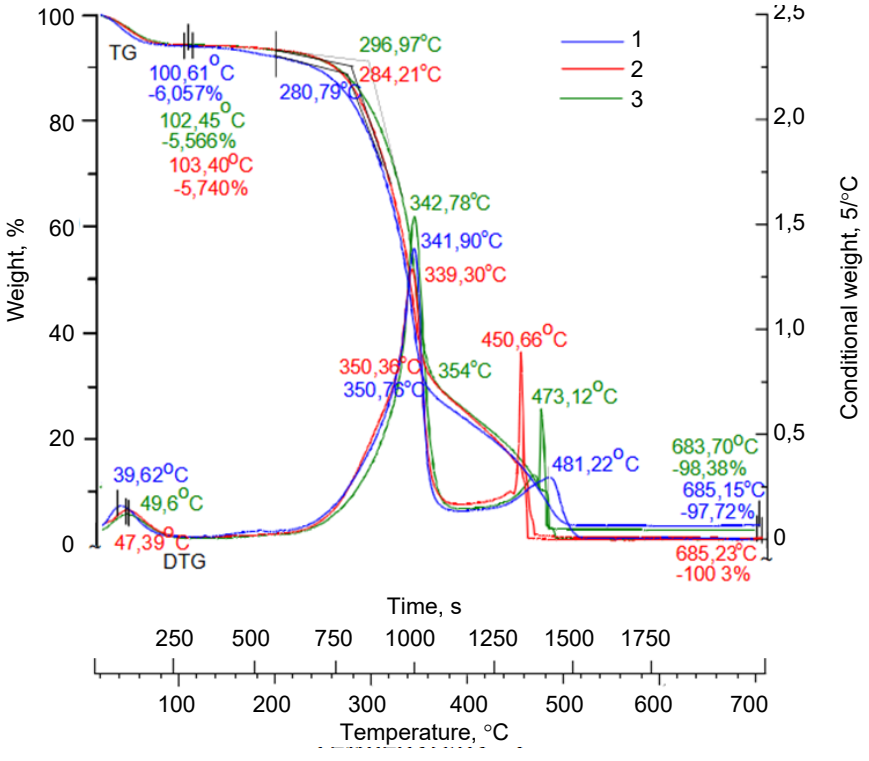


Fig. 4. Thermogravimetric analysis curves for wood samples: 1 — dry pine wood affected by a fungus of the family *Ceratostomaceae*; 2 — dry pine wood; 3 — wood from undisturbed drying stands; TG — mass loss curve depending on the increase in temperature; DTG — differentiated TG curve

Table 2

The value of the highest calorific value

Wood sample	Highest calorific value Q_{HHV}, MJ/kg
pine wood from stands not weakened by drying	18.7
dry pine wood affected by a fungus of the *Ceratostomaceae* family	19.3
dry pine wood	20.1
dry pine wood 3 years of drying	20.5
dry pine wood 5 years of drying	20.7

Table 2 demonstrates that dry pine wood has the greatest value of the highest calorific value since it has lost free, chemically unbound, hygroscopic water. Water loss is a consequence of the drying out of weakened trees caused by pathological processes that take place from fungal damage, the colonization of the tree by various pests, etc. Regarding the sample of dry pine wood affected by a fungus of the *Ceratostomaceae* family, the intermediate value of the higher calorific value can be explained by the fact that the fungus is forced to gradually give its moisture to the wood. A humidity of 24–30 % is not favorable for the development of fungi because, under these conditions, the mycelium penetrates the wood to a depth of 10–20 mm. Humidity in the range of 50–90 % is optimal for *Ceratostomaceae*. At a humidity of 110÷130 %, fungi develop well on wood with a volumetric weight of less than 0.40, and on wood with a volumetric weight of more than 0.40, their growth energy weakens.

Thus, fungi for their reproduction give their moisture to dry wood, which, in turn, reduces the highest calorific value. There was a difference in the highest calorific values for the studied wood samples, ~1 MJ/kg.

Taking into consideration the results of determining the heat of combustion of pine wood (Table 2), statistical processing of the results was carried out using a three-factor simplex-central method of experiment planning in the mathematical environment Statistica 12.

As factors of variance, we selected wood density, kg/m^3 (factor X_1), and the number of years of drying (factor X_2) (Table 3).

Table 3

Variance factors

Factor	Code	Level of variance			Range of variance
		–1	0	+1	
the number of years of drying	X_1	0	2.5	5	2.5
wood density, kg/m^3	X_2	350	400	450	50

As the initial parameter (response function), the heat of combustion of the material was chosen, the value of which was recorded on samples exposed to fire. The experiment planning matrix and its mathematical implementation are given in Table 4.

As a result of modeling, regression equations were derived and ternary surfaces of changes in the output parameter were constructed depending on changes in variance factors (Fig. 5).

Regression equation:

$$Y_{calc} = 18.62 + 1.10X_1 - 0.52X_2 + \\ + 1.29X_1^2 - 0.66X_2^2 - 0.35X_1X_2. \quad (1)$$

Based on our computer simulation, the best value of wood density was determined, which provides the highest value of the heat of combustion of wood, which is obtained at a density of 375 kg/m^3 and the number of years of drying of about 5.

Table 4

Experiment matrix and its implementation

No. of entry	Factor, form		Planning matrix		Response function	
	X_1	X_2	the number of years of drying	wood density, kg/m^3	Y actual	Y estimated
1	1	1	5	450	20	19.48
2	1	–1	5	350	20.7	21.21
3	–1	1	0	450	18.7	17.98
4	–1	–1	0	350	18	18.31
5	1	0	5	400	21	21.01
6	–1	0	0	400	18.4	18.81
7	0	1	2,5	450	16.2	17.44
8	0	–1	2,5	350	19.3	18.47
9	0	0	2,5	400	18.2	18.62
10	0	0	2,5	400	19.8	18.62
11	0	0	2,5	400	19.1	18.62

6. Discussion of results of studying the properties of dry wood

In the study of the bending strength of pine wood, as follows from our results (Fig. 2, Table 1), the process of reducing the resistance of dry pine wood to bending depending on the level of damage by the fungus of the *Ceratostomaceae* family of dry wood is natural. This is due to a change in the structure of the wood during drying, which shows a decrease in density. Thus, the data obtained by the method of IR spectroscopy with a Fourier transform indicate minor structural changes in cellulose, lignin, and xylene, which are associated with the intramolecular restructuring of wood components and changes in intermolecular bonds between them.

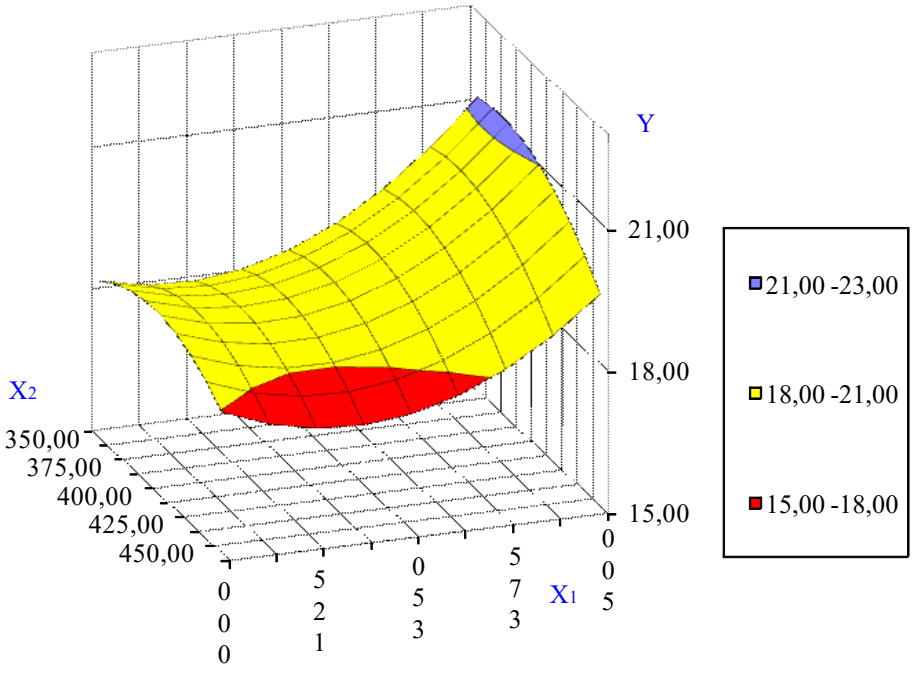


Fig. 5. Ternary surfaces of changes in the output parameter depending on changes in the factors of variance of wood density

It should be noted that a decrease in the density of wood is associated with a change in the structure of dry wood, which decreased at a constant rate from lower to higher decay classes. It is evident that such a mechanism of decomposition of wood is the factor in regulating the process due to which the thermal decomposition of dry wood increases. In this sense, there is an interpretation of the results of thermogravimetric analysis, namely the loss of mass of samples after thermal decomposition. When it reaches 700 °C, dry wood burns out completely, and samples of dry pine wood of the fungus-stricken family *Ceratostomaceae*, and wood from unaffected drying stands have unburnt remnants of inorganic nature. This indicates a different qualitative (H/C ratio) and quantitative chemical composition of the coke residue, namely polyaromatic hydrocarbons.

This means that taking this fact into account opens the possibility for effective use of wood directly under the conditions of industrial application.

A comparison of experimental studies on changes in the structure of wood during drying and studies to determine the thermal decomposition of wood indicates an increase in the heat of combustion. Since the heat of combustion of wood from undisturbed drying of wood stands did not exceed 18.7 MJ/kg (Table 2). This does not diverge from practical data well known from works [3, 7], the authors of which, by the way, also associate a decrease in the density of dry wood with a change in structural composition. However, unlike the results of studies reported in [6, 8], the data obtained on the effect of drying on the properties of wood, in particular, on bending, make it possible to assert the following:

– the main regulator of reducing the bending strength of dry wood is a change in the structure in the components of the wood;

– biological processes have a significant impact on the process of drying wood (damage by microorganisms, apoptosis, etc.).

Consequently, the formation of bacteria in the structure of wood is closely related to a decrease in its density, which is confirmed in [16]. At the same time, it is possible to carry out thermal modification of such wood in order to stop the development of a fungus of the *Ceratostomaceae* family or the use of antiseptics [17, 18].

Such conclusions can be considered appropriate from a practical point of view because they allow a reasonable approach to determining the heat of combustion of dry wood. This suggests the definition of the mechanism of wood drying processes, which are certain advantages of this study. From a theoretical point of view, they make it possible to argue about the definition of the mechanism of processes both reducing mechanical properties and changing the structure of wood during drying out, which are certain advantages of this study.

However, it is impossible not to note that the results of determining (Fig. 3) indicate an ambiguous effect of changes in the structure of wood on thermal decomposition. This is manifested, first of all, in the increase in the mass of the sample during the testing of wood from undisturbed drying of the stands. Such uncertainty imposes certain restrictions on the use of our results, which can be interpreted as shortcomings of the current study. The inability to remove these limitations in the framework of this study points to a potentially interesting area for further research. In particular, it can be focused on identifying the time point from which an intensive decrease in the density of wood begins. Such detection could make it possible to investigate the structural transformations of wood that begin to occur at that time and to determine the input variables of the process that significantly affect the onset of such a transformation.

7. Conclusions

1. Resistance to bending pine wood shows that when the wood shrinks, the tensile strength decreases depending on the degree of damage by the fungus. Namely, with an area within 30÷50 %, the strength limit decreases by more than 1.3 times, and if the fungus affects the area within 80÷100 %, the wood becomes softer, and more ductile while the strength limit decreases by 1.1 times. At the same time, samples of regular pine and dry wood are characterized by crushing of fibers at the loading point with slight chipping, and for samples whose surface is 50 % affected by the fungus, complete destruction is observed under the action of the load.

2. Based on our results of physicochemical studies, the following conclusions can be drawn:

– the revealed discrepancies in the IR spectra indicate structural changes in the constituent components of wood – a decrease or absence of intensities of absorption bands of some functional groups and the appearance or intensification of others;

– wood samples in determining the highest heat of combustion show a slight but noticeable difference in values, which is explained by structural changes in wood components caused by biological processes (damage by microorganisms, apoptosis, etc.);

– thermogravimetric analysis data indicate complete burnout of dry pine wood. Wood with undisturbed drying stands behaves in a similar way, although its coke residue burns out at a higher temperature than in dry wood. Wood with blue pigmentation affected by microorganisms has significant differences from dry wood and wood with undisturbed drying of stands in the region of heating 400–700 °C. The nature of the burnout of the coke residue in wood samples allows us to make assumptions about the different qualitative and quantitative composition of the coke residue, which is formed due to structural changes in wood components.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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