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DEFINING THE PATTERNS OF WOOD FLAMMABILITY REDUCTION CONSIDERING COMBUSTION PROCESSES AND THERMAL OXIDATIVE DESTRUCTION

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This study explores the mechanism and processes behind thermal oxidative destruction and the formation of char and pyrolysis layers in wood.

The task addressed is to establish patterns of wood combustibility and features in the formation of pyrolysis and char layers at heating in order to improve the effectiveness of fire protection.

The experimental results established that for untreated wood the average depth of the pyrolysis layer is 4 mm for birch and 7 mm for pine, while the char layer reaches 8 mm and 12 mm, respectively. When applying a fire-retardant coating, these values decrease to 1 mm (pyrolysis) and 2 mm (char) for birch, and to 2 mm (pyrolysis) and 4 mm (char) for pine. Thus, the use of fire-retardant compositions leads to a reduction in the depth of thermal oxidative destruction by 3–4 times and a significant decrease in the intensity of char formation.

The findings indicate that fire-retardant coatings modify the mechanism of thermal decomposition of wood, limit heat and mass transfer processes, reduce the release of combustible gaseous products, as well as promote the formation of a thinner but more stable protective char layer.

A quantitative relationship between the depth of pyrolysis and char layers and the type of wood (birch, pine) under surface fire-retardant treatment has been established. The results show a reduction in combustibility parameters compared to untreated samples.

The findings could be used in the design and optimization of fire-retardant compositions, as well as for improving fire protection measures for wooden structures

Keywords: pyrolysis zone, thermal oxidative destruction, charring rate, fire-retardant coatings

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1. Introduction

Ensuring the safety of construction sites and their structural elements from fires, reducing fire hazard while simultaneously protecting against the negative effects of harmful insects, fungal, and other wood diseases, is a complex task. Solving it is associated with issues of chemical kinetics: homogeneous-heterogeneous combustion mode, thermal destruction, gasification of products, as well as with issues of inhibition of both chemical and physical reactions in fire protection of products. Establishing the mechanisms of heating wood during combustion, the processes of thermal destruction of wood and coatings applied to its surface makes it possible to devise effective measures to reduce its combustibility.

In order to reduce the pyrolysis zone under the influence of fire, it is necessary to use fire-retardant combinations of substances that can act in parallel in several directions, which ensure the reduction of the pyrolysis zone to a minimum. At present, there are many fire-retardant combinations that provide reliable fire protection with deep impregnation, double or triple application, under conditions of aging in autoclaves. Currently there are no fire-retardant compositions that would provide effective fire protection with a single-layer application due to the combined action. Accordingly,

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determining the patterns of wood flammability taking into account the features of its combustion and thermal oxidative destruction is a complex scientific and technical task, the implementation of which requires analyzing thermal oxidative destruction and the process behind formation of charring and pyrolysis layers.

Increasing the efficiency of fire protection of wood and determining these features will indicate ways to ensure high-quality fire protection of wood with a substance that is applied to the surface of wood in one layer and in the form of putty. Therefore, studies aimed at establishing features of thermal oxidative destruction of wood and the influence of fire-retardant compositions on its combustion processes are relevant. This is confirmed by fires in which wooden structures treated with fire-retardant compositions lose their load-bearing capacity more slowly during combustion, which makes it possible to increase the time for evacuation or extinguishing. It should also be noted that this problem is especially relevant now during the war, when almost every hit ends in a fire of wooden structures, which is confirmed by analytical data on 23–25 years [1].

If we compare the data, the total number of fires has increased by more than 2 times and almost every fire involves burning wood. In addition, it is important to ensure the proper operational characteristics of wood, in particular, preserving its integrity. At the same time, wooden structures must comply with domestic DBN V.1.1-7 and DSTU-N B EN 1995-1-2, and European ISO 834, EN 1363, the requirements of which are generally reduced to one thing – wood must lose minimal weight when exposed to fire.

Regarding the issue of fires in other countries, it should be noted that in the countries of Scandinavia, the Balkans and, for example, Japan, dozens of fires occur every year in religious and other wooden structures [2–4]. Work [2] indicates that these cultural monuments are very vulnerable to fire. Therefore, when a fire occurs inside such a cultural monument, it is not enough to prevent it from burning out or spreading to other buildings. It is extremely important to suppress the fire at the earliest stage in order to protect the cultural monuments inside. During the fire at Surijo Castle in Japan on October 31, 2019, a security guard went to the source of the fire shortly after the heat detector was activated but was unable to begin initial extinguishing due to the already dispersed smoke. In [3], a temporal analysis of fires in wooden structures that occurred from 2010 to 2014 in rural settlements in Serbia (Žabal, Žitište) and in the urban area of Novi Sad from 2011 to 2013 was conducted.

Paper [4] reports the results of the project "Can we learn from the loss of heritage in fire?", within the framework of which Finland, Norway, and Sweden exchanged experience and knowledge on fires and fire protection of historical buildings. Based on this, it should be noted that this is only a small number of studies that describe fires in wooden structures for various purposes. Given the fairly recent data of those publications, we can conclude that fire protection of wood is extremely relevant now.

Thus, based on a significant number of fires, research aimed at establishing the regularities of wood flammability, the processes of its thermal-oxidative destruction, and the design of effective fire-retardant compositions with a combined effect, which implies more effectively blocking gas evolution and the formation of a stable foam-coke layer, is relevant.

2. Literature review and problem statement

The issue of wood combustion and reducing its combustibility has been actively studied over the last decade due to the increased demand for timber as an inexpensive, widespread, and operationally advantageous building material. A significant part of the work is focused on the kinetics of pyrolysis of lignocellulosic components, the mechanisms of carbon layer formation, and the design of flame retardants and intumescent coatings. Thus, in [5], modern approaches to modeling pyrolysis and mechanisms of fire protection of wood were analyzed. The authors considered in detail the stages of thermal destruction and the role of phosphorus-containing flame retardants; however, the issue of the relationship between the kinetics of pyrolysis, heat and mass transfer, and the rate of carbon layer formation, as we can see from our analysis, was left at the level of qualitative description.

Quantitative models do not simultaneously integrate oxygen diffusion, ash layer growth, and heat balance in real fire conditions. In work [6], a deep morphological and structural characterization of the wood combustion process was carried out, including the heterogeneous combustion phase, which is emphasized the most. It was shown that the reactivity of the layer significantly depends on the pyrolysis conditions. At the same time, the work does not consider the macroscale thermal conductivity of the layer and its influence on the rate of heating of wood during flame combustion. Thus, the microstructural results are not related to the engineering parameters of fire hazard.

In [7], the authors investigated the effect of pyrolysis temperature on the chemical and reaction properties of biochar. They found that increasing the temperature contributes to an increase in the degree of aromatization of the structure. However, the issue of predicting the rate of charring under conditions of variable heat flux and limited oxygen diffusion remains unresolved.

In [8], the effectiveness of intumescent coatings for wooden structures was considered. A decrease in heat flux and charring rate was shown. However, the mechanistic relationship between the kinetics of thermal oxidative destruction of the base and the performance of the coating is presented fragmentarily. At the same time, in studies that consider the use of thermosetting resins, it was found that their use can contribute to the formation of a protective carbon layer. In particular, the authors of [9] argue that phenolic resins intensify carbonization processes and contribute to the formation of a heat-insulating layer of coal when the ignition temperature is reached, which improves the fire-retardant properties of wood.

The authors of [10] additionally established that the modification of wood with phenol-formaldehyde and melamine-formaldehyde resins increases its thermal resistance, which is confirmed by the results of thermogravimetric analysis: the presence of aromatic structures in the resins causes their decomposition at higher temperatures and, accordingly, slows down the thermal-oxidative destruction of the material. Paper [11] established that the modified samples are characterized by a lower charring rate and the formation of a denser layer of pyrolysis carbon, which provides an additional thermal insulation effect and improves the fire-retardant properties of wood.

Most studies focus on the effective indicators (time to ignition, depth of charring) but do not build a generalized

physicochemical model of the process. At the same time, one of the key parameters is the charring rate, which, according to the authors of [12] is defined as "the distance from the initial surface of the material to the boundary of the carbon layer, referred to the time of thermal exposure." Despite the widespread use of this indicator, its relationship with pyrolysis kinetics and heat and mass transfer processes often remains poorly substantiated.

The authors of [13] investigated the kinetics of carbon oxidation in flow conditions at high temperatures. The resulting kinetic parameters are relevant for describing the heterogeneous combustion stage; however, these results were obtained on model samples and do not take into account the complex multilayer structure of wood and the influence of its humidity. In [14], the chemical structure of the wood cell wall as a three-dimensional biopolymer composite formed by cellulose, hemicelluloses, and lignin was considered. It was shown that the ratio of these components determines the physicochemical properties of wood, but the direct connection with the processes of pyrolysis and charring was not detailed. In [15], the features of the pyrolysis of the main components of wood – cellulose, hemicellulose, and lignin – were investigated. It has been established that hemicellulose decomposes at lower temperatures, while cellulose and lignin are characterized by different thermal stability, but the interaction of these components under real combustion conditions is described to a limited extent.

Our review of the literature [5–15] allows us to highlight a number of unresolved issues, namely, the lack of an integrated model that simultaneously takes into account the kinetics of pyrolysis of lignocellulosic components, thermal conductivity and heat capacity of wood, oxygen diffusion through the ash and carbon layers, as well as the mass burning rate, insufficient connection between microstructural studies of the carbon layer and engineering indicators of fire hazard (charring rate, pyrolysis depth). This is also due to the fragmentation of approaches to assessing the effectiveness of flame retardants since most works evaluate the final effect but do not explain how the mechanism of thermal oxidative destruction changes. At the same time, the reasons for the unsolved problem are both objective and methodological in nature. This is explained by the fact that there are objective reasons, such as the complexity of the multiphase process (simultaneous course of homogeneous and heterogeneous reactions), the anisotropic and porous structure of wood, and the nonlinear dependence of heat and mass transfer on temperature and air flow velocity.

Wood is a complex mixture of natural high-molecular polymers and a porous substance with a void volume of 50–75%. Its elemental composition is carbon 40–50%, hydrogen 5–6%, oxygen 39–47%, nitrogen 0.5–1.5%, trace elements up to 5%. The basic components are cellulose (≈50%), hemicellulose (≈25%) and lignin (≈25%), as well as absorbed moisture (4–7%) [10]. Cellulose is a high-molecular polysaccharide with the formula $(C_6H_{10}O_5)m$, while hemicelluloses are represented by a mixture of pentosanes, hexozanes, and polyuronides; their ratio differs for hardwood and coniferous wood species [11]. Lignin is a complex aromatic polymer compound, the content of which is 20–30% in hardwoods and up to 50% in coniferous wood [11], and its molar mass is several thousand a.u.m. [12]. Hemicellulose is the least heat-resistant component of wood, while lignin has the greatest thermal stability.

The authors of [16] emphasize that at lower pyrolysis temperatures, lignin is the main source of carbon residue formation. Therefore, wood species with a high lignin content are more heat-resistant. Thus, the problems identified in the analyzed works can be summarized as a general unsolved scientific problem. This problem is the lack of a scientifically substantiated comprehensive approach to reducing the combustibility of wood. The authors of [5] directly note that there is a very obvious lack of research in the form of review articles that cover all aspects of wood combustibility. Their study [5] confirms that the burning behavior of wood depends to a large extent on several factors, including species, moisture content, experimental conditions, density, heat exposure time, etc. However, it is quite clear that the combustibility of wood is a very complex process due to the fact that the three main components – cellulose, hemicellulose, and lignin – "degrade" at different temperatures.

Therefore, it is advisable to conduct a study on the integrated influence of the mechanisms of thermal-oxidative destruction, heat and mass transfer, and the formation of a protective carbonaceous foam coke layer and a possible gas-blocking mineralized shell, which would help maximally protect the wood surface under real fire conditions.

3. The aim and objectives of the study

The purpose of our study is to determine the patterns of combustion and reduction of flammability of wood, including wood treated with fire retardant compositions, taking into account the processes of its combustion and thermal oxidative destruction. This will make it possible to determine the initial conditions for designing new means of wood protection, with the simultaneous action of several mechanisms of wood protection, with maximum efficiency in preserving the structure of wood.

To achieve the goal, the following tasks were set:

– to quantitatively describe the two-phase combustion of wood using kinetic equations, to determine the factors influencing them, and to consider the role of the carbon layer as a regulator of the wood combustion process;

– to experimentally investigate the features of thermal oxidative destruction, to determine the depth of the pyrolysis and charring zones of untreated and treated with a fire retardant composition wood samples of different species and to establish the nature of their species dependence.

4. The study materials and methods

Object of our research: mechanism and processes behind thermal oxidative destruction and formation of charring and pyrolysis layers of wood.

The principal hypothesis assumes that the pyrolysis layer and the carbon layer are formed mainly after 2 minutes of burning. At the same time, scientific sources do not contain data on the influence of the flame retardant composition on the depth of the corresponding layers outside the standard tests, which is the basis for the theoretical and experimental determination of factors and parameters in the specified time range.

Our work assumes that wood is a homogeneous substance without internal defects or inhomogeneities, the chemical composition of the flame retardant does not change during the experiment and is evenly distributed in the thickness of the

wood. When conducting the experiment, the influence of air humidity, ultraviolet or mechanical loads was not taken into account. The simplification was also adopted that the temperature and intensity of the flame are assumed to be constant, and the thermal conductivity of wood is considered constant.

In order to determine the depth of the layers of heterogeneous combustion and pyrolysis of wood, a study was conducted with wood samples of standard sizes (Fig. 1) (bars 150 × 60 × 30 mm). Before testing, the material humidity was stabilized to 12 ± 2% in order to exclude the effect of water evaporation. Each sample was characterized by species, density, and fiber direction.

The test was carried out in a furnace (Fig. 2), the structure of which is given in GOST 16363-98, under the standard fire regime according to ISO 834. The temperature of the gas medium was raised to 500–600°C, and the duration of flame exposure was 15 minutes. The heat flux to the surface of the samples was kept within 35–50 kW/m^2, which simulates the effect of an open flame.

Fig. 1. Test furnace according to GOST 16363-98

After testing, the samples were cooled and cut perpendicularly to the surface. The depth of the charred layer was determined, characterized by a clear border of the black zone. The value was measured at several points on each sample, after which the average values were calculated. In addition to the charred layer, the depth of pyrolysis was recorded.

The results were processed by calculating the average values for each wood species and comparing them with the normative data according to EN 1995-1-2 (≈ 0.65 mm/min for conifers and ≈ 0.5 mm/min for hardwoods). Based on the data, the range of charred depths for the standard flame exposure time was determined.

5. Results of determining the regularities in a wood combustion process and experimental determination of pyrolysis and charring zones

5. 1. Features of the wood combustion process and the formation of pyrolysis and charring zones

The combustion of wood is significantly different from the combustion of other substances since it can occur under several modes at once: both homogeneous and heterogeneous. Therefore, two phases were distinguished during the combustion of wood: homogeneous (that is, flaming) combustion of decomposition products and heterogeneous oxidation of the solid carbon residue formed [14].

At the first stage, when an ignition source acts on the wood, the process of material decomposition, or pyrolysis, occurs, and several characteristic stages can be distinguished. The first stage is drying of the material at t = 110–130°C, followed by the decomposition of hemicellulose at t = 150–200°C. Then there is dehydration of lignin at t = 180–300°C and actual pyrolysis of wood at t = 250–450°C with the formation of carbonized structures and the release of volatile substances [14]. At the same time, the main mass (about 40% of the maximum possible amount) of combustible and non-combustible gases (CO_2, H_2, CH_4, C_2H_4, and so on) was released. The gas mixture that was formed is already capable of ignition from an ignition source. The concentration of pyrolysis products exceeds the lower concentration limit of flame propagation through volatile decomposition products. [15]. At the same time, under conditions of counter-diffusion of the oxidant, transient exothermic reactions of the following type occurred:

$$2CO + O_2 = 2CO_2 + 543 \text{ kJ/mol},$$

$$2H_2 + O_2 = 2H_2O + 242 \text{ kJ/mol},$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 891 \text{ kJ/mol},$$

$$C + H_2O = CO_2 + H_2 + 40.4 \text{ kJ/mol},$$

$$C_2H_4 + 2O_2 = 2CO_2 + 2H_2O + 1412 \text{ kJ/mol}.$$

The rate of release of gaseous products became equal to the rate of their diffusion combustion. In general, the rate of homogeneous chemical reactions that occur in a flame is expressed by the Arrhenius equation (1) [16]

$$\frac{dG_c}{d\tau_{hr}} = C_c^n * C_o^m * k_0 \exp\left(\frac{-E_a}{RT}\right), \quad (1)$$

where G_c – amount of reactant, mol/(m^3*s);

τ_{hr} – reaction time, s^{-1};

C_c, C_o – mass concentrations of combustible decomposition products and oxidant, mol/m^3;

k_0– pre-exponential factor, s^{-1};

R – gas constant, J/(mol*K);

E_a – activation energy J/mol;

T – absolute temperature;

n, m – stoichiometric coefficients of fuel and oxidant in the combustion reaction equation.

Based on equation (1), the reaction rate at the first stage of homogeneous combustion is determined by the mutual concentration of components in the reaction zone, the process temperature, and the activation energy. In this case, there is an autoregulation of the flame volume and the contact area of combustible products of thermal destruction with the oxidant [17]. Thus, taking into account the C_c, C_o coefficients and mass concentrations of combustible decomposition products and oxidant in equation (1), it was established that the combustion rate of mixtures (CO, C, H_2, CH_4) is determined by their content. Then for each reaction, equality (2) will be valid [17]

$$dG_i = C_i^{ni} * k_{0i} \exp\left(\frac{-E_a}{RT}\right) d\tau_{hr}. \quad (2)$$

The increase in the rate of release of pyrolysis products led to an increase in the flame volume and an increase in the area of contact of combustible products with the oxidant and vice versa. Thus, the concentration of the components of the combustible mixture in the combustion zone is approximately constant during the process under the conditions of the established diffusion and combustion regime [18]. The higher the temperature, the faster the pyrolysis process. The structural elements of coal condense more and more, forming flat lattices similar to the crystal lattice of graphite, at t = 500–600°C pyrolysis is completed, the yield of volatile products is sharply reduced, and a carbonaceous residue is formed [19].

The coal formed on the surface of the wood does not burn, although it is in an incandescent state; the combustion of coal during this period is prevented by the intense combustion of gaseous decomposition products, due to which oxygen cannot diffuse to the surface of the coal [14]. The carbon layer is a good thermal insulator, and as it thickens, it protects the inner layers of the material from the thermal effects of the flame; this is the principle behind the operation of intumescent coatings [21]. As the concentration of gaseous decomposition products decreases sharply, flaming combustion gradually ceases and oxygen access to the coal surface heated to ~600°C is opened. The second stage begins – heterogeneous oxidation of the carbon layer, in which the temperature can rise to 750–850°C [14]. The flaming combustion stage took a shorter time but was associated with the release of 55–60% of the heat, while the second phase gives 40–45% of the total heat release [5]. Heterogeneous processes occurred directly on the coal surface; the rate of the chemical reaction was determined by the local concentration of the oxidant and described by the corresponding kinetic relations (3) and mass transfer (mass transfer coefficient γ) [17]

$$\frac{dG_c}{d\tau_{hr}} = C_o^m * k_0 \exp\left(\frac{-E_a}{RT}\right). \quad (3)$$

The process of burning out the carbonized layer (recarbonization) included the following primary reactions:

$C + O_2 = CO_2 + 394$ kJ/mol,

$2C + O_2 = 2CO + 219$ kJ/mol,

as well as secondary reactions with CO_2 and H_2O (carbon reduction reactions), which are described in the literature with corresponding calorific values and kinetics [22]

$C + CO_2 = 2CO - 175.5$ kJ/mol.

The red-hot carbon reacted with water molecules present in the combustion products, or pyrolysis products, of the decomposition of the wood layers, which are below:

$C + H_2O = C + H_2 - 130.5$ kJ/mol,

$C + 2H_2O = CO_2 + 2H_2 - 132$ kJ/mol.

Free hydrogen released in previous processes can react with carbon to form methane or other hydrocarbons.

$C + 2H_2 = CH_4 - 79.4$ kJ/mol [23].

Carbon monoxide and hydrogen, which reached the coal surface, had the ability to burn under a homogeneous mode with the release of a significant amount of heat. The ash layer significantly limited the diffusion of oxygen to the surface, which makes the combustion diffusion-limited, and the rate of carbonization is approximately 0.1–0.2 mm/min under real conditions. Coming to the surface and mixing with air, carbon monoxide (CO) and hydrogen (H_2) burn under a homogeneous mode. This combustion is often visible as a bluish flame above the coal surface [24]. The thermal effect of the CO combustion reactions is given in the form:

$2CO + O_2 \rightarrow 2CO_2$ $\Delta H = -571$ kJ/mol,

$2H_2 + O_2 \rightarrow 2H_2O$ $\Delta H = -231$ kJ/mol.

These values are consistent with thermochemical tables and thermochemistry reviews [23].

Considering the formation of an additional resistance to the diffusion of the oxidant to the carbon layer by the ash layer on the wood surface and a decrease in the partial pressure of oxygen at the coal surface boundary, which accordingly leads to a diffusion-limited combustion regime [14]. From this it is concluded that if this process is improved, heterogeneous combustion will proceed at a lower speed and with the formation of a less heated layer of wood (up to 1–3 mm).

The plot below (Fig. 1) illustrates the dependence of carbon layer thickness δ angle (mm) on the linear pyrolysis velocity V_l (m/s). The plots (Fig. 2, 3) are constructed based on the results reported in study [10]. According to the thermal conductivity model, the thickness of the carbon layer is inversely proportional to the burning rate

$$\delta_{carb} = \alpha / V_l, \quad (4)$$

where $\alpha = 1.8 \cdot 10^{-7}$ m^2/s – effective heat transfer coefficient.

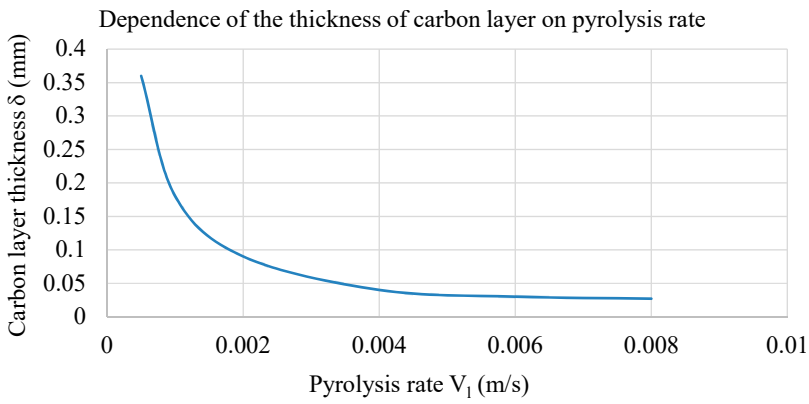


Fig. 2. Dependence plot of carbon layer thickness on pyrolysis rate [7]

The plot below (Fig. 2) [10] demonstrates the dependence of the pyrolysis temperature of wood on linear burning rate V_l. The calculation is based on the heat balance (5)

$$T(V_t) = T_0 + q_0 / (\rho \times c \times V_t) - Q_p / c, \quad (5)$$

where T_0 = 300°C – initial temperature;
q_0 = 20000 W/m^2 – heat flow;
ρ = 500 kg/m^3 – density;
c = 1800 J/(kg·K) – heat capacity;
Q_p = 250000 J/kg – heat of pyrolysis.

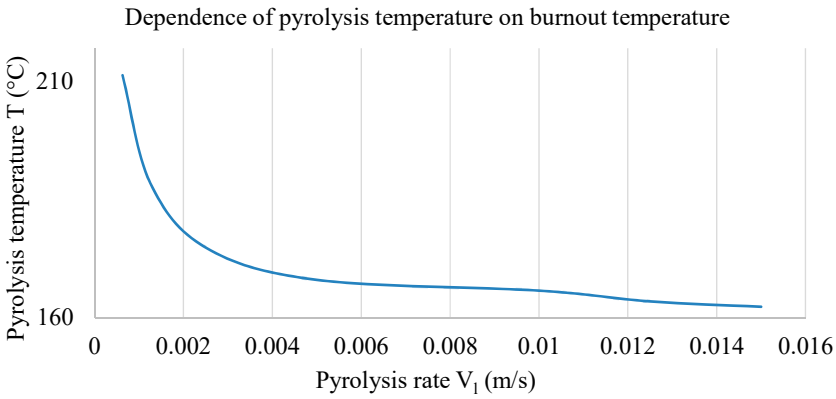


Fig. 3. Plot of pyrolysis temperature versus temperature [10]

The diffusion flow of air (Fig. 3) through the ash shell is described by the classical Fick law taking into account the effective diffusion coefficient D_i through the porous ash structure and the layer thickness T (6)

$$G_{1i} = \frac{D_i}{RT}\frac{p_{1\Delta}}{x_{\text{ash}}}. \quad (6)$$

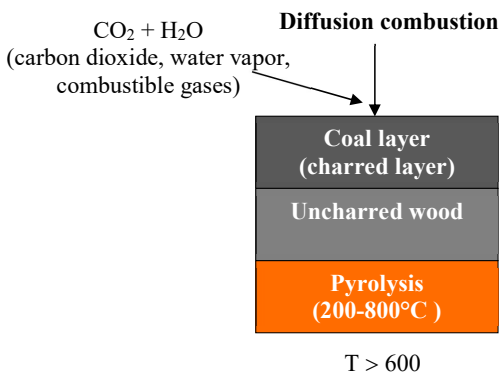


Fig. 4. Diffusion flow of oxygen through the ash layer

In the quasi-stationary approximation, the air flow to the surface is related to the rate of carbon burnup in the carbon layer (7)

$$G_{1i} = \rho_C \frac{dx_{ash}}{d\tau}, \quad (7)$$

which allowed us to obtain analytical expressions for the thickness of the ash layer (8)

$$x_{ash} = \sqrt{\frac{2D_i * p_{1\Delta}}{RT * \rho_C}\tau}, \quad (8)$$

and carbonization rates (9)

$$G_C = G_1 = \sqrt{\frac{D_i * p_{1\Delta} * \rho_C}{2RT * \tau}}, \quad (9)$$

at given physicochemical parameters of the material and convection conditions [23].

Thus, the practical conclusion from our analysis of the mechanism behind wood combustion is as follows. The ash layer increases the diffusion resistance, therefore, as it increases, the charring rate decreases in proportion to the increase in the ash thickness; this leads to a dependence of the rate on time, close to the inverse proportionality of the square of the process time.

In real fires, the rate of charring of wood is usually 0.1–0.2 mm/min but can increase with the intensification of the air flow that washes the surface and improves oxygen diffusion [14]. When studying the processes occurring during combustion, one of the important ones is the process of heat transfer in the combustion zone and heat release in the flame [20]. The heat released during exothermic reactions in the flame is spent on drying and further heating of the wood to the temperature of the onset of thermal destruction with the formation of gaseous products. The condition of heat and mass transfer between the combustion zone and the wood can be written in the form of the following equation

$$q_0 = v_v\left[c_p\left(T_p - T_o\right) + Q_p + Q_{s.c.}\right], \quad (10)$$

where q_0 – intensity of the flow coming from the combustion zone to the wood surface, W/m^2;

v_v – mass burning rate, kg/(m^2*s);

T_p, T_0 – pyrolysis temperature and initial surface temperature, °C;

Q_p, $Q_{s.c.}$ – heat of decomposition and heating of solid carbon residue, J/kg.

With steady burning on the wood surface, the constant temperature is T_{srf} = 923–1073°C. The temperature distribution in the depth of the material is described by the Michelson equation (11)

$$T_x = T_0 + \left(T_{srf} + T_0\right)\exp\left(\frac{-v_l * c_p * \rho * x}{\lambda_t}\right), \quad (11)$$

where λ_t is the thermal conductivity of the material, W/(mK);

ρ is the density of the material, kg/m^3;

c_p is the heat capacity of the material, J/(kg/K);

V_l is the linear burning rate, m/s;

T_x is the temperature at a depth x from the burning surface, °C.

Thus, along the depth of the burning wood, there are regions with different physical and physicochemical characteristics. They can be conditionally divided into four zones: 1 – charcoal, consisting of 99% carbon; 2 – wood with varying degrees of pyrolysis; 3 – non-pyrolysis dry wood; 4 – wood in its original state.

Table 1 gives generalized temperatures for the processes of thermal decomposition of wood.

Table 1

Characteristic temperatures for the combustion process

Process name	Index	Temperature, °C
Destruction temperature	T_d	653
Charring temperature	T_c	1423–1473

The increase in the thickness of the carbon layer leads to an increase in thermal resistance, and therefore to a decrease in the rate of heating and pyrolysis of wood. With a significant thickness of the carbon layer and the absence of convective air flows, self-extinguishing of the combustion

process is possible, which can occur with a significant density of wood. With a significant density, partial blocking of gas flows from the depth of the wood will occur and, accordingly, an increase in the carbon layer at the beginning of wood combustion.

Table 2 gives density and thermal conductivity data for different types of wood.

Table 2

Density and thermal conductivity of wood [10]

Wood species	Density (kg/m^3)	Thermal conductivity λ (W/(m·K))	Notes
Pine (Pinus)	500–550	0.12–0.15	Softwood, medium density, quick ignition
Birch (Betula)	600–650	0.14–0.17	Medium density, quick off-gassing

According to preliminary data in Table 2, it was found that the density of wood is one of the main factors that, taking into account equations (10) and (11), will affect the parameters of the pyrolysis and carbonization layers. Thus, for comparison and experimental determination of wood parameters, indicator wood species were selected – pine and birch, which have almost the same thermal conductivity of approximately 0.15 (W/(m K)), but slightly different densities. Pine – 500–550 (kg/m^3) and birch – 600–650 (kg/m^3).

The plot of thermal decomposition of common wood species is shown in Fig. 4.

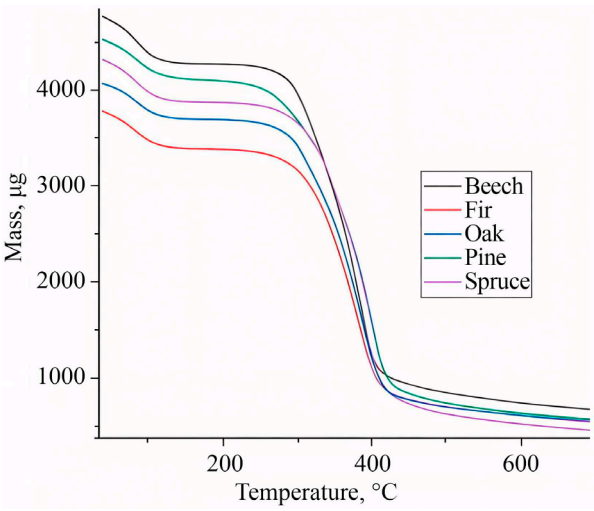


Fig. 5. Thermal decomposition plot of wood species [5]

As can be seen from Fig. 5, approximately all wood species had different pyrolysis rates but, at temperatures above 250°C, this value becomes almost the same for all wood species. At the same time, the average depth of the pyrolysis layer of wood is from 15 mm to 28 mm for pine and beech, respectively (Table 3).

It was established that the aforementioned processes are influenced by the density, thickness of the pyrolysis and charred layers, as well as the rate of diffusion of pyrolysis gases through them. Based on this, the indicator species pine and birch were selected due to their difference in wood density. If we take into account hard wood species, then based on the data given in Table 3, the depth of the pyrolysis layer is somewhat greater than that of species with low density. It was established that the most significant factors affecting the wood combustion process are the rate of diffusion of gaseous products from the pyrolysis and charring zones, based on the equations of Michelson et al. Accordingly, the rate of gas formation as a result of these processes is significantly reduced, which leads to a decrease in the size of the diffusion flame.

Table 3

The average depth of the pyrolysis layer of wood [5, 14]

Wood species	Average depth of pyrolysis layer (mm)	Conditions ($T \approx$ 500–600°C, time ≈ 30 min)
Pine (Pinus)	15–25	Fast ignition, thinner layer
Spruce (Picea)	15–20	Lower density, fast heating
Oak (Quercus)	20–30	Thick carbon layer,
Beech (Fagus)	20–28	Stable pyrolysis process
Birch (Betula)	18–25	Medium density
Poplar (Populus)	18–22	Light wood, minimal thermal conductivity
Balsa (Ochroma)	10–15	Very light, minimal thermal conductivity

The given parameters (depth of the pyrolysis layer, charring rate) were obtained in standard fire tests according to the methodologies enshrined in international standards (ISO 834, EN 13631, EN 199512 "Eurocode 5". In order to determine the characteristics and factors that affect the processes of combustion and thermal destruction, as well as the formation of pyrolysis and charring layers, two wood species were selected – pine and birch. These species were selected due to their characteristics with opposite parameters: minimum and maximum density, almost the same heat capacity, but not critical for impregnation with a fire retardant, and their widespread use.

Under the influence of high temperatures, complex physicochemical processes occur in wood, in particular, heating of the material, thermal oxidative destruction, pyrolysis and formation of a charring layer. In the process of thermal decomposition, combustible gaseous products are formed, which contribute to the development of flame combustion and the spread of fire. This leads to destruction of the surface of the material, a decrease in its strength and a loss of the bearing capacity of wooden structures. The intensity of these processes largely depends on the temperature regime, the rate of heat transfer into the thickness of the material and the features of the formation of pyrolysis and charring zones. In the absence of an effective fire-retardant coating, the pyrolysis zone quickly spreads deep into the wood, which leads to accelerated destruction of its structure and a decrease in mechanical strength. The use of such compositions should ensure maximum preservation of the surface and structure of the wood even under conditions of prolonged fire exposure.

5. 2. Experimental study on the features of thermal-oxidative destruction and determining the depth of pyrolysis and charring zones

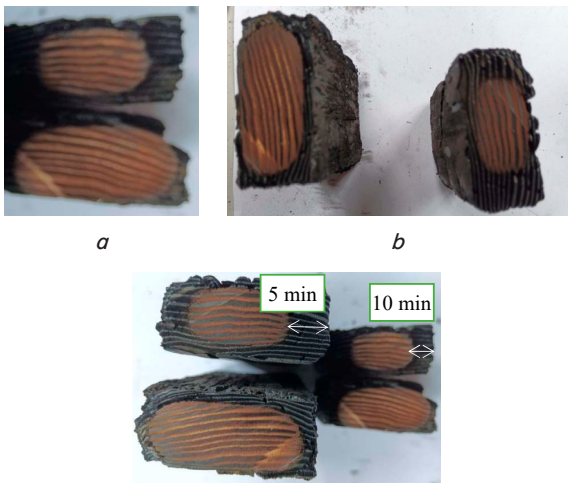
The study was conducted on 2 ordinary and treated wood samples of each species. Fig. 5 shows the prepared ones treated with one layer of fire-retardant coating AMOK-1 [22]

The flame retardant fire retardant composition AMOK-1 consists of orthophosphoric acid 60%, starch – 5–10%, formalin 2.5%, 60% formaldehyde solution, dicyandiamide 25%, urea 7%, potassium bicarbonate (2%), and polyvinyl acetate emulsion 85–95% – from 5% to 25% [22].

The authors of work [22] determined the fire retardant efficiency according to DSTU 9330:2025 and established that the composition AMOK-1 has good fire retardant characteristics even when applied in a single layer to the surface of wood, while the loss of wood mass is on average 6%. When coated with one and two layers, the difference is insignificant and differs in the direction of improvement up to 1%. The specified composition has the ability to be applied to the surface in all geometric positions without flowing off it and effectively adhering to it.

a *b*

Fig. 6. Samples of wood prepared for testing and coated with one layer of AMOK-1: *a* – pine; *b* – birch



a *b*

c

Fig. 7. Untreated wood samples after testing: *a* – untreated pine and birch samples after 10 min of thermal exposure; *b* – untreated pine and birch samples after 5 min of thermal exposure; *c* – comparison of sample sizes after testing on 5 and 10 minutes of untreated samples

As can be seen from Fig. 7, after a fire test lasting 10 min, the depth of the carbon layer is 8 mm with a loss in dimensions of up to 55% of the initial (Fig. 7, *a*). When testing for 5 min, the thickness of the carbon layer is about 15 mm, and the dimensions of the sample themselves are 75% of the initial (Fig. 7, *b*). Comparison of the sizes of the samples showed that after 10 min of testing, the dimensions became half as small (Fig. 6, *c*), and the thickness of the carbon zone is almost 2 times smaller at 10 min of testing.

The appearance of the untreated and treated samples after testing from the side is shown in Fig. 8. As can be seen, the untreated wood sample was significantly damaged and covered with cracks. Fig. 8, *b* shows the physical appearance of the treated sample, which has almost no cracks, and those that are there are up to 3 mm deep.

Fig. 8 shows the physical appearance of untreated and treated wood samples after testing.

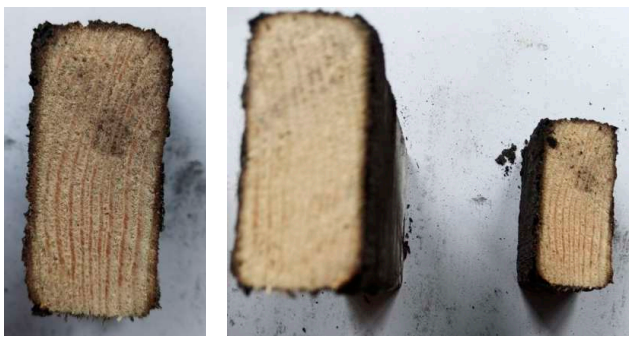
a

b

Fig. 8. Wood samples after testing: *a* – untreated pine sample; *b* – treated pine sample, test time 5 min

In order to determine the effect on the charring and pyrolysis layers, treated pine and birch samples were tested for fire resistance and depth of thermal oxidative destruction according to ISO 834. The test results are given in Table 4.

Fig. 9 shows the physical appearance of sections of treated wood samples after fire testing with the AMOK-1 fire retardant.



a *b*

Fig. 9. Samples of wood treated with the fire-retardant composition AMOK-1 after 5 minutes of fire testing: *a* – effect on the treated pine sample; *b* – effect on the treated birch sample

After removing the char layer, an additional visual analysis of the condition of the wood was carried out. Local blackening of the surface is observed on the cleaned samples (Fig. 10), which indicates the influence of elevated temperatures and the course of the initial stages of thermal decomposition. The presence of surface cracks was also found, which are a consequence of thermal stresses during heating and cooling of the material. At the same time, it was found that the deeper layers of the wood underwent minor changes: the structure of the material was mainly preserved,

and no significant signs of deep thermal oxidative destruction were detected. This indicates the limited nature of the thermal effect and the localization of pyrolysis processes mainly in the surface layers.

a

a

Fig. 10. Cleaned samples of wood treated with the fire retardant composition AMOK-1 after testing under a temperature regime of 5 min

From the sizes of the pyrolysis and charring zones, it was found that the fire-retardant composition AMOK-1 significantly affects their sizes, which proves its fire-retardant efficiency and a significant reduction in the pyrolysis zone. The results shown in Fig. 8 indicate that the pyrolysis zone almost disappears, and a small charring zone remains, which is smaller than the zone on untreated samples by an average of 4 times. In addition, from the results of the experiment (Table 4) it was found that on the treated samples the wood species does not affect the sizes of these zones.

Table 4

Results of an experiment to determine the size of pyrolysis and charring zones on minute 5

No.	Wood species	Average depth of charring and pyrolysis layers without fireproof coating		Average depth of charring and pyrolysis layers with fire retardant coating	
		Pyrolysis	Charring	Pyrolysis	Charring
1	Birch	4 mm	8 mm	1 mm	2 mm
2	Pine	7 mm	12 mm	2 mm	4 mm
3	Birch	4 mm	8 mm	1 mm	2 mm
4	Pine	7 mm	12 mm	2 mm	4 mm

6. Discussion of results based on the experimental study on the features of thermal oxidative destruction and determination of the sizes of pyrolysis and charring zones

Our experimental results, given in Table 4 and shown in Fig. 5–8, are attributed to the significant influence of the fire retardant AMOK-1 on the mechanism of thermal oxidative destruction of wood.

The features of the experimental results are that for untreated samples a clear dependence of the depth of the pyrolysis and charring zones on the wood species was established, which correlates well with the data reported in [5, 10–19]. Based on our results, birch was characterized by a greater depth of both the pyrolysis and charred layer compared to pine. This is consistent with the differences in density, pore structure, and thermal conductivity of wood of different species, which is confirmed in [10–13]. But it should be noted that, accordingly, in the untreated state, the process of thermal destruction has a species-dependent nature and is determined by the intensity of heating the material and the rate of release of volatile products – CO, H_2, H_2O, CO_2, CH_4, etc., which, accordingly, have considerable thermal effects of combustion based on the equations given in the previous section. Thus, when treated with a fire-retardant layer, wood during combustion does not receive a total of about 2000 kJ/mol, which causes a significant decrease in the intensity of combustion. The test methodology is based on standard fire tests in a furnace, the samples are heated according to the ISO curve, after which the thickness of the charred layer is measured. The obtained data are averaged and expressed as the depth of the layer (mm) and the charring rate (mm/min).

In order to determine the effect of the fire-retardant composition on the thickness of the pyrolysis and charring layers, one layer of the AMOK-1 composition was applied, after which a fundamentally different picture was observed in the thickness of the aforementioned layers. After conducting the experiment, it was determined that the depth of charring decreased several times, and the pyrolysis zone practically disappeared. This indicates a change in the dominant mechanism of heat and mass transfer and corresponds to the conclusions from equations (7) to (9). And if we return to the results of the previously conducted analysis, it is necessary to note that if in untreated wood the process is determined by internal heating and pyrolysis kinetics, then in the case of treated samples it passes into a heat-insulating-controlled mode, which corresponds to the conditions for creating wood burning zones, the parameters of which are consistent with equation (11). These results are important in reducing the fire hazard of objects and installations when using ignition mixtures and volumetric fire extinguishing systems [23–25].

As a result of our analysis of the experiment, it was found that the difference between wood species after their treatment with a fire retardant practically disappeared. This means that the intumescent layer (foam coke) and the mineralized gas barrier formed under the influence of temperature neutralize the influence of the physical and mechanical characteristics of the material. Thus, natural anisotropy and differences in density cease to play a decisive role, and the main factor becomes the thermal resistance of the protective layer and the gas barrier. Of particular importance is the established fact that even a relatively small thickness of the formed foam coke layer provides a significant reduction in the depth of thermal oxidative destruction. This indicates the high efficiency of the intumescent swelling mechanism, in which a porous heat-insulating structure with low thermal conductivity and increased resistance to oxygen diffusion is formed.

Thus, it has been experimentally confirmed that the action of AMOK-1 is realized by reducing the heat flux to

the wood surface, limiting the heating of the material to active pyrolysis temperatures, reducing the rate of formation of volatile combustible products, and transferring the process to a diffusion-limited mode with a minimum depth of damage. The described processes of increasing fire resistance occur due to the formation of a foam coke layer, which is formed and a solid molten layer on the surface of the foam coke, as well as a mineralized layer on the surface of the wood, which blocks cracks and reduces the release of gases. Thus, the fire-protective effect of the AMOK-1 composition is formed due to the synergistic interaction of the acid, carbon, and gas-forming components. The formation of a foam coke layer with low thermal conductivity provides an effective reduction in the thermal effect on the wood and a slowdown in the processes of ignition and flame spread, which confirms the prospects for using the AMOK-1 composition for fire protection of wood and cellulose-containing materials. After drying, a composite material is formed, and it can be said that the starch formed a gel, in which the phosphates provided crystallization in the form of granules (Fig. 5). All this together creates a multicomponent matrix, which when heated will turn into foamed foam coke, the pores will expand, foam coke will form a black barrier, and the resins stabilize the structure. In this case, the starch gel matrix forms the base, partially retains water, and when heated, it dehydrates and forms a black carbonaceous char as the frame of the foam coke. Phosphate components (KH_2PO_4, K_2HPO_4) ensure the formation of crystalline inclusions and stabilize the structure, and when heated, they cause a flame retardant effect, reduce runoff, and a gas-resistant barrier [22]. This creates the initial conditions for the design of new wood protection products that would have a combined effect by creating a blocking surface layer of gas flows from the depth of the wood and a dense foam coke layer with a surface that forms a physical gas-tight thermal insulation barrier. Designing such a product will lead to the preservation of the wood surface and its mechanical characteristics even under prolonged fire exposure.

Regarding the shortcomings of this study, one should note that it is advisable to conduct tests with a longer fire exposure on wood samples treated with the fire-retardant composition AMOK-1.

The results are consistent with the theoretical provisions on the role of the carbon and ash layer as a heat and mass transfer barrier and confirm the feasibility of using intumescent systems with the formation of a mineral layer on the surface of wood to stabilize the fire behavior of wooden structures during prolonged fire exposure. In addition, new data were obtained, not available in the scientific literature, which show the state of the wood surface after fire exposure. The results of our work are important for the design of fire-retardant coatings with the maximum degree of fire protection while preserving the wood surface from thermal effects and charring.

The limitations of the study are that the experiment was conducted only on two types of wood (pine and birch). The experiment used a standard test setup, which does not fully reflect all scenarios of a real fire. The experiment was conducted under dry conditions, without taking into account the influence of humidity or atmospheric factors. Only one type of fire retardant AMOK-1 was applied for the experiment.

Possible areas for further research are additional studies on the mechanism behind gas blocking and thermal insulation of harder wood species, as a basis for designing effective fire retardant compositions with a combined broad-spectrum effect with the maximum effect of preserving the wood surface.

7. Conclusions

1. The two-phase combustion of wood has been described, the essence of which is as follows. The ash layer increases the diffusion resistance; therefore, as it increases, the charring rate decreases in proportion to the increase in ash thickness, which indicates a dependence of the rate on time, close to the inverse proportionality of the square of the process time. It has been established that the most significant factor affecting the wood combustion process is the rate of diffusion of gaseous products from the pyrolysis and charring zones, based on the equations of Michelson et al. It has been established that the increase in the thickness of the carbon layer at the beginning of the wood combustion stage leads to an increase in thermal resistance and, therefore, to a decrease in the rate of heating and pyrolysis of wood. With a significant thickness of the carbon layer and the absence of convective air flows, self-extinguishing of the combustion process is possible, which can occur with a higher density or application of a flame retardant layer to the surface of the wood.

2. It has been experimentally established that when treating wood with the fire retardant AMOK 1, the pyrolysis and charring zones are reduced by up to 3 times due to the formation of a foam coke layer and the creation of a gas-tight mineralized surface, which partially blocks the cracks through which pyrolysis gases escape, and also creates a heat-insulating barrier. In addition, it was established that the depth of the charring and pyrolysis layers is minimal, 2–4 mm, and almost the same for the studied wood species, which indicates a significant role of the gas-tight mineralized barrier, which affects the intensity of combustion and the preservation of the operational characteristics of wood during fire exposure.

As a result of our experiment, it was established for the first time that the thickness of the charring and pyrolysis layers in samples treated with the fire retardant composition practically does not depend on the wood species and is almost the same for species with different densities. Based on this, the conditions for effective fire protection of the wood surface have been established, which consist in a combined action – blocking gas diffusion flows from the wood surface and installing a thermal foam coke barrier on its surface, which indicates and determines the conditions for developing more effective fire protection means for wood with the maximum protective ability of its surface from fire exposure during its combustion.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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Use of artificial intelligence

The work employed artificial intelligence GPT-5 mini (OpenAI).

AI tools were used to search for sources for literature review and grammar editing. Using AI tools, sources for literature review were found by keywords and their summary and description were highlighted. The results of the AI search were checked by the authors by personally reviewing these sources and their content. The results of the literature source search influenced the more effective identification of shortcomings of past research and objects that have not been researched so far. The text was also checked for grammatical errors by the AI.

Authors' contributions

Volodymyr Balanyuk: Conceptualization, Writing – review & editing, Supervision; **Viktor Pykus**: Validation; **Yurii Kopystynskyi**: Formal analysis; **Pavlo Pastukhov**: Resources; **Oleksandr Harasymiuk**: Validation; **Katerina Kudrynska**: Validation.

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