

THERMAL DECOMPOSITION OF MONO- AND DIETHANOLAMINEBORATE MODIFIED WOOD IN AIR ATMOSPHERE

IRINA STEPINA* and YULIA ZHEGLOVA**

*Department of Building Materials Science, Moscow State University of Civil Engineering
(National Research University), Yaroslavskoye Shosse, 26, Moscow, 129337, Russia

**Department of Information Systems, Technologies and Automation in Construction, Moscow State
University of Civil Engineering (National Research University),

Yaroslavskoye Shosse, 26, Moscow, 129337, Russia

✉ Corresponding author: I. Stepina, sudeykina@mail.ru

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For cellulosic materials used in various branches of the economy, the issue of increasing thermal stability is still relevant today. Especially acute is the problem of fire resistance for wood materials used in building structures. In our work, we investigated the effect of mono- and diethanolamine borates on the thermal decomposition of wood in an air atmosphere. It has been previously found that mono- and diethanolaminoborates, when used as surface modifiers, provide 100% biostability to plant raw materials. In this regard, the purpose of the study was to identify the flame retardant effect of the described modifiers.

In the course of the study, it was found that the developed compositions, the main components of which are boron-nitrogen compounds, effectively reduce the combustibility of wood materials, suppress smoldering, and reduce the burning rate of wood. Since it is the smoldering of wood after the liquidation of the fire that is the main cause of structural collapse, which prevents evacuation during the fire, the use of the developed compositions for fire protection of wooden structures is extremely appropriate. A regression model of the dependence of activation energy on conversion has been obtained and substantiated on the basis of correlation and regression analysis. The presented semi-logarithmic model can be further applied to predict the dependence of the activation energy value of the thermal decomposition process of modified wood on the degree of conversion.

Keywords: cellulose, wood, thermal analysis, activation energy, boron-nitrogen compounds, regression model, semi-logarithmic model

INTRODUCTION

Increasing the thermal stability of cellulose-based products is as relevant as ever, as researchers are still searching for effective ways to modify cellulosic materials for their fire protection. In recent work,¹ polysiloxane grafted cellulose acetate was successfully synthesized by employing mild reaction conditions and characterized using various techniques. Thermogravimetric analysis (TGA) and pyrolysis combustion flow calorimetry (PCFC) results showed that functionalized cellulose materials have thermal and flame retardant properties that are superior to the control cellulose acetate. Better thermal stability, high char yield and less heat release capacity can make the polysiloxane grafted cellulose acetate a potential candidate as an environmentally safe flame retardant material

for fire resistant (FR) textile applications. Other authors² successfully developed two efficient flame retardant recipes, using trimethyl phosphate (TMP) with bio-based crosslinker succinic acid, as well as TMP with urea-glyoxal under different polymerization atmospheres and conditions. When treated under normal atmosphere and without using catalyst or initiator, the fabric sample was fully burned for each assessed recipe involving succinic acid and TMP. Similarly, when nitrogen atmosphere was used for the treatment, the fabric sample was fully burned for each of the prepared recipes. However, the addition of catalyst sodium hypophosphite (SHP) and initiator potassium persulfate (PPS) to the recipes with TMP and succinic acid improved the flame retardancy. The optimum result in the case of

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succinic acid was obtained when 10% succinic acid was polymerized with 10% TMP, along with catalyst 8% SHP and 0.5% PPS at 75 °C under nitrogen atmosphere. The coke residue mass for this best recipe was higher than that corresponding to the 40% Pyrovatex based recipe and lower than that of the 20% Pyrovatex based recipe. Pyrovatex is the commercial name for a flame retardant based on n-methyloldimethylphosphonopropionamide.

Similarly, in the case of polymerization between TMP, urea, and glyoxal, the best results were obtained under nitrogen atmosphere. The above-mentioned optimized recipes also exhibited improved performance in terms of loss-on-ignition (LOI), shrinkage control, antimicrobial and crease recovery properties. Energy dispersive X-ray spectroscopy (known as EDX analysis) confirmed the presence of adequate phosphorus amounts in the two best recipes. Scanning electron microscopy (SEM analysis) indicated the successful application of the identified recipes on the fabric samples. Both recipes are non-toxic and formaldehyde free. However, the succinic acid based recipe is more sustainable, as it is a biobased product. Hence, the proposed recipes provide potential alternatives to existing hazardous flame retardants for textile materials.

In the study of D. Y. Aydin *et al.*,³ antimony fluoroborate was synthesized by the wet method, which is an economical process, using antimony trioxide and fluoroboric acid. The effects of reactant mole ratio, temperature and stirring rate as synthesis parameters on the product yield were investigated. The maximum yield of 94% was achieved at the reactant mole ratio ($n\text{HBF}_4/n\text{Sb}_2\text{O}_3$) of 6:1, temperature of 70 °C and stirring rate of 300 rpm. The flame retardancy effect and the thermal behavior of antimony fluoroborate were investigated by the vertical flame and LOI tests, and TGA, respectively. Antimony fluoroborate solutions were prepared at different concentrations and fabrics were impregnated for the tests. TGA results indicate that the treated fabric has higher thermal stability, compared to that of untreated fabric. The fabrics impregnated with antimony fluoroborate solutions passed the vertical flame test when add-on values were 6% and 12%. Their char lengths were less than 50% of the original fabric, with no after flame and after-glow times. The LOI value of the 12% antimony fluoroborate solution impregnated fabric is more than twice the LOI value of the

untreated fabric. The vertical flame test and LOI test results imply that antimony fluoroborate exhibits excellent flame retardancy for cellulosic fabrics. G. Çölük *et al.* developed flame retardant and antimicrobial paper coatings with rosemary oil and barium borate. Their findings have shown that the color difference among the coated papers is too small to be distinguished by the naked eye, and all the coatings have inhibitory properties against *E. coli* and *S. aureus*. Moreover, all the coatings have made the paper flame retardant, but barium borate imparts better flame retardancy. When examining the contact angles, it has been established that rosemary oil makes the starch coating slightly hydrophobic, while barium borate makes it hydrophilic, and thus, the printability of the paper surface is improved when using both components in the coating formulation. All coated papers were successfully printed with screen printing.

The problem of fire resistance is particularly acute for cellulose materials used in building structures. Building structures designed for dozens of years of use under normal conditions can collapse in a few minutes in a fire. Combustible structures burn when exposed to high fire temperatures for certain periods of time, while non-combustible structures change their mechanical properties and collapse. When a structure collapses, fire damage reaches maximum values. Preserving load-bearing building structures significantly reduces the damage from fires. Therefore, protecting structures from destruction and ensuring their sufficient strength and stability under conditions of high temperatures is of paramount importance in providing fire protection for buildings. According to Mnuskina Y. V. *et al.*,⁵ the absolute way to protect wood from the open flame has not yet been invented by science. All available means can only slow down the ignition and give time to eliminate the fire. The main method of protection is based on introducing a sufficient amount of a chemical substance (flame retardant) into the wood. The protective effect of flame retardants can be active or passive. The action is based on a combination of physical and chemical processes occurring under the action of an open fire on the wood. Easily fusible substances that are part of the flame retardants (salts of boric acid, salts of phosphoric acid, and salts of silicic acid) melt. Due to melting in the form of a film on the surface of the wooden element, a non-combustible

crust is formed, which limits the access of oxygen. A significant amount of heat is used to melt the flame retardant. Heat energy is not enough to ignite the wood, as there is an increase in the overall thermal resistance of the structure. The decomposition of gas-forming substances releases ammonia or sulfur dioxide – these volatile substances do not support combustion. The decomposition of salts leads to emission of non-combustible gases that push oxygen away from wooden surfaces and prevent combustion. Flame retardants based on organophosphorus compounds expand upon contact with fire, forming a protective foamy shell on the wood surface. An additional protective layer is formed by the gases that are released during this process. The foaming “coat” prevents the contact of the wood surface with the flame and slows down the spread of the fire. The main area of application of flame retardants is the fire protection of wood, wood products, building materials, cables, metal structures, and organic fabrics. Also, flame retardants are components of fire retardant paints, plasters, pastes, varnishes, impregnations, and fire retardant sealants.⁵

The vast majority of fires occur from low-calorie ignition sources. Under these conditions, flame-retardant materials successfully prevent fires or localize the resulting fire.⁶⁻⁹ The multitude of flame retardants offered on the market do not always meet all the increasing needs, forcing the creation of new products to reduce fire safety. Fire protection of wood materials is achieved by introducing the right amount of chemicals into the wood, which are capable of preventing it from burning at a given concentration. Attempts to reduce the combustibility of wood have been made by many researchers. Flame-retardant coatings and plasters, flame-retardant varnishes, paints, and impregnations have been created.¹⁰⁻¹⁴ The study by H. Čekovská *et al.*¹⁵ is devoted to the risk of possible ignition and combustion of wood. The article proposed an environmentally acceptable method of improving the fire-resistant properties of wood by heat treatment. The authors evaluated the effect of thermal modification on the fire resistance of wood, including weight loss and burning rate. A new test method was developed to provide sufficient sensitivity to control fire performance. The results showed that heat-modified spruce wood has a lower weight loss than untreated wood.

One of the most revealing indicators of treatment efficiency is the mass loss of wood due to its thermal degradation.¹⁶ However, implementing a fast and accurate system for measuring mass loss and/or elemental composition on an industrial scale is very difficult. Nevertheless, effective quality control measurement is of paramount importance to assess the quality of heat-treated wood, as well as optimize process parameters. Color tests provide a quick assessment of the durability of heat-treated wood, but such a measure is not accurate or effective enough, given the variability of the wood and the heterogeneity of the treatment. Spectroscopic analyses, such as near infrared (NIR) or Fourier-transform infrared spectroscopy (FTIR), can provide information on the extent of the process (by estimating mass loss) and the properties that are relevant to this wood modification and use of heat-treated wood (*e.g.*, equilibrium moisture content (EMC), dimensional stability, and rot resistance) from a combined single spectrum averaged over the hard surface of a heat-treated wood sample. Thus, given that NIR spectrum acquisition can be done quickly and easily on the hard surface of samples using a fiber probe, and spectral data processing can be done immediately thereafter, this is a methodology with interesting potential for process and product quality control after calibration and model testing of treated wood species. More recently, the use of mechanical testing of wood before and after the thermal modification process (non-destructive methods, such as beam identification by non-destructive grading (BING®)) could allow quick and easy acquisition of resonance frequency spectra to evaluate the properties of heat-treated wood. Although this method is widely and effectively used commercially on natural wood, it requires calibration steps so that it can be properly used on modified wood material. Finally, the use of a relative area indicator from wood temperature kinetics is readily achievable on an industrial scale using a heat treatment device that allows the wood temperature to be dynamically recorded in the process. Even though this indicator gives the manufacturer a global estimate of the quality of the modified wood output from a single heat-treated batch, this method does not provide quality control for every wood board from that batch. This latter method seems to be more efficient, simpler, and cheaper when considered on an industrial site, but it needs to be

investigated for different heat-treated wood modification processes and on an industrial scale.

In our work, we investigated the influence of mono- and diethanolamineborates on the process of wood thermal decomposition in an air atmosphere. Earlier, it was found that mono- and diethanolamineborates, when used as surface modifiers, provided 100% biostability to plant raw materials.¹⁷ In this regard, the purpose of the study was to identify the flame retardant effect of the described modifiers. In addition, we tried to obtain and justify regression models of the dependence of activation energy on conversion based on correlation and regression analysis. The originality of the presented research is given by the lack of data on the flame retardant effect of mono- and diethanolamineborates applied to the surface of wood in the literature.

EXPERIMENTAL

Air-dry pine sapwood samples were used as a substrate. 50% aqueous solutions of mono- and diethanolamine borates (composition 1 and composition 2, respectively) were used as wood surface modifiers. Modification of samples was carried out at room temperature, where the modifier was applied by brush, with a consumption of 150 g/m². Then, the samples were air-dried to constant weight. Thermal analysis (TGA) was carried out on 0.75 mm-thick plate-type elements prepared from the surface layer of pine wood samples pre-treated by brush application.

To obtain the kinetic parameters of thermal degradation of modified wood (integral method), an automated modular thermoanalytical system – Du Pont 9900 thermoanalyzer – (Wilmington, Delaware, United States) was used. The studies on TGA-951 thermobalances were carried out in the dynamic mode of heating in an air atmosphere at heating rates of 5, 10, and 20 °C/min.^{18,19}

Thermoanalytical curves were processed using special software: File Modification V 1.0, General V 1.0 and TGAKin V 1.0, installed on the Du Pont 9900 thermoanalyzer; The Universal Analysis 2000 program of TA Instruments, Version V 4.0C (Intertech Corporation, Tampa, Florida, United States).

The kinetic parameters of the degradation processes were calculated by a graphical solution of the equation:

$$E = -(R/0.457) \cdot \Delta(\log \beta) / \Delta(1/T) \quad (1)$$

where E is activation energy, $1/T$ – inverse temperature, $\log \beta$ – logarithm of the heating rate, R is the universal gas constant.

RESULTS AND DISCUSSION

Three temperature intervals can be distinguished in the process of wood thermal

degradation in an air atmosphere (Figs. 1-3). In the first temperature interval (30–186 °C), the mass loss of the studied samples is not high (on average, it is 7.5%) and is associated with the evaporation of capillary-condensed and surface-adsorbed moisture.²⁰

The increase in the surface polarity of wood samples modified with compositions 1 and 2, due to the grafting of polar amino- and protolytic OH-groups included in four-coordinated boron-nitrogen compounds, promotes stronger retention of water molecules at the surface of modified wood due to the formation of hydrogen bonds between water molecules and the polar groups of modifiers. The evaporation of water, in this case, is accompanied by additional energy expenditure, since part of the energy is spent on breaking the formed hydrogen bonds.²¹ This results in less weight loss due to water evaporation in modified wood samples, compared to unmodified samples, at a heating rate of 5 °C. However, as the heating rate increases, the mass loss of the modified wood samples increases and exceeds the mass loss of the control samples at a heating rate of 20 °C per minute. Perhaps, in this case, part of the heat is spent on the dehydration of the polysaccharide complex in the wood. The presence on the surface of modified samples of protolytic OH-groups, providing an acidic environment, catalyzes this process,²² which leads to an increase in weight loss.

In the second temperature interval (150–423 °C), the thermal degradation of wood components produces low molecular weight compounds capable of diffusing into the gas phase, and the formation of carbonized residue begins. At this stage, weight loss increases with increasing heating rate both for unmodified wood samples and for modified samples, and surface modification of wood with composition 1, and especially with composition 2, leads to a decrease in weight loss at all heating rates compared to control samples.

It can be assumed that the modifier molecules, interacting chemically with the reactive groups of the ligno-carbohydrate complex of wood and with the products of their decomposition, contribute to the enlargement of fragments, which helps to reduce the yield of low-molecular-weight compounds that form the fraction of combustible volatile products.²¹ The participation of hydroxyl groups at the C6-atom of the pyranose cycle in the modification reactions leads to inhibition of the

process of cellulose depolymerization into an easily flammable intermediate, levoglucosan,²³ which also increases the flammability of modified samples. In addition, inert nitrogen oxides and water vapor emitted during the decomposition of the components of the used compositions dilute the gas-air mixture near the surface of the modified samples and thus isolate them from air oxygen.⁶ The formed thin film of boron oxide reflects some of the heat flux and prevents the release of volatile products, but, according to literature data,⁶ the contribution of this factor is insignificant.

In the temperature range of 380–650 °C, the processes of oxidation of carbonized residue

occur, and for modified wood samples, this interval, as well as the temperature of maximum oxidation of coke, shifts to higher temperatures (by 150 °C and 35 °C for composition 1 and composition 2, respectively). This indicates a significant increase in the thermal stability of carbonaceous structures formed during the thermal degradation of wood modified with the developed compositions. A significant decrease in coke oxidation rate (~2 times) leads to an increase in carbonized residue on the surface of protected samples, due to which the thermal insulation of the wood substance is increased.

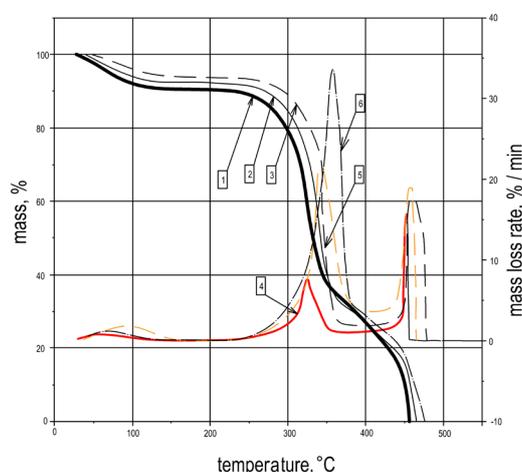


Figure 1: TG (1, 2, 3) and DTG (4, 5, 6) curves of unmodified pine wood samples (air atmosphere): 1, 4 – heating rate 5 °C/min; 2, 5 – heating rate 10 °C/min; 3, 6 – heating rate 20 °C/min

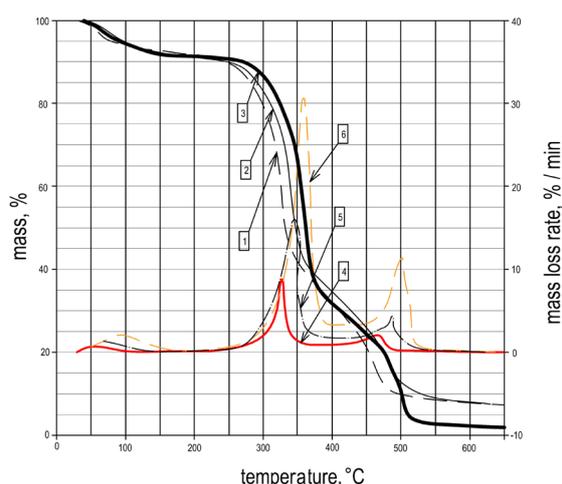


Figure 2: TG (1, 2, 3) and DTG (4, 5, 6) curves of pine wood surface layer samples modified with composition 1 (air atmosphere): 1, 4 – heating rate 5 °C/min; 2, 5 – heating rate 10 °C/min; 3, 6 – heating rate 20 °C/min

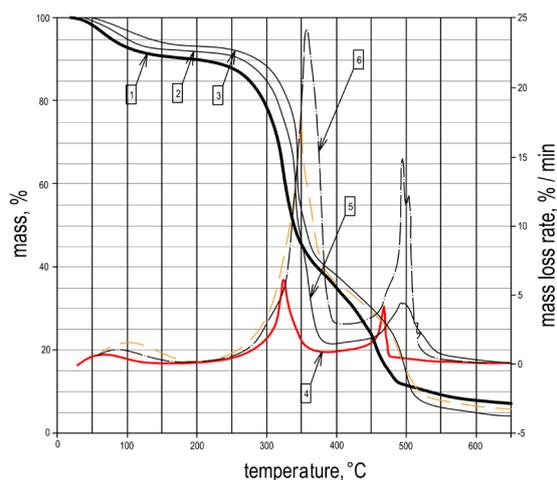


Figure 3: TG (1, 2, 3) and DTG (4, 5, 6) curves of pine wood surface layer samples modified with composition 2 (air atmosphere): 1, 4 – heating rate 5 °C/min; 2, 5 – heating rate of 10 °C/min; 3, 6 – heating rate 20 °C/min

The kinetic parameters of the processes of thermal degradation of modified and native wood are given in Table 1, where we can see that the values of activation energy of protected wood samples are lower than those of unmodified samples. The activation energy of the thermal decomposition of wood samples modified with compositions 1 and 2 decreases by ~2.5 and ~2 times, respectively, relative to unprotected wood samples. According to literature sources,⁸ the fact that the activation energy decreases indicates that at the beginning of the combustion process, it is not the wood that undergoes thermal destruction, but the modifier located on its surface. This leads to the formation of new products with increased thermal stability with respect to further decomposition and reduced combustibility, *i.e.*, the four-coordinated boron-nitrogen compounds present in the surface layer of modified samples increase the thermal stability of the wood composite. The dependence of activation energy on the degree of transformation of the studied samples is graphically presented in Figure 4. The graphs show that, as the degree of transformation of the modified samples increases, the value of activation energy increases as well (activation

energy at 70% conversion is ~2 times higher compared to the original value). This is due to the fact that, as modifiers are consumed as a result of chemical transformations, the wood material begins to undergo thermal degradation.

Thus, the developed compositions, the main components of which are boron-nitrogen compounds, effectively reduce the combustibility of wood materials, suppress smoldering, and reduce the burning rate of wood. Since the smoldering of wood after the elimination of fire is the main cause of the collapse of structures, which prevents evacuation during the fire, the use of the developed compositions for fire protection of wooden structures is extremely appropriate.

Using a pairwise regression, let us select the type of mathematical function $y = f(x)$ characterizing the dependence between conversion (%) and activation energy (kJ/mol). We will apply the analytical method of regression equation type selection. This method is based on the study of the material nature of the relationship between the studied attributes. The data on the kinetics of thermal degradation listed in Table 1 will be used here.

Table 1
Kinetics of thermal degradation in an air atmosphere

Conversion, %	Activation energy, kJ/mol	
	Pine + composition 1	Pine + composition 2
5.0	55.4	81.0
10.0	81.5	108.6
15.0	93.8	116.2
20.0	101.7	120.0
30.0	113.0	125.6
40.0	121.5	128.5
50.0	123.7	128.2
60.0	122.1	127.9
70.0	120.8	132.0

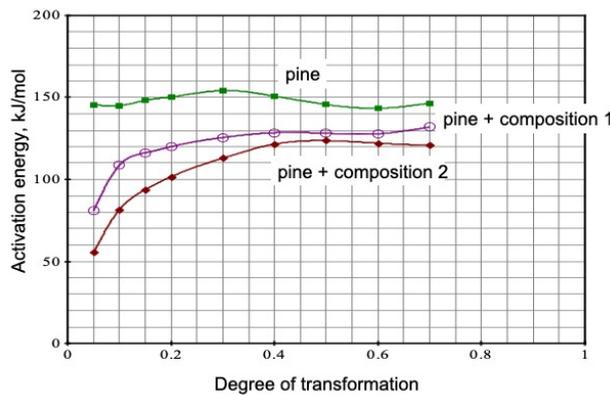


Figure 4: Dependence of activation energy (E) on degree of transformation (α)

Consider the linear and nonlinear models. In the linear model, the parameters of the linear pairwise regression equation $y = a + bx$ are calculated. For this purpose, we will use the formulas:²⁴

$$a = \bar{y} - b \cdot \bar{x}, \quad (2)$$

where $\bar{x} = \frac{1}{n} \sum x$, $\bar{y} = \frac{1}{n} \sum y$

$$b = \frac{\text{cov}(x, y)}{\sigma_x^2}, \quad (3)$$

where $\text{cov}(x, y) = \overline{y \cdot x} - \bar{y} \cdot \bar{x}$ – the covariance of features x and y , $\sigma_x^2 = \overline{x^2} - \bar{x}^2$ – the variance of the trait x and $\overline{y \cdot x} = \frac{1}{n} \sum y \cdot x$, $\overline{x^2} = \frac{1}{n} \sum x^2$.

The regression equation is always supplemented by the closeness of the relationship. The indicator of the closeness of the relationship, the linear correlation coefficient r_{xy} , is determined by the formula:²⁵

$$r_{xy} = b \cdot \frac{\sigma_x}{\sigma_y} = \frac{\text{cov}(x, y)}{\sigma_x \cdot \sigma_y}. \quad (4)$$

The linear correlation coefficient is in the range $-1 \leq r_{xy} \leq 1$: the closer the absolute value of r_{xy} is to unity, the stronger the linear relationship between the factors.

To assess the quality of the linear function selection, the coefficient of determination is calculated, which is determined by the formula:²⁵

$$r_{xy}^2 = 1 - \frac{\sigma_{ost}^2}{\sigma_y^2} \quad (5)$$

where

$$\sigma_{ost}^2 = \frac{1}{n} \sum (y - \hat{y}_x)^2, \quad \sigma_y^2 = \frac{1}{n} \sum (y - \bar{y})^2 = \overline{y^2} - \bar{y}^2.$$

The quality of the regression equation is determined by Fisher's F -criterion:²⁵

$$F = \frac{\sigma_{fact}^2}{\sigma_{ost}^2}. \quad (6)$$

The actual value of Fisher's F -criterion is compared with the table value $F_{table}(\alpha; k_1; k_2)$ at significance level α and degrees of freedom $k_1 = m$ and $k_2 = n - m - 1$ (where n is the number of observations and m is the number of parameters in the variable x). In this case, if the actual value of the F -criterion is greater than the tabulated one, then the statistical significance of the equation as a whole is recognized.²⁵

To assess the statistical significance of regression and correlation coefficients, we calculate Student's t -criterion and confidence intervals for each of the indicators:²⁵

- standard error of the regression coefficient:

$$m_b = \sqrt{\frac{S_{ost}^2}{\sum (x - \bar{x})^2}} = \frac{S_{ost}}{\sigma_x \cdot \sqrt{n}} \quad (7)$$

where $S_{ost}^2 = \frac{\sum (y - \hat{y}_x)^2}{n - 2}$ – the residual variance per one degree of freedom;

- the standard error of the parameter a :

$$m_a = \sqrt{S_{ost}^2 \cdot \frac{\sum x^2}{n \cdot \sum (x - \bar{x})^2}} = S_{ost} \cdot \frac{\sqrt{\sum x^2}}{\sigma_x \cdot n} \quad (8)$$

The significance of the linear correlation coefficient is tested on the basis of the error value of the correlation coefficient m_r :²⁵

$$m_r = \sqrt{\frac{1 - r^2}{n - 2}} \quad (9)$$

The actual value of the Student's t -criterion is defined as $t_r = \frac{r}{m_r}$. There is a relationship

between Student's t -criterion and Fisher's F -criterion:²⁵

$$t_b = t_r = \sqrt{F} \quad (10)$$

In order to have a general judgment about the quality of the model from the relative deviations for each observation, the average error of approximation is determined:²⁵

$$\bar{A} = \frac{1}{n} \sum \left| \frac{y - \hat{y}_x}{y} \right| \cdot 100\% \quad (11)$$

The average approximation error should not exceed 8-10%.

Let us construct a linear model for the relation between activation energy and conversion. To calculate the coefficients, formulas (2) and (3) will be used. The regression equation for composition 1 is as follows:

$$y = 0.8549x + 75.225 \quad (12)$$

The linear regression equation for composition 2 is as follows:

$$y = 0.5332x + 100.89 \quad (13)$$

The results of the calculations and analysis of this model are presented in Table 2. Tabular value ($k_1 = 1$, $k_2 = n - 2 = 7$, $\alpha = 0.05$): $F_{table} = 5.59$.²⁶ Since for both compositions $F > F_{table}$, the statistical significance of the equation as a whole is recognized. The tabular value of Student's t -

criterion for $\alpha = 0.05$ and the number of degrees of freedom $\nu = n - 2 = 7$ is $t_{table} = 2.365$.²⁶ Since the inequalities $t_b > t_{table}$, $t_a > t_{table}$, and $t_r > t_{table}$ are fulfilled for compositions 1 and 2, we admit the statistical significance of the regression parameters and the closeness of the relationship.

The graphs of the linear regression model for “Pine + composition 1” and “Pine + composition 2” are shown in Figure 5 (a, b). Based on these estimates, we can conclude that the linear regression model is not suitable for composition

1, as the average error of approximation is $\bar{A} = 11.38\%$, which is unacceptable. The average error of approximation for composition 2 $\bar{A} = 6.66\%$ shows that the regression line approximates the initial data, but not well enough. The coefficient of determination $r_{xy}^2 = 0.5961$ for composition 2 shows that 59.61% of the variation of the resultant sign is explained by the variation of the factor sign and 40.39% falls on the share of other factors, so this model is also unreliable.

Table 2
Data from linear regression model analysis

	Pine + composition 1	Pine + composition 2
r_{xy}	0.8439	0.7721
r_{xy}^2	0.7121	0.5961
F	17.31	10.33
m_b	0.2055	0.1659
m_a	2.7252	2.2000
m_r	0.2028	0.2402
t_b	4.1609	3.2145
t_a	27.6037	45.8606
t_r	4.1609	3.2145
\bar{A}	11.38	6.66

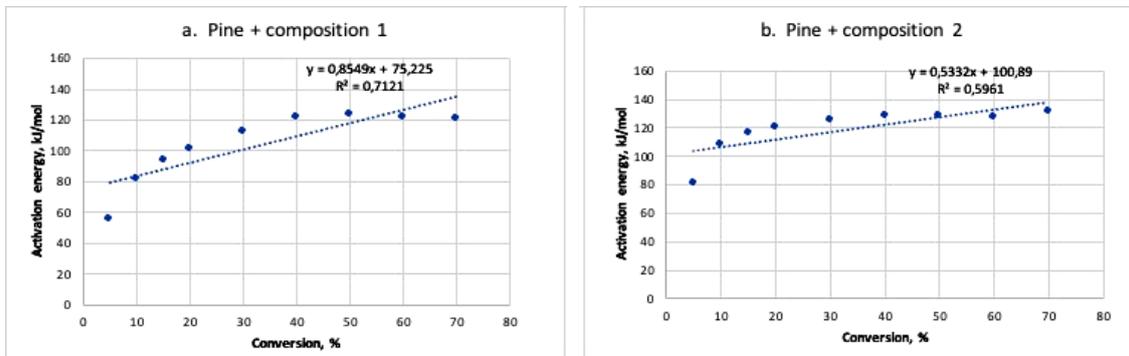


Figure 5: Linear regression model

When considering nonlinear regression models, the nonlinear regression equation, as well as in the case of linear dependence, is supplemented by an indicator of the closeness of the relationship. In this case, it is a correlation index.²⁵

$$\rho_{xy} = \sqrt{1 - \frac{\sigma_{ost}^2}{\sigma_y^2}} \tag{14}$$

where $\sigma_y^2 = \frac{1}{n} \sum (y - \bar{y})^2$ – total variance of the result indicator y , $\sigma_{ost}^2 = \frac{1}{n} \sum (y - \hat{y}_x)^2$ residual dispersion.²⁵

The value of this indicator is in the range $0 \leq \rho_{xy} \leq 1$. The closer the correlation value is to unity, the closer the connection between the considered attributes is, and the more reliable the regression equation is.

The square of an index of correlation carries the name of an index of determination and characterizes a share of the dispersion of a

resultant sign y , explained by regression, in the general dispersion of a resultant sign:²⁵

$$\rho_{xy}^2 = 1 - \frac{\sigma_{ost}^2}{\sigma_y^2} \quad (15)$$

The coefficient of determination ρ_{xy}^2 can be compared to the coefficient of determination r_{xy}^2 to justify the possibility of applying a linear function. The greater the curvature of the regression line r_{xy}^2 , the smaller the value is ρ_{xy}^2 . The closeness of these indicators indicates that there is no need to complicate the form of the regression equation, and a linear function can be used.²⁵

The determination index is used to test the significance of the regression equation as a whole by Fisher's F -criterion:²⁵

$$F = \frac{\rho_{xy}^2}{1 - \rho_{xy}^2} \cdot \frac{n - m - 1}{m} \quad (16)$$

where ρ_{xy}^2 – index of determination, n – number of observations, and m – number of parameters in variable x . The actual value of the F -criterion is compared with the table at the level of significance α and the number of degrees of freedom, $k_2 = n - m - 1$ (for the residual sum of squares) and $k_1 = m$ (for the factor sum of squares).²⁵

The quality of the nonlinear equation can also be judged by the average error of approximation,

which, as in the linear case, is calculated by formula (11).

It can be suggested that the regression has a non-linear character. Let us suggest a power model for the data in Table 1. Having calculated the coefficients, we obtain that the equation of regression for the treatment with composition 1 will look like this:

$$y = 40.274 x^{0.2853} \quad (17)$$

while for the treatment with composition 2:

$$y = 71.247 x^{0.1556} \quad (18)$$

The results of the stepwise regression analysis are presented in Table 3. The initial data and the power regression model for “Pine + composition 1” and “Pine + composition 2” are presented in Figure 6 (a, b). Based on the results of the analysis, we can conclude that the power regression model approximates the raw data for both compositions well enough, and the calculated values of Fisher's F -criterion significantly exceed the table $F_{table} = 5.59$.²⁶ The average error of approximation \bar{A} does not exceed 8%. In the case of composition 2, the regression line approximates the initial data better than it does for composition 1. The index of determination is high enough: for composition 1 it is 12.01% and is the share of other factors, and for composition 2 it is 18.27%. The given percentage is rather high, so we suggest trying to apply another nonlinear model.

Table 3
Data from power regression model analysis

	Pine + composition 1	Pine + composition 2
ρ_{xy}	0.9377	0.9040
ρ_{xy}^2	0.8793	0.8173
F	50.99	31.31
\bar{A}	7.05	4.89

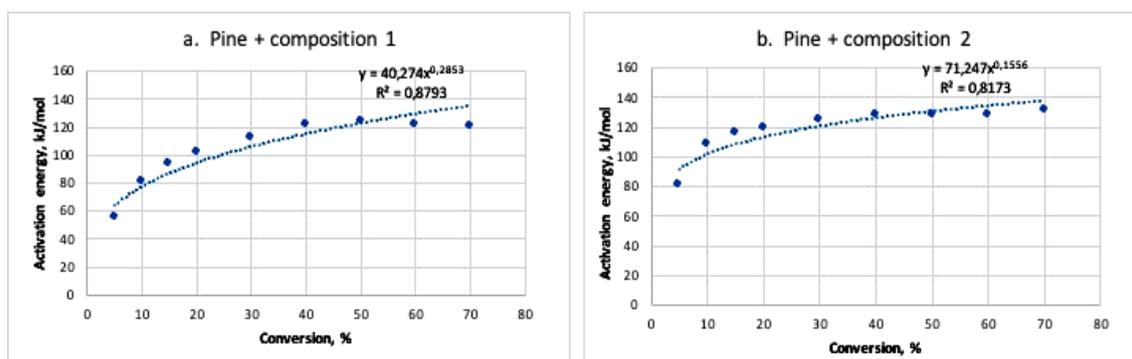


Figure 6: Power regression model

Table 4
Data from semi-logarithmic regression model analysis

	Pine + composition 1	Pine + composition 2
ρ_{xy}	0.9724	0.9301
ρ_{xy}^2	0.9456	0.8651
F	121.59	44.9
\bar{A}	4.77	4.19

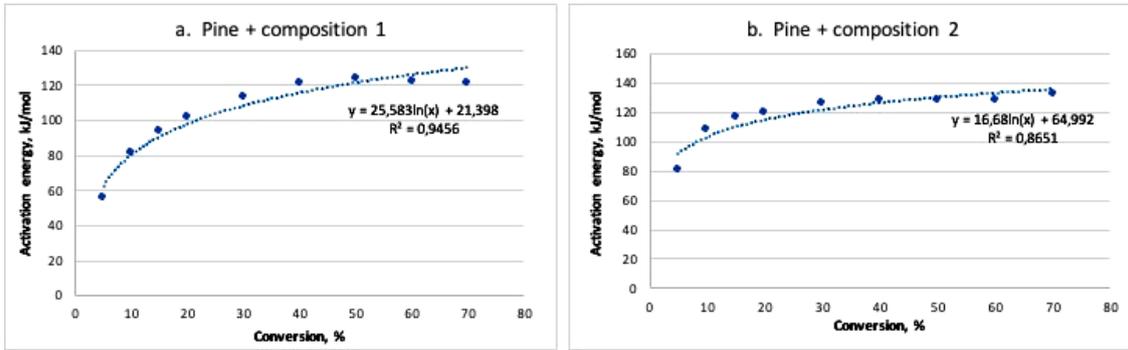


Figure 7: Semi-logarithmic regression model

Let us build a semi-logarithmic regression model. Having calculated the coefficients, we will obtain regression equations for a semi-logarithmic model for each composition. The equation of semi-logarithmic regression will take the following form for the treatment with composition 1:

$$y = 25.583 \ln(x) + 21.398 \tag{19}$$

and for the treatment with composition 2:

$$y = 16.68 \ln(x) + 64.992 \tag{20}$$

The results of the analysis of the semi-logarithmic regression model are presented in Table 4. Figure 7 (a, b) shows a semi-logarithmic regression model for each composition “Pine + composition 1” and “Pine + composition 2”. Based on the results of the analysis, we can conclude that the semi-logarithmic regression model approximates well the raw data for both compositions, and the calculated values of Fisher's F-criterion significantly exceed the table $F_{table} = 5.59$.²⁶ The average error of approximation \bar{A} for composition 1 is 4.77%, and for composition 2, it is 4.19%, which shows that the regression line approximates the data for each composition well. The index of determination for both compositions is very high (strong): for the composition 1, 94.56% of the variation of the resultant sign is explained by the variation of the attribute-factor, and only 5.44% is the share of other factors; for composition 2, 86.51% of the variation of the resultant sign is explained by the

variation of the attribute-factor, and 13.49% is the share of other factors, which is much higher than for the power model. It can be concluded that this nonlinear model approximates the original data well.

When considering to build an exponential model, the regression equations for the model will take shape as follows – for the treatment with composition 1:

$$y = 74.188 e^{0.0092 x} \tag{21}$$

and for the treatment with composition 2:

$$y = 99.967 e^{0.0049 x} \tag{22}$$

The results of the exponential regression model analysis are presented in Table 5. Figure 8 (a, b) shows an exponential regression model for each composition.

From the analysis, we can conclude that this model is not suitable for data approximation, as in accordance with the calculated index of determination the share of other factors for composition 1 is 38.26%, and for composition 2 is 44.44%. The average error of approximation for the second set is high enough and makes 7.84%, and for the first set $\bar{A} = 12.74\%$, which is unacceptably high.

To summarize, the results of the analysis of the models built by the determination index and the average error of approximation are presented in Tables 6 and 7. Table 6 shows that the best model for composition 1 is the semi-logarithmic model, since the determination index for this model is

closest to 1, and the average error of approximation is the smallest. Table 7 shows that the best model for composition 2 is also the semi-logarithmic model, as it is for composition 1, as it

has the greatest index of determination and the smallest average error of approximation, which indicates that this model is reliable.

Table 5
Data from the analysis of the exponential regression model

	Pine + composition 1	Pine + composition 2
ρ_{xy}	0.7858	0.7454
ρ_{xy}^2	0.6174	0.5556
F	11.297	8.75
\bar{A}	12.74	7.84

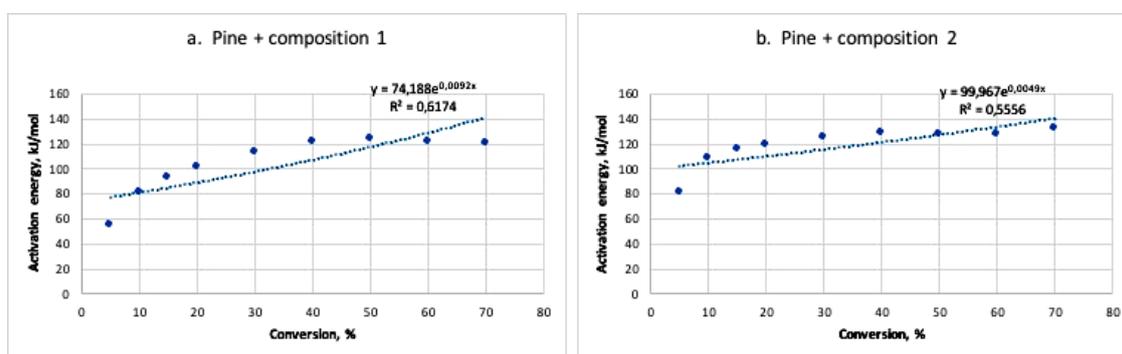


Figure 8: Exponential regression model

Table 6
Comparative analysis of the considered models for composition 1

Model	Determination index, R^2 (r_{xy}^2, ρ_{xy}^2)	Average approximation error, \bar{A} , %
Linear model	0.7121	11.38
Power regression model	0.8793	7.05
Semi-logarithmic model	0.9456	4.77
Exponential model	0.6174	12.74

Table 7
Comparative analysis of the models under consideration for composition 2

Model	Determination index, R^2 (r_{xy}^2, ρ_{xy}^2)	Average approximation error, \bar{A} , %
Linear model	0.5961	6.66
Power regression model	0.8173	4.89
Semi-logarithmic model	0.8651	4.19
Exponential model	0.5556	7.84

Based on our analysis, we conclude that the semi-logarithmic model approximates the experimental data the best. Therefore, it should be chosen to relate the dependence of activation energy and conversion, discarding all other models, which were considered and analyzed in

this article, because of their lower statistical reliability.

CONCLUSION

The developed compositions, the main components of which are boron-nitrogen

compounds, effectively reduce the combustibility of wood materials, suppress smoldering, and reduce the burning rate of wood. Since it is the smoldering of wood after the liquidation of the fire that is the main cause of structural collapse, which prevents evacuation during the fire, the use of the developed compositions for fire protection of wooden structures is extremely appropriate.

A regression model of the dependence of activation energy on conversion has been obtained and substantiated on the basis of correlation and regression analysis. The presented semi-logarithmic model can be further applied to predict the dependence of the activation energy value of the thermal decomposition process of modified wood on the degree of conversion.

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