Thermodynamic foundations of wood's operational properties

Fedor Portnov¹, Daria Mikhailova¹
¹Moscow State University of Civil Engineering, Yaroslav shosse, 26, Moscow 129337, Russian Federation
E-mail: wastingtimefilmart@gmail.com

Abstract. The paper shows trends in the study of building materials. Thermodynamic approaches to analysis of the condition of building materials as a thermodynamic system, including in thermal decomposition conditions, are described. As part of the experimental part, the proposed methods analysed the effect of phosphorus organic materials on the fire danger of wood. The correlation of thermodynamic criteria (Gibbs energy) and identified physical and chemical behaviors of modified wood has been revealed.

1. Introduction
Currently, research trends are aimed at reducing the procedure for evaluating the characteristics of building materials and structures to fundamental methods based on the basic characteristics of materials. Such methods include the study of a microscopic structure, but it is also possible to move to more significant physical-chemical methods of chemical research methods, based on the analysis of thermodynamic systems.

Choosing a rational method of research using physical-chemical assessment methods is the goal of this work. To achieve this, the goal is to analyze experimental data from the assessment of the energy properties of wood building materials, as well as to study their correlation with methods of evaluating operational properties, one of which is flammability.

Based on the first postulate on thermodynamic equilibrium, as well as on the law of Hess, we can conclude that the processes that occur with building materials do not depend on the path of these processes, but depend only on the initial and final state, as well as on the nature of external influences affecting the material. It is obvious that the most important in any analysis of the behavior of building materials is to obtain data on the properties of building material, as well as on the impact factors. In addition, detailed information on the impact of external factors on the material will allow to conduct a forecast of the behavior of similar properties of building materials (Figure.1).
Analyzing the factors affecting the material can be identified the main two types of influences - destructive and modifying. The first class of exposures include thermooxic decompositions in the impact of elevated temperatures, aging, exposure to aggressive environments, chemical exposure, biological impact. The modification can include chemical, mechanical, and thermal modification. It should be noted that destructive and modifying effects are more often always counter-in-character. The source material is modified to increase resistance to negative destructive effects (Figure 2).

As a typical situation, we will analyze the thermal decomposition of wood, modified by elemental compounds. It is obvious that the process of thermal decomposition (burning) of wood is a vivid example of changes in the physical and chemical characteristics of the material, which in turn opens up great possibilities for analysis. In addition, the burning of wood materials is of considerable practical interest because of the high risk of fire emergencies in the residential sector, where wood building materials are often used, as structural and finishing elements.

2. Experimental part
20% of water solutions of phosphorus acid esters (diphenylphosphate (DMF), dietylphosphate (DEF), dipropylphosphate (DPF), dibutylphosphate (DBF), diphenylphosphate (DFF) and ammonium polyphosphate were used as modifiers. Typical for this type of compound, the chemistry of interaction with wood pulp is represented in Figure 3.
It is worth noting that the modification took place in soft conditions, that is, the modification components were carried out on the surface of the material at a temperature of 20 °C with a consumption of 300 g/m². In such conditions, there is no additional heating or the use of complex equipment for deep impregnation. This approach is of great practical interest and is presented in a number of scientific papers [1,6].

Each of the samples was subjected to thermal decomposition in differential-scan calorimetry (until full combustion at an even increase in temperature) and in the conditions of smouldering mode of thermal decomposition (until the end of active smoke at the border with thermal impact leading to ignition).

The results of the thermal analysis are shown in Figure 4.

Based on these results, we can note a decrease in the intensity of exothermic reaction in thermal decomposition of modified wood, as well as the shift of the first stage of thermal decomposition to the area of lower temperatures. This picture is typical of the action of fire retardant materials of this type. Nevertheless, it is worth noting that for the DEF modifier there is no brightly expressed exothermic peak in the first stage of thermal decomposition, which is of great interest.

To study the features of this effect and analyze its impact on performance, an analysis should be conducted on the changes in the thermodynamic characteristics of the system under study. As
mentioned earlier, the basic postulates of thermodynamics indicate the need to assess the original and final state. This analysis will be carried out in accordance with the diagram shown in Figure 5, which shows the source and endpoints of the analysis.

*Figure 5.* How to analyze the building material depending on the position of the system.

The energy properties are characterized by changes in the following thermodynamic characteristics: the edge angle of wetting, surface tension and changes in the isobarn-isothermic potential of the surface in modification.

The surface energy intensity factor is surface tension. The calculation of the change in isobarn-isothermic potential of the modified surface was made on the basis of the combined I and II laws of thermodynamics.

To assess free surface energy for systems with a permanent chemical composition, the combined equation I and II of the laws of thermodynamics has the appearance of:

\[
dG = -SdT + Vdp + \sigma dS_{sp} + \mu dn
\]

(1)

where \( G \) - Gibbs energy, \( S \) - entropy system, \( T \) - temperature, \( V \) - volume, \( p \) - pressure, \( \sigma \)-surface tension (work of surface unit formation), \( S_{sp} \) – specific surface, \( \mu \) - chemical potential of the substance that makes up the condensed phase, \( n \)- number of moles

In isobarn-isothermic conditions and the constant amount of matter, the differential of the equation (1) has the appearance of:

\[
\Delta G = \sigma dS_{sp} + S_{sp} d\sigma
\]

(2)

The following methods were used to obtain key characteristics: capillary nitrogen capillary condensation (to estimate the specific surface area) and the neutral drop method (to assess surface tension).

The porometry was carried out using specialized equipment - the installation of the nova 4200e quantachrome. The concept of the installation is shown in Figure 6.

*Figure 6.* Installation to determine the edge angle of wetting.
The analysis and calculation of the data obtained resulted in the results shown in Table 1.

### Table 1. Evaluation of changes in isobarn-isothermic capacity of samples.

| Surface layer modifier | DMF | DEF | DPF | Dbf | DFF | PFA-1 |
|------------------------|-----|-----|-----|-----|-----|-------|
| Before thermal decomposition |     |     |     |     |     |       |
| JG. J                   | -12.68 | -14.5 | -4.94 | -6.97 | -10.16 | -2.71 |
| After thermal decomposition |     |     |     |     |     |       |
| JG. J                   | 14.31 | -14.48 | 4.05 | 2.43 | -13.69 | 12.35 |

According to the provisions of thermodynamics, on the one hand, the most negative value of the change in isobarn-isothermic potential characterizes the most active processes of system change, on the other hand, the value of the change in isobarn-isothermic potential close to zero characterizes the stability of the system in the thermodynamic process. In the analysis of the results, there is a high activity in the process of chemical modification in the use of modifiers DMF, DEF, DF, with the greatest resistance in thermal decomposition observed for wood modified DEF.

Tests were conducted to assess the operational properties for the selected samples, as well as to determine the smoke-forming ability.

### Table 2. Test results to determine fire retardant efficiency of the samples studied.

| Sample               | Loss of mass. % | Fire retardant Efficiency Group |
|----------------------|-----------------|-------------------------------|
| Native wood          | 79.0            | III                           |
| Wood modified DMF    | 7.9             | I                             |
| Wood modified DEF    | 8.5             | I                             |
| Wood modified DFF    | 9.5             | II                            |
| Wood modified PFA-1  | 8.7             | I                             |

### Table 3. Test results to determine the smoke-forming ratio of the samples studied.

| No p/p | Sample               | Dₘₑₙmₘ²/kg/kg |
|--------|----------------------|---------------|
| 1      | Wood - DMF           | 450-470       |
| 2      | Wood - DEF           | 130-140       |
| 3      | Wood                 | 640-680       |
| 4      | Wood                 | 600-640       |
| 5      | Wood - DFF           | 740-780       |
| 6      | Wood - PFA-1         | 400-440       |
| 7      | Wood - PFA-2         | 820-860       |
| 8      | Original wood        | 970-1030      |

Based on the data obtained, it can be concluded that the most effective modifiers are DMF and DEF in terms of fire retardant efficiency, yet the smallest smoke is observed for wood modified by DEF.

### 3. Discussion of results

The Based on the results, you can build a number of dependencies. The high activity of the previously mentioned modifiers is due to their high activity in interaction with wood. Particular attention should be paid to the nature of thermal decomposition in DSK analysis. As noted earlier in the area of the first stage of thermal decomposition there is no exothermic peak in the case of wood combustion, modified DEF. This effect is reflected in the results of the determination of the change in isobarn-isothermic combustion potential for this sample.
For a more detailed analysis, the results of the elemental analysis for the content of phosphorus in the surface layer of the objects studied (table 4) were obtained, as well as a picture of an electron microscope of wood modified by DEF after thermal decomposition (Figure 7).

| Surface layer modifier | DMF | DEF | DPF | Dbf | DFF | PFA-1 |
|------------------------|-----|-----|-----|-----|-----|-------|
| Before thermal decomposition | %P | 2.87 | 3.57 | 2.6 | 2.65 | 2.45 | 2.21 |
| After thermal decomposition | %P | 0.85 | 4.7 | 0.41 | 0.37 | 1.06 | 0.35 |

**Table 4.** The results of elemental analysis of modified wood.

The new data confirms the correlation between the nature of thermal decomposition and the energy characteristics of the surface layer of wood. The electron microscope image shows a stable structured surface. The result of this effect is an effective chemical interaction, confirmed by the data of elemental analysis - after thermal decomposition in the corner layer there is the presence of chemically bound phosphorus.

The data confirm the operational characteristics of the wood (fire hazard and smoke-forming ability). It is obvious that the stability of thermodynamic stability of the samples is due to the fact that the thermal decomposition of samples occurs with a relatively low intensity, in addition, it determines the resistance to diffusion in the atmosphere of solid dispersed wood particles, which is the reason for the low smoke-forming ability of the respective samples.

4. Conclusions
Based on the experiment and analysis of the data, the following conclusions can be drawn:

The main objective of the work, which is to select the best methods for assessing the performance of wood, was achieved through the use of the method of assessing the energy characteristics of the surface of the sample.
- The results are correlated with the assessment data of thermal analysis methods and fire-dangerous characteristics of modified wood.

- The proposed approach to assessing the performance of building materials based on micro-level and supramolecular level assessments can be used more widely, taking into account the practical significance of this method.

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References
[1] E.N. Pokrovskaya, F.A. Portnov, A.A. Kobelev, D.A. Korolchenko, Fire and Explosion Safety, 10, 40-46 (2013)
[2] A.A Stenin, Construction - the formation of the environment of life, 553-559 (2013)
[3] V.A. Shamaev, International Scientific and Technical Conference "Modern Problems of Mechanical Wood Technology", 11-17 (2010)
[4] E.U. Tariva, VI International Scientific and Technical Conference "Actual problems of construction and construction industry", 55-56 (2005)
[5] E. N. Pokrovskaya, Preservation of monuments of wooden architecture with the help of organoelement compounds (2009)
[6] E. N. Pokrovskaya, Chemical and physical basis for increasing the longevity of wood (2003)
[7] V.I. Roldugin, Physicochemistry of the surface (2011)
[8] A.S. Tutygin, A.A. Shinkaruk, A.M. Aisenstadt, V.S. Lesovik, J. of International Scientific Publications: Ecology & Safety, 8, 54-61 (2014)
[9] A.S. Tutygin, A.A. Shinkaruk, A.M. Aisenstadt, M.F. Frolova, T.A. Pospelova., J. of International Scientific Publications: Ecology & Safety, 7, 37-45 (2013)
[10] A.M. Aisenstadt, Innovative materials and technologies for construction in extreme climatic conditions, 244 (2014)
[11] B.V. Deryagin, I.I. Abrikosova, E.M. Lifshits, Successes in physical sciences, 3, 494-526 (1958)
[12] B.V. Deryagin, N.V. Curaev, Wetting membranes (1984)
[13] P. Dzh. Gudkh'yu, Practical Methods in Electron Microscopy (1980)
[14] Dzh. Gouldsteyn Practical raster microscopy (1978)
[15] B.A. Kalin, Raster electron microscopy. Laboratory work (2008)
[16] A.A. Abramzon, L.Ye. Bobrova, L.P. Zaychenko, Surface phenomena and surface-active substances: handbook (1984)
[17] A.S. Vyacheslavov, Ye.A. Pomerantseva, Measurement of surface area and porosity by the method of capillary nitrogen condensation (preparation of masters - operators of modern scientific equipment): Methodological development (2006)
[18] YU.A. Podkamennyy, A.A. Nosenko Innovative method for determining the specific surface area of disperse systems and porous materials. Available at: http://conf.sfukras.ru/sites/mn2013/section060.html (2013)
[19] Interstate Standard 53292-2009. Fire protection compounds and substances for wood and materials based on it. General requirements. Test methods (2007)
[20] Interstate Standard 12.1.044–89*. Occupational safety standards system. Fire and explosion hazard of substances and materials. Nomenclature of indices and methods of their determination (1989)