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DETERMINATION OF THERMOPHYSICAL PROPERTIES OF PARTLY PYROLYZED FIRE RETARDANT-TREATED SAWDUST

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Experiments were carried out to investigate the effect of pyrolysis temperature and phosphorus-containing impregnating compounds on thermal properties of specimens made of compacted sawdust.

Prediction of ignition delay time and solution of the problem of propagation of a combustion wave require information about the material as a source of combustible volatiles, a heat source or sink, and the thermal properties of the condensed phase (λ, a, c), which enter into the main calculation equations. It is necessary to take into consideration that thermal conductivity and specific heat are not constant and can change as the condensed phase burns up and when the material is impregnated with various kinds of impregnating compounds.

The problem of decreasing the ignitability and combustibility of polymer materials, including wood, is extremely urgent. The ignition of wood mainly depends on the behavior of cellulose, which is its most reactive component [1]. It is known that in cellulose subjected to heating the direction of break of cellulose links, the condensed phase yield, and the chemical reaction rate are very sensitive to catalytic effects and, consequently, depend on additives of inorganic salts, in particular, phosphorus-containing impregnating compounds introduced into the polymer [2]. In this connection, treatment of wood with various kinds of protective agents that contain derivatives of phosphoric acids is a promising process that could yield more-fire-resistant materials.

In the literature one can find information about the thermal properties of intact wood but there are almost no data on partly pyrolyzed products of both intact and preservative-compound-impregnated wood. It is also interesting to study the effect of impregnation of wood with fire retardants on its thermal properties.

In the present work we measured the specific heat and thermal conductivity of compacted sawdust treated with carbamide compounds [3, 4] based on orthophosphoric (compound I) and polyphosphoric (compound 2) acids as well as products of their thermooxidative decomposition in the temperature range 20–500°C.

The wood specimens studied were produced by cold-and-hot bath impregnation of conifer sawdust (the fraction $2 < X < 5$ mm). The modulus of the impregnation bath (the ratio of the mass of the solution to the mass of the sawdust) for treatment of the specimens was 15. Half of the sawdust impregnated with both compounds was subjected to heat treatment under isothermal conditions at 150°C for 40 min. In this process, cellulose (in conifer wood its content can reach 50%) and lignin (its content can be 17%) are etherified, which results in introduction of phosphoric acid groups into these compounds. After etherification, the material was carefully flashed with boiling distilled water to a neutral medium. Then, specimens with a 8% moisture content that had been dried and modified with compounds 1 and 2 were subjected to thermooxidative pyrolysis at 150, 220, 300, 400, and 500°C. In Fig. 1 one can see curves of thermogravimetric decomposition of speciments on a Q-1000 derivatograph (MOM, Hungary).

As can be seen from the present data, the highest condensed phase yield (52%) is observed in wood modified with polyphosphoric acid. In the material with residues of orthophosporic acid in ether groups it is a little lower (46%). The yield of the product pyrolyzed at 500°C is lower for impregnated sawdust than for modified

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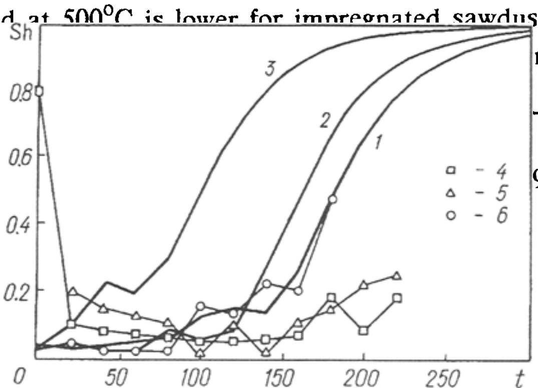

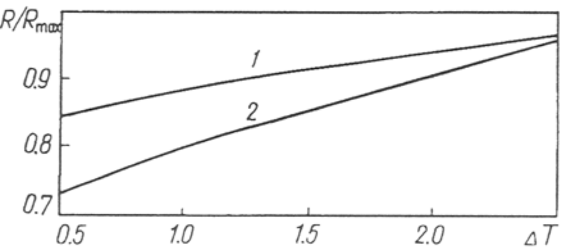

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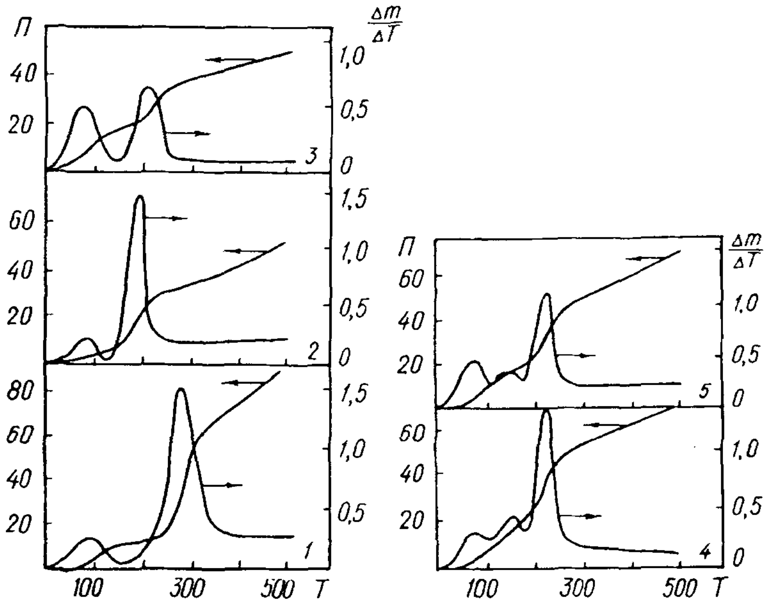

Fig. 1. Thermogravimetric curves of decomposition (in integral and differential forms) of wood specimens: 1) initial, 2) modified with carbamide and polyphosphoric acid (compound 1), 3) modified with carbamide and polyphosphoric acid (compound 2), 4) impregnated with compound 1, 5) impregnated with compound 2.

Estimation of the fire resistance of wood materials produced with polyphosphoric acid-based biological fire-retardant BAN (compound 2) developed at the Institute of General and Inorganic Chemistry of the Academy of Sciences of Belarus shows the high fire-retarding efficiency of the protective agent.

Surface treatment of the carbohydrate-lignin complex of wood with this agent provides fireproof materials (with a mass loss of 13–18% (GOST 16363) in estimation of fire resistance). Modification or autoclave impregnation of wood with a reagent consumption of 250 kg/m^3 ensures production of fireproof materials with a minimal mass loss.

The specific heats of the materials studied were determined with the comparative dynamic c-calorimeter method [5]. The essence of the method can be described as follows. The test specimen is placed into a metal ampoule and monotonically heated together with the ampoule by heat flux that is supplied to the system from the base through a heat-measuring device. The ampoule and specimen can be thermally connected with the environment only via the heat-measuring device. During heating the lateral sides of the surface are separated from the environment by an adiabatic shell. The measuring cell is designed in such a way that during heating in the developed heating stage the temperature field of the heat-measuring device is almost steady and linear, and all parts of the system are heated at similar rates. The heat flux that passes through the heat-measuring device can be inferred from its thermal conductivity $K_{\text{h.m}}$ and the temperature drop ΔT in it. At small temperature drops at the heat-measuring device, the temperature lag time $\tau_{\text{h.m}}$ at the device can be measured instead of ΔT. With the assumptions just mentioned, the calculated formula for the specific heat has the form

$$c = \frac{K_{\text{h.m}}}{M_{\text{s}}} (\tau_{\text{h.m}} - \tau^0_{\text{h.m}}) .$$

The "constants" $K_{\text{h.m}}$ and $\tau^0_{\text{h.m}}$ of the measuring cell are found during calibration in experiments with a standard copper specimen ($K_{\text{h.m}}$) and an empty ampoule ($\tau^0_{\text{h.m}}$).

The thermal conductivity of the specimens was measured with the monotonic heating method in a λ-calorimeter. Calculations were carried out with the formulas:

$$\lambda = h/P_{\text{s}} , \quad P_{\text{s}} = \Delta T_{\text{s}}\, S\, (1 + \sigma_{\text{s}})/\Delta T_{\text{h.m}}\, K_{\text{h.m}} - P_{\text{con}} , \quad \sigma_{\text{r}} = C_{\text{s}}/2\, (C_{\text{s}} + C_{\text{r}}) ,$$

TABLE 1. Specific Heat Capacities and Thermal Conductivities of Pyrolyzed Wood

Wood specimen	T,°C	20	150	220	300	400	500
Initial	c	1723	1729	1725	1737	1757	–
	λ	0.23	0.23	0.31	0.25	0.30	0.25
Impregnated with compound 1	c	2317	2919	2433	2060	2117	2010
	λ	0.51	0.66	0.45	0.34	0.39	0.43
Impregnated with compound 2	c	2062	2884	2210	–	1598	1670
	λ	0.5	0.52	0.3	0.57	0.31	0.48
Modified with compound 1	c	1854	1744	1761	1955	1749	1768
	λ	0.30	0.33	0.32	0.33	0.37	0.32
Modified with compound 2	c	1869	1890	1903	1815	1662	1662
	λ	0.31	0.30	0.28	0.29	0.33	0.32

where ΔT_s and $\Delta T_{h.m}$ are temperature drops across the specimen and the heat-measuring device. The parameters P_{con} and $K_{h.m}$ do not depend on the properties of the specimen and are determined during calibration of the instrument. For determination of the thermal conductivity and specific heat of specimens treated with the different compounds, pellets with a diameter of 15 mm and a height of 2–3 mm and 10 mm were formed with a press (50–100 kg/cm^2). For the decomposition products of the specimens, in the temperature range 150–220°C, carboxymethylcellulose (CMC) (a drop of 8% CMC solution per pellet) was used as a binder in compression of the pellets.

The measurement results are summarized in Table 1. The data were analyzed, bearing in mind that the pellets of sawdust are a fibrous disperse system that consists of particles which are organic swelling compounds. In this complicated multiphase system, heat can be transfered by conduction in all the phases, by convection, and by radiation. Since in the present case, the test samples are coarse disperse particles with a low (up to 8%) moisture content of the material and measurements are conducted at temperatures close to room temperature, heat conduction is the dominant process in heat transfer. The specific heats of the disperse specimens are affected by the thermal conductivity of the material itself, the impregnation compound, and the temperature level. As can be seen from Table 1, the specific heat of the sawdust pellets of 1750 J/(kg·K) is almost the same over the whole temperature range of study. We obtained heat capacities of specimens from intact sawdust (at 20° and 8% moisture contents) that agree within 2% with the values reported in [6] and are 7% lower than the values obtained in [7]. As the pyrolysis temperature increases, in the specimens studied some chemical reactions take place that result in destruction of the material. Decomposition of cellulose and its satellites stops in wood mainly by 350°C, and properties of a specimen are determined by the properties of the carbon residue. In spite of substantial changes in the composition and structural and chemical parameters of the wood that take place in the temperaturte range of heating, the specific heat of the pellets of untreated pyrolyzed sawdust does not change markedly.

It is known that thermal decomposition of cellulose has a nonuniform order [8]: first of all it starts in areas with the lowest density and then, as temperature increases, propagates to highly ordered regions. Therefore, along with the destruction of polysaccharide links, pores are formed in the wood structure due to burn-up of disordered microregions [9, 10]. The porous product formed absorbs water, which results in an increase in the specific heat of the pyrolyzed carbon. It is likely that a possible decrease in the heat capacity due to changes in the polymer composition could be partly compensated by the increased heat capacity of the porous air-dry carbon residue.

The effective thermal conductivity of studied untreated specimens given in Table 1 also changes slightly as the pyrolysis temperature increases from 20 to 500°C. This can be explained both by a slight change in λ of the material itself and by the fact that in a disperse system the nature of the material affects the thermal conductivity not directly, but via the dispersity and mechanical composition of the particles.

Table 1 also contains dependences of the thermal conductivity and specific heat on the pyrolysis temperature for specimens treated with impregnation compounds 1 and 2. As can be seen from the data given in the table, the behavior of the functions $\lambda = f(T)$ and $c = f(T)$ substantially differs from that of similar functions for the untreated specimens. For example, the specific heat capacity is 15–30% higher in comparison with the intact specimens. The heat capacity of pellets of impregnated compressed sawdust is composed of the heat capacity of the wood itself and the heat capacities of the impregnating compound and water contained in the specimen. When sawdust is kept in the hot impregnating compound, the fibers (cell walls) and voids between the cells are saturated with the compound. When drying occurs in air at room temperature, the moisture that is bound to the least extent evaporates from the cells first. Hygroscopic moisture is removed from fibers much less easily. By similarity, it can be suggested that the increase in the thermal conductivity and specific heat capacity that is obseved in the impregnated specimens at 20°C is caused not only by the presence of additional chemical elements of the impregnating compound in the specimen, but also with the presence of additional hygroscopic moisture. Moreover, specimens that are impregnated with compounds 1 and 2 and subjected to hydrolysis have sharp maxima of thermal conductivity and specific heat capacity at 150°C. In the temperature range 140–160°C lignin and cellulose are etherified by phosphoric acids, and as a result the phosphoric acid residues that occur in the ether groups are introduced into the compounds, and water and ammonia are released. As the temperature of the treatment increases further from 150 to 300°C in the sawdust-impregnation compound system the etherification reaction with primary alcohol groups of cellulose that are free of intra- and intermolecular interaction continues. Moreover, the carbohydrate-lignin complex is dehydrated to produce a phosphorus-containing carboniferous material. All these factors affect the thermal properties of the test specimens.

Table 1 also contains dependences of the thermophysical characteristics of sawdust specimens modified by compounds 1 and 2 on temperature. Here, the specific heat capacities are slightly different (within 12%) from those quantities of the initial specimens at different pyrolysis temperatures. In the range of pyrolysis temperature within 300°C the difference between the thermal conductivities of the modified sawdust specimens and the initial wood can reach 35%, which suggests different mechanisms of thermal decomposition of the initial and treated cellulose.

The present results make it possible to estimate the specific heat capacities and thermal conductivities of compacted sawdust specimens subjected to oxidative pyrolysis at 20, 150, 220, 300, 400, and 500°C. Since λ and c were measured not only during the pyrolysis, but also after it, the measured thermal properties are not distorted by exo- and endoeffects that accompany thermal decomposition of material. Moreover, the present studies reveal the effects of various impregnation compounds on the thermal properties of the specimens. In combination with other studies (thermographic, determination of adsorption properties, chromatography, etc.), the present data give a more complete picture of thermal decomposition of complex organic materials.

NOTATION

λ, thermal conductivity, W/(m·K); a, thermal diffusivity, m^2/sec; c, specific heat capacity, J/(kg·K); $K_{\mathrm{h.m}}$, heat conductance of heat-measuring device, W/K; $\tau^0_{\mathrm{h.m}}$, temperature lag time in heat-measuring device, sec; M_s, mass of specimen, kg; h, height of specimen, m; P_s, thermal resistance of specimen, (K·m^2)/W; P_{con}, contact thermal resistance, (K·m^2)/W; S, cross-sectional area of specimen, m^2; σ_s, correction for heat capacity of specimen; C_s, total heat capacity of specimen, J/K; C_c, specific heat capacity of core, J/K; X, linear dimensions of fraction, mm; Δm, mass loss, mg; Π, relative mass loss, %; ΔT, temperature drop, °C.

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