

**INFLUENCE OF RETARDANTS TO BURNING LIGNOCELLULOSIC  
MATERIALS**

Ivana TUREKOVÁ, Jozef HARANGOZÓ, Jozef MARTINKA

**Abstract**

*The paper deals with monitoring retardant changes of lignocellulosic materials. Combustion of lignocellulosic materials and fire-technical characteristics are described. In assessing the retarding effect of salt  $NH_4H_2PO_4$ , fire-technical characteristics as limiting oxygen index (LOI) were measured, and by using thermoanalytical TG and DSC methods. High-temperature process of cellulose degradation at various flame concentrations was studied.*

**Key words**

*burning, fire-technical characteristics, limiting oxygen index, thermal analysis*

**Introduction**

The aim of the testing was to assess the impact of retardants to flame and flameless burning propagation of cellulose. Retarding effect of salt  $NH_4H_2PO_4$  by thermoanalytical methods was observed. The advantage of research is that the changes in biopolymer materials were recorded by increasing temperature. The thermogravimetry and the differential scanning calorimetry were carried out by testing of concentrated samples of different significant results. For evaluation of retarding effects of TG and DSC methods were used to assess the retarding effect on the process of burning, while the changes were recorded in reaction enthalpy (DSC), the maximum rate of active degradation (DTG), resistant residue at 600 °C (TG), the starting temperature of active decomposition (TG) and impact of oxidation of the atmosphere on the course of thermal decomposition (DSC, TG).

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Ivana Tureková, Assoc. Professor, Ph.D., Jozef Harangozó, MSc. Eng., Jozef Martinka, Ph.D. - Institute of Safety and Environmental Engineering, Faculty of Materials Science and Technology, Slovak University of Technology in Bratislava, Botanická 49, 917 24 Trnava, e-mail: >ivana.turekova@stuba.sk<, >jozef.harangozo@stuba.sk <, >jozef.martinka@stuba.sk<

As a result of biochemical processes of plants, wood is a complex of substances with distinct chemical and physical properties. To give an idea of the complex substance, it is necessary to research the structure of macromolecules of wood parts. It is important to know the character and properties of substances. Particular wood substances cannot be observed separately; it is therefore important to focus on the perspective of interaction and reciprocal connection. When we separate one of the main substances, there are such important changes in the wood that we cannot talk about the same substance as in the natural wood [1].

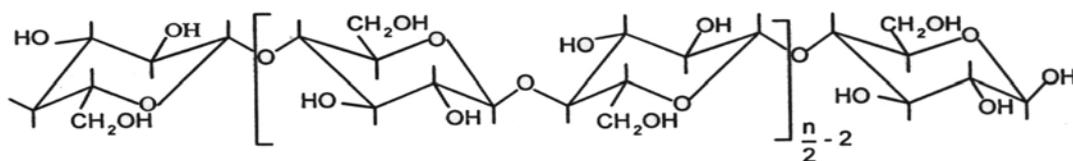
This also applies in the case of thermal degradation of wood respectively wood substances. Considering all these facts, the processes of wood heat degradation will depend on:

- chemical properties (chemical content),
- physical properties (humidity, thermal conductivity, specific heat),
- mechanical properties (decreased solidity properties caused by cracks),
- environmental atmosphere (the concentration of fouling, speed and direction of air flux),
- antipyrene wood treatment [2].

The theory of wood burning comes from the general burning theory of solid substances. The issue of wood combustibility, in wooden or other materials, is based on a determination of present conditions and factors that influence the burning process. Combustibility is not a physical unit; it only characterizes the value of substance behaviour by certain conditional factors. When comparing the combustibility of materials, we compare the changes in chemical content and the changes in the physical and mechanical properties, caused by the thermo-oxidizing reaction. [3].

Wood is a biopolymer because of its base, which has high energetic potential, mostly in covalent bonds of polysaccharides and lignin. The electrons of covalent bonds are excited to the higher energetic level due to a sufficient supply of energy (heat). Thus, the excited covalent bonds can be split and react with other reactive substances.

The most important component of wood is cellulose. Pure cellulose is an unbranched homopolymer with repeated cellobiose components. Cellulose is a basic structural component of cell walls in wood. Cellulose consists of two  $\beta$ -D anhydroglucopyranosis units links which are connected in positions 1 $\rightarrow$ 4- $\beta$ -D by a glucosidic bond. The neighbouring units are connected to one another and turned by 180° (Fig. 1) [4, 5].



*Fig. 1 Structural formula of the cellulose macromolecule[3]*

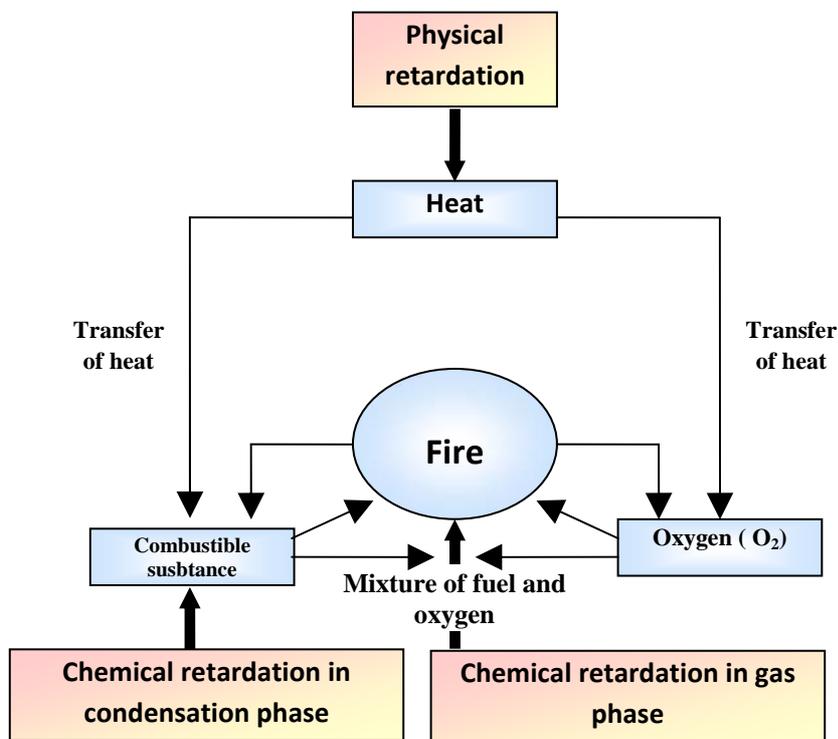
### **Fire-technical characteristics**

Substances are characterized by physical-chemical properties and fire-technical characteristics. The physical-chemical properties have a character of parameters of substance defining. The fire-technical characteristics are the common values depending on the whole

group of factors including the way of their determination. The fire-technical characteristics can be defined as the numeral values, which reflect the behaviour of substances or materials by the initiation and process of burning to its termination. These characteristics relate to certain partial process phases of ignition and combustion, as ignition, time to flame forming, rate and time of burning, flame propagation rate, amount of formed heat and smoke, amount and kind of gas products of burning, mass reduction, amount and properties of carbonized rest after burning and others. A certain set of fire-technical characteristics is needed for a complex evaluation of fire danger of a substance, material or product [6, 7].

### Principle of fire retardation

During the process of fire retardation, it is necessary to affect those events that cause the termination of burning. In fact, these influence the rate of formation (intake) or rate of heat removal from the reaction zone of fire. Flame fire of chemical reactions takes place in the gas phase, but all the process passes through several intermediate stages of combustion (Figure 2) [6, 8, 9].



*Fig. 2 The scheme of three fire elements and possible retardation*

Fire retardants change the process of active thermal decomposition of cellulose-based materials by catalyzing the reactions by lower temperatures and limiting the rate and extent of the main decomposition reaction.

## Assessing thermal stability of protected and unprotected cellulose

### Sample preparation

FILTRAK 389 quantitative filter paper was used as cellulosic material in the experimental measurements. It is a filter medium fast filtering, ash-free. The cellulose samples (they were prepared according to the test method) conditioned in desiccators for 24 hours at  $20 \pm 1$  °C and then weighed on an analytical balance. The  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  was used as a retardant for testing and applied to cellulose by inserting it to solutions of different concentrations.

### Testing protected and unprotected cellulose

The methods that were applied for material testing are described below:

1. The method of thermal analysis TG and DSC that characterize the material behaviour by high-temperature degradation. We used METTLER Toledo thermo analyzer (Switzerland) to measure DSC TG 20 or 50, together with Graphware TA - 72.2/5 evaluation software. The thermoanalytic methods belong to the methods of elementary research.
2. The method of limited oxygen index, which defines combustibility and rate of burning.

### Thermogravimetric analysis (TGA)

TGA is the most important thermo analytic method, which we used in the study of thermoanalysis process and biopolymer burning. The heating rate in testing was  $10$  °C.min<sup>-1</sup>. The thermo gravimetric analysis was performed at the temperature of  $600$ ° C. According to the results of measurements in dynamic air atmosphere, various intermediate grades of decay, mass reduction and temperature by maximum reduction rate were carried out (Table 1).

THERMAL CHARACTERISTICS OF PARTICULAR DISINTEGRATION OF PROTECTED AND UNPROTECTED CELLULOSE  $\text{NH}_4\text{H}_2\text{PO}_4$  by TG METHOD Table 1

| Quantity<br>$\text{NH}_4\text{H}_2\text{PO}_4$<br>[g.m <sup>-2</sup> ] | Integrates of<br>disintegration | Temperature<br>interval<br>[°C] | Mass<br>reduction<br>[%] | Temperature by<br>max. reduction rate<br>[°C] |
|--|---------------------------------|---------------------------------|--------------------------|---|
| pure cellulosis  | I. grade                        | 277.3 – 353.0                   | 79.60                    | 333.7   |
|  | II. grade                       | 353.0 – 495.4                   | 15.24                    | 480.7   |
| 44.08  | I. grade                        | 166.2 – 292.4                   | 33.82                    | 263.7   |
|  | II. grade                       | 292.4 – 600.0                   | 34.98                    | .   |
| 22.15  | I. grade                        | 176.3 – 288.4                   | 35.06                    | 259.0   |
|  | II. grade                       | 288.4 – 600.0                   | 36.81                    | .   |
| 10.72  | I. grade                        | 183.4 – 282.3                   | 40.61                    | 252.0   |
|  | II. grade                       | 282.3 – 600.0                   | 42.36                    | 495.2   |
| 5.25   | I. grade                        | 185.4 – 308.5                   | 46.18                    | 266.0   |
|  | II. grade                       | 308.5 – 600.0                   | 41.98                    | 495.2   |

In Figures 3 - 7, there are thermograms of protected and unprotected cellulose with different quantity retarder. On the basis of the thermoanalytical measurements, we can conclude that fire resistance of the examined lignocellulose material increases with the amount of  $(\text{NH}_4)_2\text{HPO}_4$  applied. The increasing amount of retarder influenced also the process of flameless combustion of cellulose, where thermal maximum was not observed in the case of lower concentrations of flame.

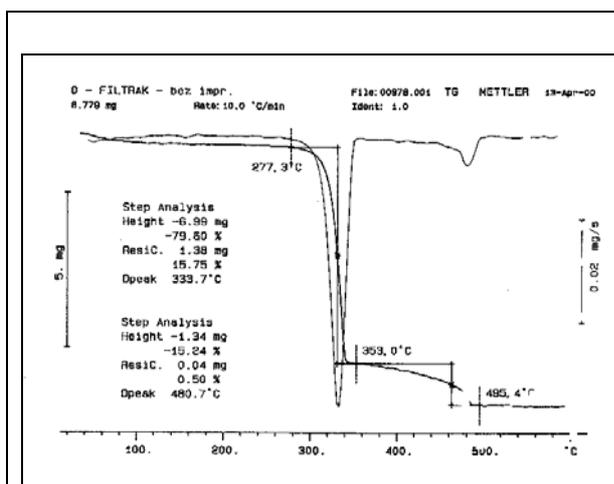


Fig. 3 TG record of unretarded cellulose

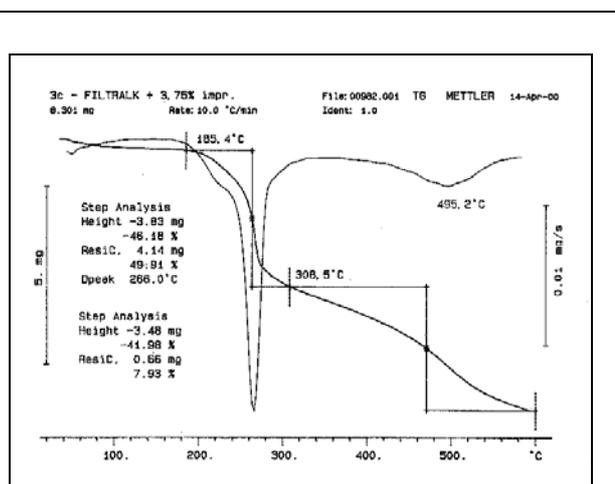


Fig. 4 TG record of retarded cellulose with retardant amount  $\text{NH}_4\text{H}_2\text{PO}_4$   $5,25 \text{ g.m}^{-2}$

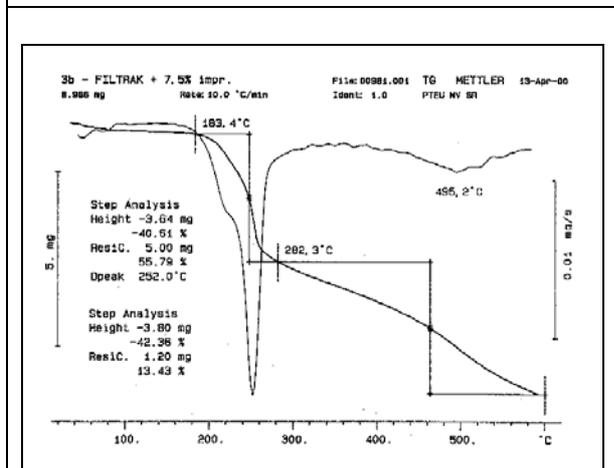


Fig. 5 TG record of retarded cellulose with retardant  $\text{NH}_4\text{H}_2\text{PO}_4$   $10,72 \text{ g.m}^{-2}$

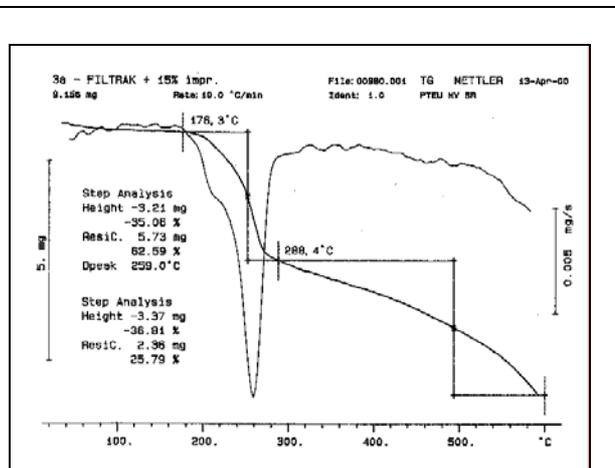
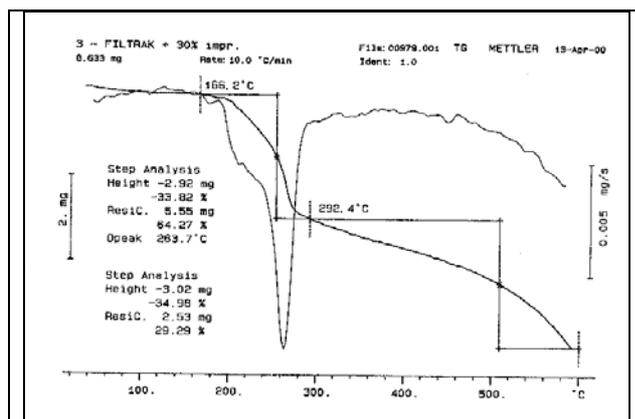


Fig. 6 TG record of retarded cellulose with retardant  $\text{NH}_4\text{H}_2\text{PO}_4$   $22,15 \text{ g.m}^{-2}$



**Fig. 7** TG record of retarded cellulose with retardant  $\text{NH}_4\text{H}_2\text{PO}_4$   $44,08 \text{ g.m}^{-2}$

### Diferencial scanning calorimetry (DSC)

DSC method was used to measure the changes in reaction enthalpies of fuel-forming thermal generation processes by thermal disintegration of testing samples. The reaction heats in the selected interval of exothermic (endothermic) reactions were determined, and the maximum rate of heat formation was characterised by the maximum temperature of exothermal peak on the thermoanalytical curve between 25 - 600 °C in dynamic air atmosphere. In this way, the determined changes of reaction enthalpy are not identical with the enthalpic measurements in a calorimetric bomb, but they do provide better information about the heat released by thermal degradation. They also provide information about thermal colour reaction in the individual grades of thermal disintegration in testing sample.

#### CORRELATION OF CHANGE PROCESS BY REACTION ENTHALPY OF PURE CELLULOSE AND CELLULOSE PROTECTED WITH $\text{NH}_4\text{H}_2\text{PO}_4$ METHOD DSC

Table 2

| Quantity<br>$\text{NH}_4\text{H}_2\text{PO}_4$<br>[ $\text{g.m}^{-2}$ ] | Temperature<br>interval<br>[°C] | Change of reaction<br>enthalpy<br>[ $\text{J.g}^{-1}$ ] | Temperature by<br>max. peak<br>[°C] |
|---|---------------------------------|---|-------------------------------------|
| pure cellulosis   | 35.0 – 122.1                    | - 121   | 79.3                                |
|   | 311.2 – 555.1                   | 5966  | 350.8 (506.0)                       |
| 44.08   | 186.8 – 244.2                   | -1170   | 204.2                               |
|   | 244.2 – 280.0                   | 462   | 266.9                               |
| 22.15   | 185.6 – 228.0                   | - 411   | 200.2                               |
|   | 228.0 – 579.0                   | 14 942  | 307.4 (502.7)                       |
| 10.72   | 183.6 – 224.1                   | - 182   | 198.2                               |
|   | 224.1 – 593.1                   | 18 854  | 305.4 (508.9)                       |
| 5.25  | 222.0 – 598.5                   | 25 848  | 310.5 (520.0)                       |

Generally, we can say that the larger the area of endothermic peaks by fire retardants is, the more efficient they will be in the protection of polymeric materials against high-temperature degradation.

These results characterize the retardation efficiency of salts dihydrogen phosphor, which are applied in cellulose and describe the behaviour of these materials in the process of high-temperature degradation. The change of each parameter in measurement can cause the changes in the determined characteristics.

### **The method of limiting oxygen index (LOI)**

The LOI method was used in testing the retardation efficiency of fire retardants, too. LOI is defined as the lowest concentration of oxygen mixed with nitrogen, expressed as volume fraction of oxygen in 100 parts by volume mixture of  $N_2$  and  $O_2$ , in which the sample keeps burning at the conditions defined by test. This feature characterizes the ability of the material to burn even at reduced oxygen concentration, especially in the conditions of developed fires in buildings where the air supply to the area is very limited [10].

The sample is ignited on the upper end and the flame spreading in the opposite direction of the flowing oxidizing agent is observed in the interval of 180 seconds at minimum. The rate of gas flow (usually a mixture of oxygen and nitrogen) is  $4 \pm 1 \text{ cm.s}^{-1}$ . The equipment can be combined also with a set for heating a flowing mixture of oxygen and nitrogen. This modification enables the observation of the influence of temperature on the change LOI.

The equipment for determining LOI also allows us to provide the linear rate of flame spread along the surface, as well as to develop a model of the non-flame process of propagation (Fig. 8). The concentration of oxygen and nitrogen is mostly determined by flowmeters, which is the latest equipment, and paramagnetic analyzers of oxygen. The results of the LOI retarded cellulose are shown in two vertical and horizontal configurations in Table 3.



*Fig. 8 Equipment of combustibility determination by the method of oxygen index (vertical modification)*

LIMITING OXYGEN INDEX OF RETARDANT AND NON-RETARDANT  
CELLULOSE  $\text{NH}_4\text{H}_2\text{PO}_4$

Table 3

| Amount of applied<br>retardant<br>$\text{NH}_4\text{H}_2\text{PO}_4$ | LOI<br>[vol. % $\text{O}_2$ ] |                         |
|--|-------------------------------|-------------------------|
|  | Vertical distribution         | Horizontal distribution |
| Pure cellulose<br>without retardation                                | 17                            | 21                      |
| 10.1   | 34                            | 34                      |
| 19.7   | 45                            | 77                      |
| 32.1   | 66                            | 68                      |
| 39.2   | 66                            | 76                      |

A modification of counter-flow testing of vertical and horizontal distributions provided different LOI results. In the case of pure and retarded cellulose, the results of fire initiations in the vertical position were lower. The LOI value in retarded samples increased with increased retardant concentration in samples. The amount of applied retardant,  $31.1 \text{ g.m}^{-2}$  significantly affected the limit LOI which is an evidence of high substance efficiency of  $\text{NH}_4\text{H}_2\text{PO}_4$  functioning as a cellulose retardant.

### Discussion and conclusion

If to compare the effectiveness of various retarding substances, it is necessary to ensure the same standard conditions as heating rate, atmosphere, amount of sample and its pre-treatment), and to have enough knowledge about quantity of retardant. Testing the cellulose of different of  $\text{NH}_4\text{H}_2\text{PO}_4$  concentrations by using DSC and TG methods showed that the best results were achieved at the value of  $44.08 \text{ g.m}^{-2}$  wt. of pure  $\text{NH}_4\text{H}_2\text{PO}_4$  retardant in the sample.

Retardant properties showed high efficiency of the flame. It was proved that pro-degradation effect caused by dehydration reactions shifts the beginning of the reaction to lower temperatures than in the case of pure substances. To apply these retardants on wood, other factors such as the size and value of the active surface and method of application of the sample impregnation should be considered in further research. It was confirmed that  $\text{NH}_4\text{H}_2\text{PO}_4$  salt is one of the basic substances which, when applied to materials, will be subject to further research. Research confirmed that optimum interface concentration of salt is  $10.8 \text{ \% wt.} - 3.31 \text{ \% wt.}$ , where an important retarding effect on cellulose was proved.

The LOI method is a suitable method for comparison of a fire retardant's efficiency, but the visualisation of fire is advantageous in terms of searching for new testing methods. This advantage provides valuable information about the influence of external conditions on the real process of material burning.

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## Reviewers:

Milan Oravec, Professor, Ph.D. – Institute of Safety and Quality and environmental Science, Faculty of Mechanical Engineering, Košice

Danica Kačíková, Assoc. Professor, Ph.D. – Department of Fire Protection, Faculty of Wood Sciences and Technology, Technical University in Zvolen

