

Research of pyrolytic charring mechanism in natural and fire retardant treated pine wood

A. Jefimovas¹, R. Mačiulaitis²

Abstract – *There is a number of various fire retardant solutions created worldwide, however, performance research has not been carried out in detail for all of them. Furthermore, the process of wood combustion and charring is further impeded by different environmental conditions forming during fire. The work covers the thermogravimetric, microscopic and EDS research in different environmental conditions. Based on the thermogravimetric research it was determined that there had been three exo-effects recorded in the DTA curve for natural pine in the air medium, whereas for natural pine wood in the nitrogen medium and natural pine treated with BAK-1 both in the air and nitrogen media there had been six exo-effects recorded. Based on the EDS research it was determined that in the residue of both, natural and treated pine produced in the nitrogen environment, the amount of oxygen had been lower and the amount of carbon had been higher compared to the residue produced in the air environment, which means that processes in the nitrogen environment take place using the oxygen present in the wood composition, and oxidation of char in the air medium takes place in a more intensive manner. This is partially confirmed by the microscopic (SEM) research of the pine char residue. Copyright © 2014 Praise Worthy Prize S.r.l. - All rights reserved.*

Keywords: wood, fire retardants, thermogravimetric analysis, SEM, EDS.

I. Introduction

Wood is a natural product used in many areas. It is a material of plant origin, composed of cells with woody walls, and the cells are composed of organic compounds. From old times it has been widely used and loved by people due to its aesthetic properties. It is a popular material for interior and exterior decoration. Wood is widely used for construction purposes because it is light, strong, has high compression, tensile and bending strength, is elastic, has low thermal conductivity and is easy to process [1].

Wood as a building material has drawbacks as well. It is a hygroscopic, anisotropic, flammable and not resistant to decaying material. Its main drawback is considered to be fast flaming up and burning [2], [3]. Furthermore, burning wood emits gaseous products that are toxic to people and animals, and pollute atmosphere [4].

Wood combustibility is useful in case it is used as a fuel, however it is not useful when wood is used as a building material. As a rule, combustibility of timber structures is decreased by treating them with fire retardant solutions. Quite a number of works have been dedicated to research of efficiency and durability of fire retardant solutions [5 - 13].

Combustibility values of wood treated with a fire retardant solution depend on the chemical composition of the solution used, its consumption, treatment method

(subject to penetration depth of fire retardant compounds) as well as structure and characteristics of timber itself. [14 - 18].

The thermogravimetric analysis is used for research of thermal decomposition, combustion mechanism and kinetics of natural and fire retardant treated timber and its products [19]. The thermogravimetric analysis can be performed in different environment of oxidising or reducing gases. Thus, various conditions that are likely to occur during a fire and its extinguishing are simulated [19 - 21]. However, this mechanism of thermal decomposition and combustion of wood has not been investigated completely and proved by experiments yet.

The aim of this work is to investigate in more detail how pyrolysis and charring of natural and fire retardant treated wood occur in different gas media.

II. Test Equipment and Methods

II.1. Tested materials and their characteristics

For experiments pine wood was used. The moisture content in the specimens was measured using a moisture meter HPM 2000 and did not exceed 15 %.

For treating purposes the fire retardant solution BAK-1 was used. The samples cut from pine wood and dried afterwards (20 mm long, 15 mm wide and 10 mm thick) were soaked for 24 hours completely immersed in the fire

retardant. After taking them out of the fire retardant, the samples were conditioned in the room under the conditions of stable temperature and humidity according to the requirements of LST EN 13238:2010 [22].

II.2. Thermogravimetric analysis

The thermographic analysis was carried out using the thermogravimetric analyser Linseis STA PT-1600. The analysis was performed in the temperature range from 25 °C to 1000 °C. The rate of temperature increase was 10 °C/min. The analysis was performed in the gaseous media of nitrogen and atmospheric air. The flow of nitrogen and air was 0.15 l/min. For testing purposes approx. 10 mg pieces of wood were used.

II.3. SEM ir EDS research

The scanning electron microscopy (SEM) and energy dispersive spectroscopy (chemical composition, EDS) were performed with the char residue from natural and treated wood.

Char samples used for research were produced by heating wood in the thermogravimetric analyser Linseis STA PT-1600 in the air or nitrogen media and constantly increasing temperature at the rate of 10 °C/min. (maintaining the flow of 0.15 l/min.) only up to 400 °C.

The research was performed using scanning electron microscope JEOL JSM-7600F with the EDS microanalysis system Oxford INCA Energy X-Max20, having resolution of 1,5 nm, magnification from 25 to 1000000x. During the tests voltage of 4.0 kV and 10 kV was used, the surface of test specimen was coated with gold, 500 and 1000x magnification was used.

III. Overview of Results

Pyrolysis of natural pine wood in the nitrogen environment takes place in stages (Fig. 1). A few endo-effects in the DTA curve (min ~ 60, 100 °C) can be explained by eliminating moisture present in wood at low (up to 120 °C) temperatures. Here the mass loss amounts to ~7 %.

The exo-effect in the first stage occurs in the temperature range of 120–220 °C (max ~180 °C). It is likely that at that time pyrolysis and decomposition of hemicellulose take place. The mass loss in this stage amounts to ~5 %.

The second exothermal effect in the process of pyrolysis occurs in the temperature range of 220–330 °C (max ~290 °C). The mass loss in this stage amounts to ~20 %. Decomposition and combustion of cellulose are likely to prevail in this stage.

The third exothermal effect and at the same time the pyrolysis stage occurs in the temperature range of 330–

380 °C (max ~350 °C). This is likely to show the beginning of lignin destruction. The mass loss in this stage amounts to ~36 %. This essentially matches the results of the previous research [21].

After the temperature exceeds 380 °C, another three exothermal effects occur: (max ~430 °C), (max ~540 °C) and (max ~720 °C). This can be explained by continuing destruction of another fraction in lignin and also reactions taking place between carbon, its monoxide and even water vapour [23]. According to DTG, this process starts at 400 °C and ends when the temperature of 910 °C is reached. The total mass loss attributable to these three effects amounts to ~21 %.

The total mass loss amounted to ~95 %.

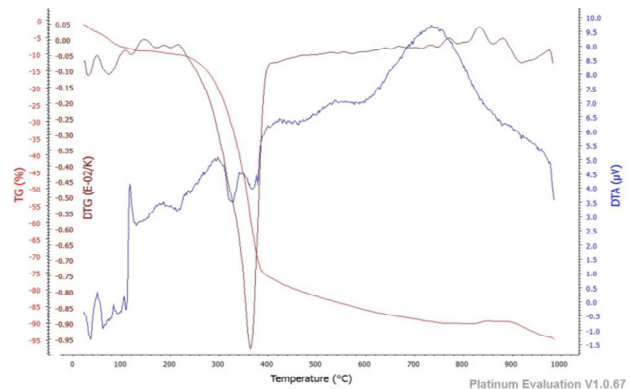


Fig. 1. Curves of thermogravimetric analysis in nitrogen medium for natural pine wood

Pyrolysis of pine wood treated with the fire retardant BAK-1 in the nitrogen environment also takes place in stages (Fig. 2). The endo-effect in the DTA curve (min ~104 °C) can be explained by eliminating capillary moisture (water) present in wood. Here the mass loss amounts to ~17 %.

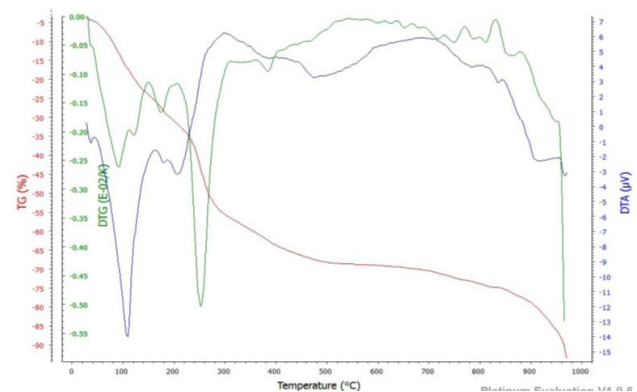


Fig. 2. Curves of thermogravimetric analysis in nitrogen medium for natural pine wood treated with BAK-1

The exo-effect in the first stage occurs in the temperature range of 105–170 °C (max ~160 °C). It is likely that at that time pyrolysis and decomposition of hemicellulose take place. The mass loss in this stage amounts to ~10 %.

The second exothermal effect in the process of pyrolysis occurs in the temperature range of 170–210 °C (max ~190 °C). Decomposition and combustion of cellulose prevail in this stage. The mass loss in this stage amounts to ~5 %.

The third exothermal effect and at the same time the pyrolysis stage occurs when the temperature exceeds 210 °C and ends at the temperature of approx. 460 °C. Its maximum is at ~300 °C. The process is much faster compared to the second stage with prevailing gasification and oxidation reactions in lignin. The mass loss in this stage amounts to ~36 %.

Later three more exo-effects occurred in the temperature range from 460 to 920 °C with corresponding maximums at the temperature of ~690 °C, ~800 °C and ~850 °C. This again can be explained by continuing destruction of another fraction in lignin and also reactions taking place between carbon, its monoxide and even water vapour [23]. The total mass loss attributable to these three effects amounts to ~14 %.

The total loss of mass amounted to ~92 %.

Pyrolysis of natural pine wood in the air environment also takes place in stages (Fig. 3). The endo-effect in the DTA curve (min ~105 °C) can be explained by eliminating moisture (water) present in wood. Here the mass loss amounts ~15 %.

The exo-effect in the first stage occurs in the temperature range of 140–420 °C (max ~350 °C). At that time pyrolysis and oxidation of hemicellulose take place. The mass loss in this stage amounts to ~64 %.

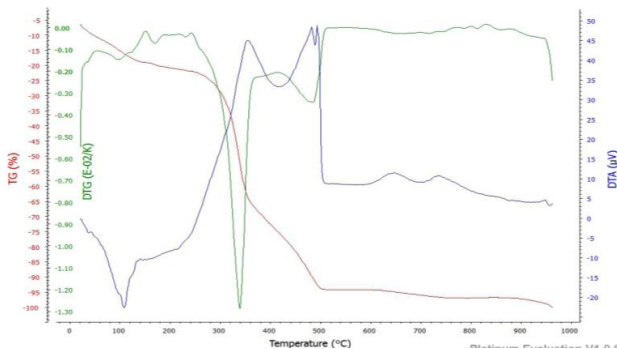


Fig. 3. Curves of thermogravimetric analysis in air medium for natural pine wood

The second exothermal effect in the process of pyrolysis occurs in the temperature range of 420–480 °C (max ~470 °C). Decomposition and combustion of cellulose prevail in this stage. The mass loss in this stage amounts to ~13 %.

The third exothermal effect and at the same time the pyrolysis stage take place in the temperature range of 480–510 °C. Its maximum is at ~490 °C. At that time gasification and oxidation reactions of lignin prevail. The mass loss in this stage amounted to ~7 %.

The total mass loss amounts to ~99 %.

Such results (Fig. 1 and Fig. 3) perfectly match the data obtained during our previous researches [21], and minor differences can be explained by the fact that tests have been performed using another identical piece of equipment with crucibles made of different material, however samples from the same set.

Gasification and combustion of pine treated with fire retardant BAK-1 in the air environment also take place in stages (Fig. 4). The endo-effect in the DTA curve (min ~110°C) can be explained by eliminating capillary moisture present in wood. The mass loss amounts to ~7 %.

The first exothermal effect in the process of pyrolysis and oxidation of hemicellulose occurs in the temperature range of 120–210 °C (max ~160 °C). The mass loss in this stage amounts to ~14 % of the total mass of the sample.

The second exothermal effect occurs in the temperature range of 210–300 °C (max ~260 °C). In this stage the mass loss is immediate and amounts to ~30 %. It means both formation of major amount of volatile gases, and prevailing decomposition and combustion of cellulose.

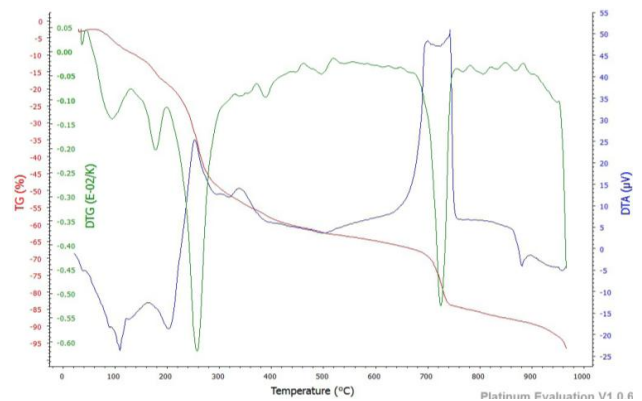


Fig. 4. Curves of thermogravimetric analysis in air medium for natural pine wood treated with BAK-1

The third exothermal effect in the process of decomposition and combustion of lignin occurs in the temperature range of 300–510 °C (max ~340 °C). The mass loss in this stage amounts to ~13 %.

Later (from 510 to 880°C) two more exo-effects with maximums at ~700 °C ~740 °C occur, which can be treated as a duplet as the DTG exhibits no interruption. The flash effect could be explained by decomposition of foamed char film itself and combustion of carbon monoxide. The total mass loss amounts to ~19 %.

Later on one more exo-effect occurs with its maximum at ~900 °C, which ends at the temperature of 960 °C. It is likely that this exo-effect can be explained by the prevailing oxidation in char. The mass loss in this stage amounts to ~3 %.

The total mass loss amounted to ~86 %.

Figures 5 through 8 show microscopic (different resolutions) pictures of the fracture surface in char

resulting from natural and treated with BAK-1 pine wood produced by heating it to 400 °C in the nitrogen or air media.

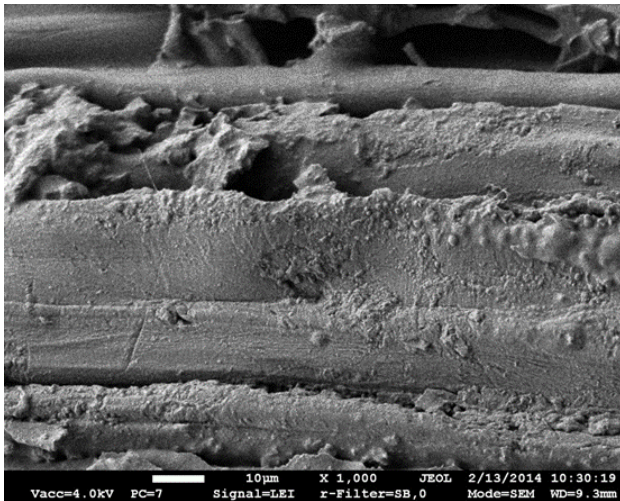


Fig. 5. Char from natural pine wood produced in nitrogen medium

The surface of char resulting from natural pine wood (Fig. 5) burnt in the nitrogen environment exhibits protrusions, irregularities, which are likely to have formed in the process of pyrolysis and decomposition by eliminating molecular oxygen from wood [21].

Whereas the surface of char resulting from natural pine wood (Fig. 6) burnt in the air environment is relatively homogeneous, clean and free of cracks.

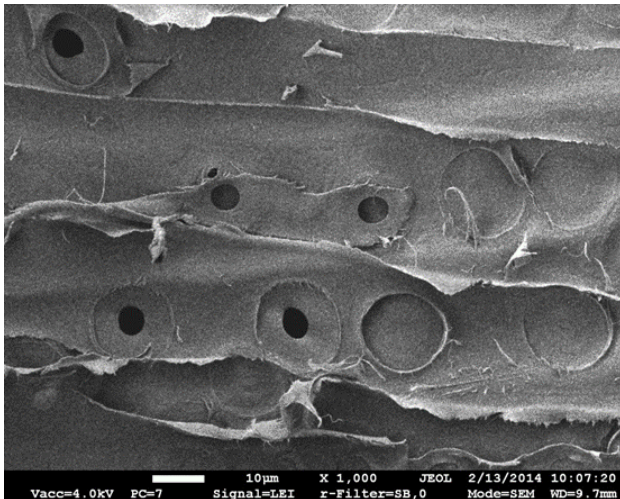


Fig. 6. View of char resulting from natural pine wood produced in air medium

Whereas the surface of char resulting from pine wood treated with BAK-1 produced in the nitrogen environment (Fig. 7) is very similar to the equivalent surface of char without fire retardant treatment (Fig. 5). The surface views of char resulting from pine wood treated with BAK-1 produced in the air environment

(Fig. 8) and nitrogen environment (Fig. 7) have only unessential differences.

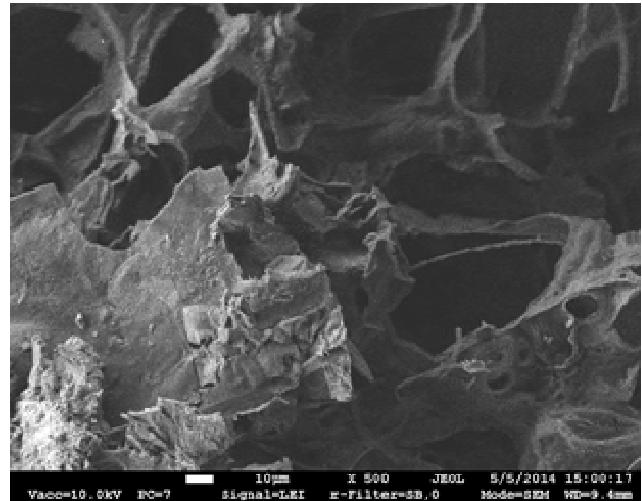


Fig. 7. View of char resulting from pine wood treated with BAK-1 produced in nitrogen medium

The typical chemical composition of char residue resulting from natural and treated with BAK-1 pine wood produced by heating to 400 °C in the nitrogen or air media is presented in Table 1. As it can be seen from the data in the table, in all cases the amount of carbon makes the largest part, the amount of oxygen is smaller and the amount of other elements is still smaller.

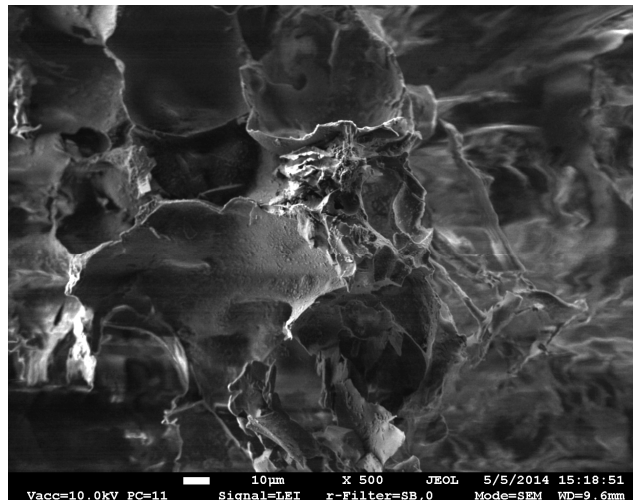


Fig. 8. View of char resulting from pine wood treated with BAK-1 produced in air medium

The amount of carbon is relatively the biggest in the char residue resulting from natural pine wood produced in the nitrogen medium – 77.9 %, its amount is lower in the char residue resulting from natural pine wood, however produced in the air medium – 73.3 %. The amount of carbon is still smaller in the char residue resulting from pine wood treated with BAK-1 produced in the nitrogen medium – 50.8 %, and the smallest

amount – 50.2 % – is in the char residue resulting from pine wood treated with BAK-1 produced in the air medium. The largest amount of oxygen is in the char residue resulting from pine wood treated with BAK-1 produced in the air medium – 36.4 %, and the smallest amount is in the char residue resulting from natural pine wood produced in the nitrogen medium – 20.4 %. The residue of natural pine wood produced in the air environment has 22.9 % of oxygen, and the residue of pine wood treated with BAK-1 produced in the nitrogen environment has 33.6 % of oxygen.

TABLE I
Prevailing chemical composition of char resulting from natural and treated pine wood

Wood (medium)	Elemental composition, %				
	C	O	Na	K	Ca
Pine (nitrogen)	77.9	20.4	0.4	0.5	0.8
Pine (air)	73.3	22.9	0.9	1.1	1.8
Pine BAK-1 (nitrogen)	50.8	33.6	0.3	14.3	1.0
Pine BAK-1 (air)	50.2	36.4	0.7	12.1	0.6

However, the amount of oxygen in char residue resulting from both, natural and treated pine wood, produced in the nitrogen environment is relatively smaller compared to the residue produced in the air environment. And referring to the amount of element carbon, everything is vice versa.

This obtained data not only confirms our previous results [21], that in the nitrogen environment the processes take place using the internal oxygen present in the composition of wood but also allow stating that in the air medium a relatively larger amount of carbon itself reacts with oxygen before it reaches the temperature of 400 °C.

Furthermore, in the char residue of pine wood resulting from pine wood treated with BAK-1 there are larger amounts of element potassium – 14.3 % and 12.1 %, compared to that in the char residue resulting from natural pine wood – 0.5 % and 1.1 %. This confirms that fire retardant is composed of a potassium compound.

IV. Conclusion

1. 3 exo-effects with maximums at the temperature of ~350 °C, ~470 °C and ~490 °C are recorded in the DTA curve of natural pine wood in the air environment, whereas in the DTA curve of pine wood treated with BAK-1 in the same environment there are 6 exo-effects recorded with maximums at ~160 °C, ~260 °C, ~340 °C, ~700 °C, ~740 °C and ~900 °C. It can be seen from these results that pyrolysis and destruction processes of treated pine wood essentially differ from those of natural wood. Having reached the temperature of ~510 °C, natural pine wood actually burns completely: the mass loss is as high as ~99 %. Whereas pyrolysis and oxidation of treated

pine wood continues up to 1000 °C, and the total mass loss amounts to 86 %.

2. In each DTA curves of both, natural pine wood and treated with BAK-1, in the nitrogen environment there are 6 exo-effects recorded, which again is different from the processes in the air medium. The maximums of the first three exo-effects (at lower temperatures) in treated pine wood occur at ~160 °C, ~190 °C and ~300 °C, and in natural pine wood – at ~180 °C, ~290 °C, ~350 °C. After the first three exo-effects the mass loss in case of treated pine wood amounts to 51 %, and in case of natural pine wood – 61 %. The maximums of other three exo-effects in case of treated pine wood occur at ~690 °C, ~800 °C and ~850 °C, and the maximums of natural pine wood – at ~430 °C ~540 °C and ~ 720 °C. After the latter three exo-effects the total mass loss in case of natural pine wood amount to 95 %, and in case of treated pine wood – 92 %.

3. The amount of element oxygen is relatively smaller and the amount of element carbon is correspondingly larger in the char residue of both, natural and treated pine wood, heated in the nitrogen environment to the temperature of 400 °C. However, the elemental carbon and oxygen ratio depends on burning environmental. This implies that a larger amount of carbon gets oxidised in the air environment and in the nitrogen environment this amount is smaller regardless the usage of structural oxygen.

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Romualdas Mačiulaitis was born in Mažeikiai at 1948. Chemist, Vilnius university, Department of Chemistry, 1972; technical science Doctor, 1981; Doctor Habil., 1993; Senior research worker, 1987; Assoc. professor, 1997; Professor 1999. Scientific interests in building conglomerates research of properties and development. He has developed 15 training books and 2 manual, has announced more than 200 scientific articles, 16 inventions and 6 patents.

Authors' information



Andrejus Jefimovas was born in Kaunas at 1985. PhD student at Dept. of building materials of Vilnius Gediminas Technical University, Vilnius, Lithuania. Research interests: research of timber charring.