ТЕРМИЧЕН АНАЛИЗ НА ДЪРВЕСИНА ОТ МЕКСИКАНСКИ БЯЛ КЕДЪР (*CUPRESSUS LUSITANICA*) ОГНЕЗАЩИТЕНА ЧРЕЗ ПЛАЗМЕНО-ПОДПОМОГНАТА ИМПРЕГНАЦИЯ СЪС ЗАБАВИТЕЛИ НА ГОРЕНЕТО

Диляна Господинова, Ивайло Иванов, Петър Динев, Люсиен Велева

Резюме: *Плазмено подпомогнатата огнезащита чрез забавители на горенето на дърво, дървени изделия и целулозни материали е замислена и разработена като резултат от появата и развитието на плазмено подпомогната капилярна импрегнация. Предшестващото капилярната импрегнация плазмено химично активиране на повърхността променя съществено електрическата, химичната и капилярната активност на порестата повърхност, което от своя страна е причина за подобряване на основни характеристики на импрегнационния процес. Термичният анализ е използван по един нов начин, за да се разкрие влиянието на плазмено подпомогнатата капилярна импрегнация върху огнезащитата на дървесина от Мексикански бял кедър (Cupressus Lusitanica).*
Ключови думи: *диелектричен бариерен разряд, плазмено подпомогната капилярна импрегнация, забавител на горенето, дървесина от кедър.*

INVESTIGATION ON PLASMA-AIDED FLAME RETARDATION OF MEXICAN WHITE CEDAR (*CUPRESSUS LUSITANICA*) WOOD BY THERMAL ANALYSIS

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Abstract: *The plasma aided flame retardation of wood, wooden products and cellulosic fibrous materials has been conceived and developed as a result of plasma aided process of capillary impregnation. The plasma-chemical surface pre-treatment substantially alters its electrical, chemical and capillary activity, thus improving some impregnation process basic characteristics, such as penetration depth, solution spreading and adsorption speed, adsorbed solution capacity. Thermal analysis has been used to reveal the impact of a new phosphor and nitrogen containing flame retardant and plasma-aided capillary impregnation on flame retardation of Mexican white cedar wood. This study has been developed as part of a large investigation on plasma activated (functionalized) wood surface and flame retardant treated wood.*
Keywords: *dielectric barrier discharge, plasma aided capillary impregnation, flame retardants, Mexican white cedar (Cupressus Lusitanica) wood.*

1. Introduction

The plasma aided flame retardation of wood, wooden products and cellulosic fibrous materials has been conceived and developed as a result of an original plasma aided process of capillary impregnation. The ability of the wood grain to adsorb water solution is of critical importance for the capillary impregnation of the wood, [1, 2, 3].

It is well known that heat treatment (drying) and machining reduces the chemical activity and wood wettability by modifying its water-reactive matrix in different ways. It was found earlier that the cold plasma pre-treatment of hard wood like cherry and oak improves such technological characteristics of the capillary impregnation process as solution spreading and flame retardant adsorption speed and quantity. The plasma-chemical surface pre-treatment modifies significantly the ionic and chemical activity of the wood surface as well as its capillary activity. As a result of that the technological characteristics of the capillary impregnation process were improved. This allows using the plasma aided retardation as a finishing process and applying it "*in line*" and "*off line*". A system of plasma device and applicators has been created to produce cold technological plasma through dielectric barrier discharge (*DBD*) at atmospheric pressure and room temperature, [1, 2, 3, 4 and 5].

Mexican white cedar, Cedar of Goa, Mexican cypress or White cedar (Scientific name: *Cupressus Lusitanica*) is a species of cypress native to Mexico and Central America (Guatemala, El Salvador and Honduras). *Cedro Blanco, Cedro de San Juan, Cypress Mexicano, Cypress de Portugal, Cypress Lusitanico* and *Teotlate* are distinctive names used in Mexico. It has also been introduced to Belize, Costa Rica and Nicaragua. It has been planted widely for commercial production: at high altitudes in Colombia, Bolivia and South Africa, and near sea level in New Zealand where it is fully naturalized.

White cedar is widely used for production of construction lumber, poles/posts, turned objects and musical instruments. But due to its fine-texture and surface inactivation it is difficult to apply flame retardants through capillary impregnation, [6, 7].

The objective of this paper was to study the effect of plasma pre-treatment on the wood surface functionalization as well as the effect of different surfactants on the ion activity of the new impregnation solution, both aiming to improve the *White cedar* wood flame retardation.

Some experimental results on *White cedar* thermal degradation (pyrolysis) depending on wood flame retardation under different conditions monitored by some methods of commonly used thermal analysis (*thermogravimetric analysis, TGA*; *differential thermal analysis*, *DTA*; and *differential scanning calorimetry*, *DSC*) are presented here: *i* - plasma-aided capillary impregnation for wood flame retardency improvement; *ii* - new phosphorous and nitrogen containing flame retardant impregnation solution for plasma-aided retardation; *iii* - conditioning of the applying impregnation solution with surfactants and spreaders.

2. Experimental investigation

White cedar soft wood (*Cupressus Lusitanica,* Yucatan, Mexico) with *average dried weight*: 470 kg/m^3; *basic specific gravity (basic*: 12 % moisture content): 40/47; *Janka hardness*: 2 240 N; *rupture strength* or *modulus of rupture*:76.40 MPa; *elastic*

strength or *modulus of elasticity*: 8.72 MPa; *radial* or *R-shrinkage*: 2.8 %; *tangential* or *T-shrinkage*: 5.9 %, and *volumetric shrinkage*: 8.1 %; *T/R* ratio: 2.1; and moisture content of 8.3 % was used in this investigation, Fig. 1

Thermal analysis test samples were made from *White cedar* heartwood

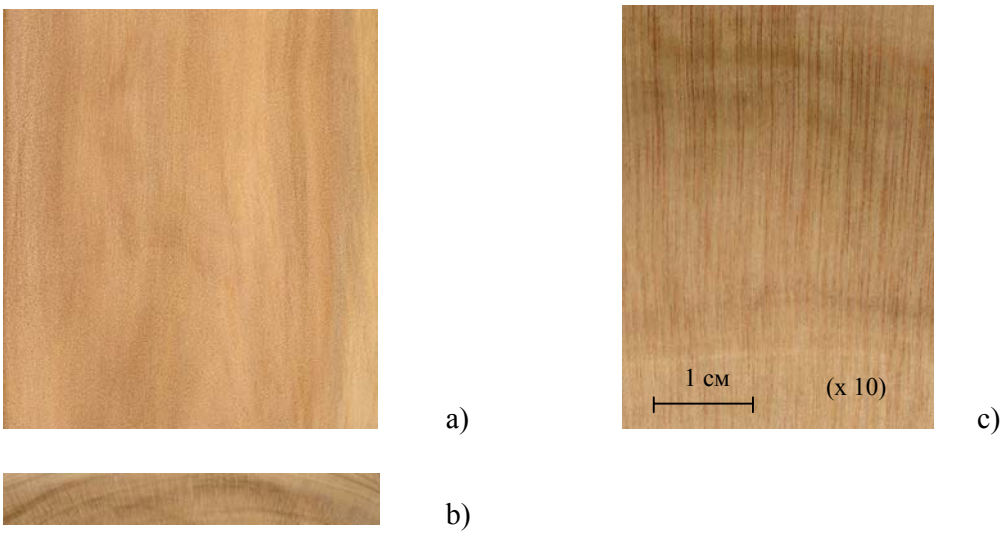

Fig. 1. Flatsawn (*a*), quartersawn (*c*) surfaces of *White Cedar* wood sample, and an end grain view (*b*) of *White Cedar* (x 10).

On the basis of prior art, as well as on our own former experience in plasma aided impregnation, [3, 5], an oxidative (nitrogen oxides, NO_x) surface plasma pretreatment has been applied on the test samples for 60 sec in a non-equilibrium cold plasma of dielectric barrier air discharge (*DBD*) at atmospheric pressure, industrial frequency (50 Hz) and 18 kV (*RMS*) or 25.4 kV (PV).

The *DBD*-technological plasma system consisted of coplanar shaped rectangular electrodes with one glass barrier (3 mm thick) closely arranged to the grounded electrode, with 6 mm operating distance between the high voltage electrode and the barrier, Fig 1a. The *DBD* was assured by a low frequency (50 Hz) voltage generator. The wood samples were disposed in operating volume and were treated for one minute (60 sec) under chosen operational regime, Fig. 1b.

A halogen-free, *phosphorus and nitrogen containing flame retardant* has been used in this investigation as a 30 wt. % water solution. A new flame retardant product (*PhNFR*) based on ortho-phosphorous acid, urea and ammonia has been produced and studied. The impregnating flame retardant water solution (*PhFRIS*, dry substance of 30 wt. %; phosphorus content of about 13 wt. %, pH = 7÷8 and density of 1.15 g/cm^3) was based on it. The replacement of the halogen containing flame retardants by halogen-free ones has been imposed by the toxicity of the halogens, [6].

The non-equilibrium air plasma treatment gives good results increasing the chemical, anionic and capillary surface activities. Anionic surfactants (*AS*, "*Aniticrystallin A*", Chimatech, Ltd., Bulgaria) in quantity of 5 vol. %, and silicone super spreader (*SSP*, Y-17113, *Momentive Performance Materials* GmbH & Co. KG, Germany) in quantity of 0.1 vol. %, as well as their combinations, have been used to control the ion activity of the flame retardant impregnation water solution after surface

plasma pre-treatment. The capillary impregnation has been applied on bare (for comparison) and plasma pre-treated *White cedar* wood samples at atmospheric pressure by spraying the corresponding flame retardant solution (390 ml.m^{-2} or 390 cm^3.m^{-2}).

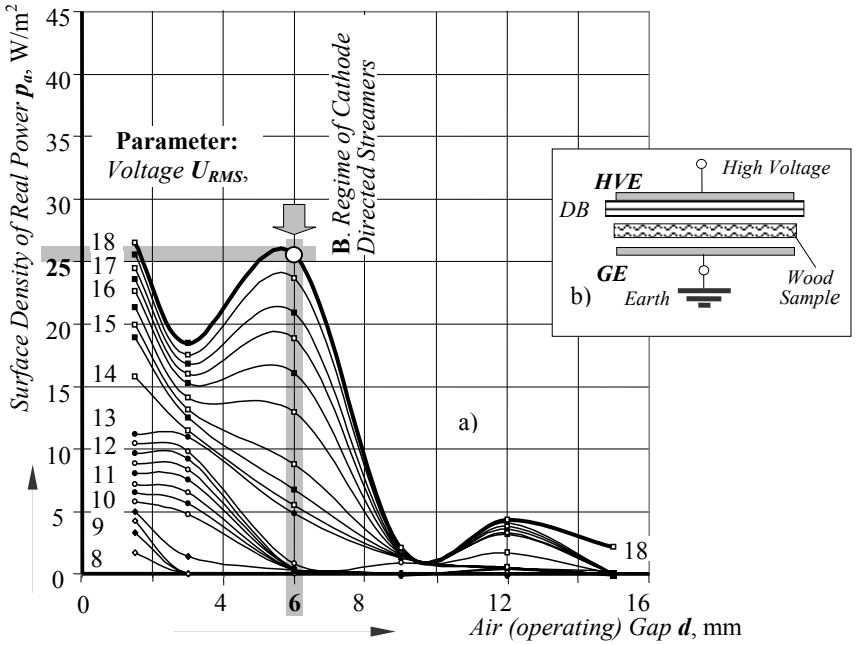

Fig. 2. Dielectric barrier air discharge (*DBD*) in asymmetric coplanar electrode system with one (alkali glass) barrier (**a**), technological discharge characteristic "p_a - U_{RMS}", and pick and choose regime (**b**) of plasma pre-treatment at industrial frequency and 18 kV (RMS).

Thermal analysis – thermogravimetric analysis (*TGA*), differential scanning calorimetry (*DSC*), and differential thermal analysis (*DTA*), have been performed in air at a heating rate of 10 ^{0}C/min within the temperature range of 25÷1 000^{0}C using *Perkins-Elmer* equipment, [8, 9].

3. Experimental results and discussion

Flame-retardency effect on heat release and mass losses

The studied *plasma-aided capillary impregnation* was based on both: plasma pre-treatment of the wood surface, Fig. 2; and flame retardant impregnating solution with ion activity optimization, expecting that an increase of the wood capillary activity and the impregnating solution adsorption speed and capacity would allow good enough flame retardant performance of porous wood surface [1, 2, and 5].

The *DBD*-surface activation effects or the expected surface reorganization and alternation of the chemical composition as a result of the plasma pre-treatment as well as the impregnation solution conditioning, have been directly monitored by the thermal behaviour of bare and flame retarded *White cedar* wood – by *TGA* and *DSC*-analyzes, Fig. 5, 6 and 7.

The pyrolysis characteristics of *White cedar* were investigated using a thermogravimetric (*TGA*) analyzer with differential scanning calorimetry (*DSC*) detector and a pack bed, Fig. 3.

In thermal analysis, the pyrolysis of hemicellulose and cellulose occurs quickly, with main weight loss of *hemicellulose* at 220÷315 ^{0}C and that of *cellulose* at

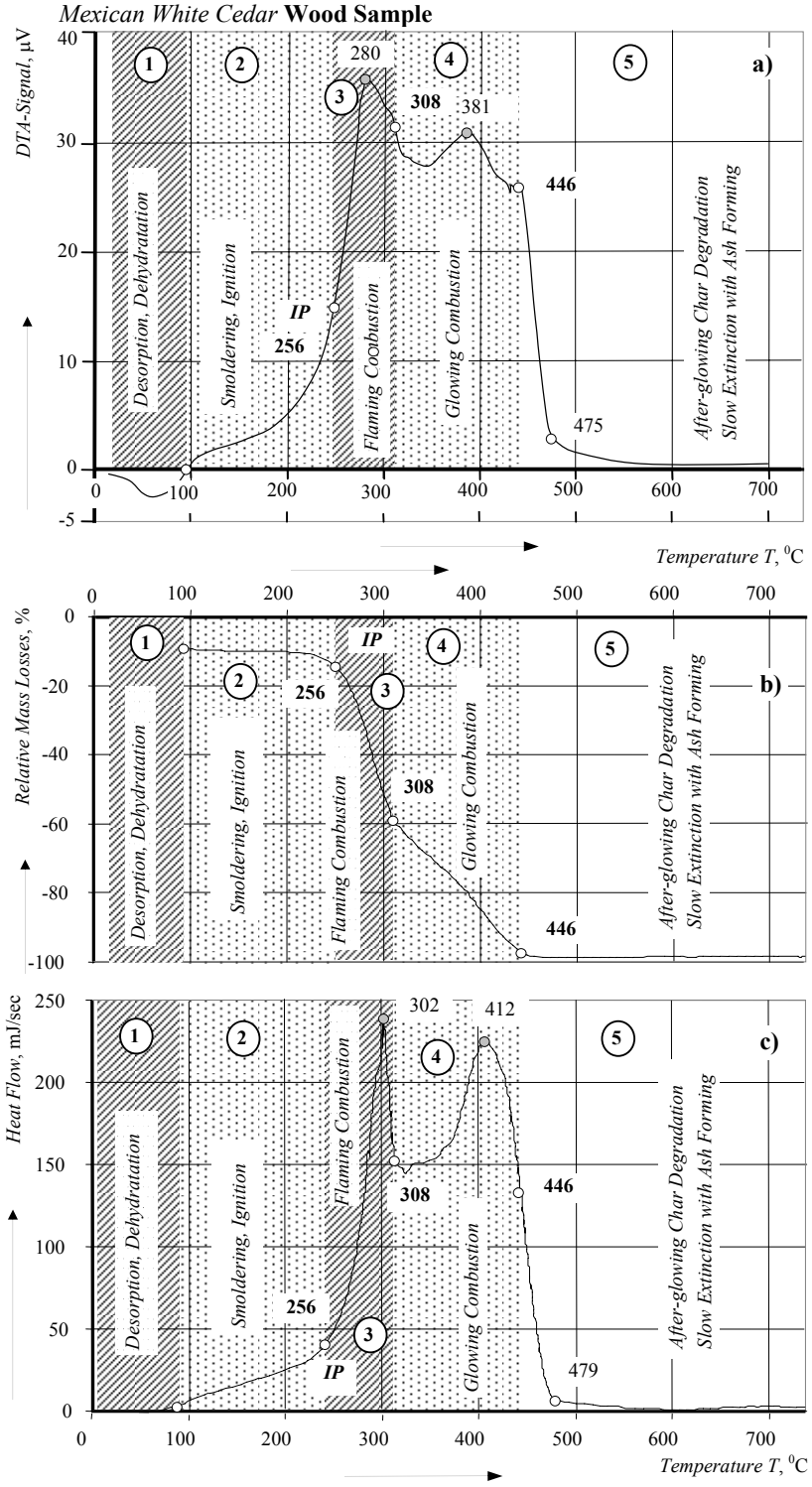

Fig. 3. Thermal analysis - *DTA*, *TGA* and *DSC*-spectra of bare *White Cedar* wood (*Cupressus Lusitanica*, Yucatan, Mexico) samples in air (heating rate: 10 ^{0}C per minute): wood pyrolysis stages identification (1, 2, 3, 4 and 5): ***a*** - by *DTA*-spectrum; ***b*** - by *TGA*-spectrum; ***c*** - by *DSC*-spectrum.

315÷400 ^{0}C. However, *lignin* is more difficult to decompose and its mass loss happens in a temperature range from 160 to 900 ^{0}C). Well known studies show that wood

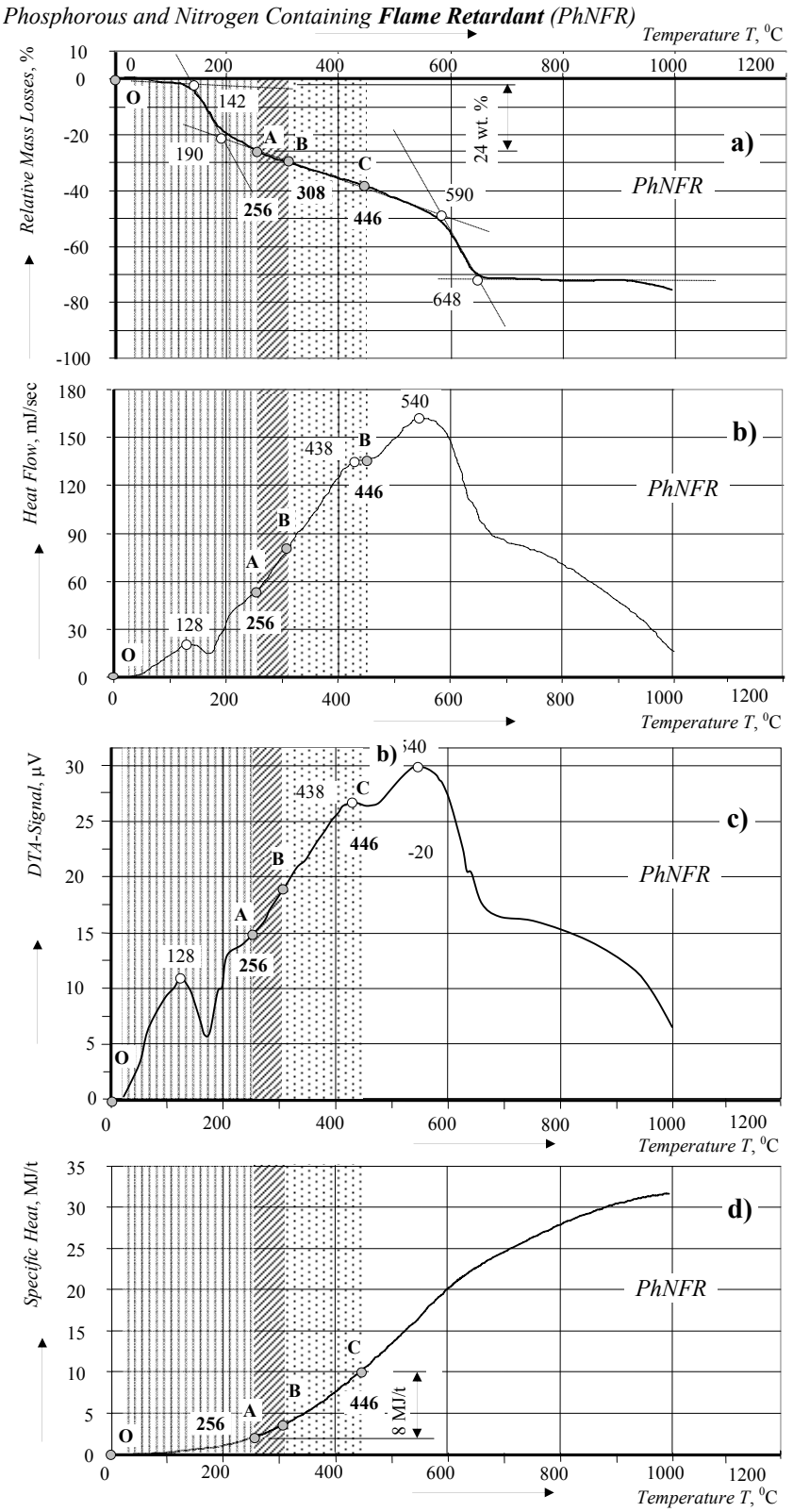

Fig. 4. Thermal analysis - *TGA*, *DSC* and *DTA*-spectra of bare phosphorous and nitrogen containing flame retardant (*PhNFR*) dried sample in air (heating rate: 10 ^{0}C per minute) in the temperature area of flaming and glowing wood pyrolysis stages (*A-B-C*): ***a*** - *TGA*-spectrum; ***b*** - *DSC*-

spectrum; ***c*** - *DTA*-spectrum; ***d*** - specific heat (by unit weight of *FR*-sample) released during the interval of wood ignition (*O-A*), flaming (*A-B*) and glowing (*B-C*).

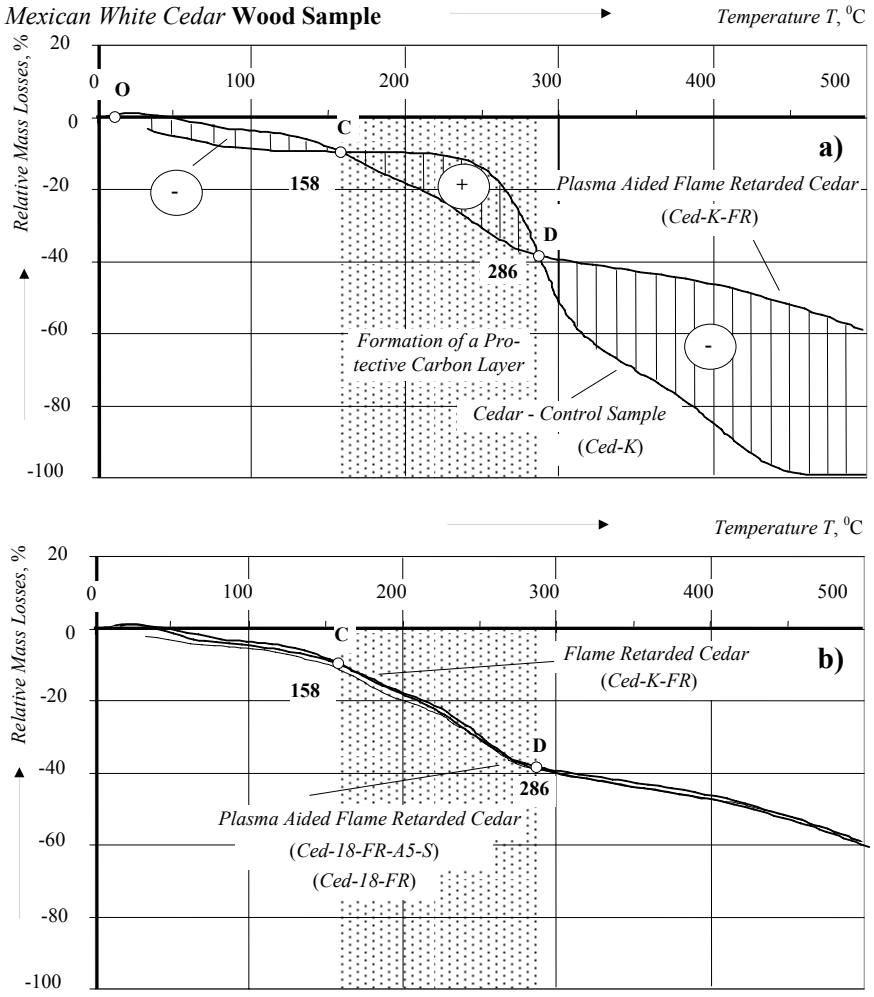

Fig. 5. Thermal *TGA*-analysis: flame retardency effect illustrated by the difference between relative mass losses demonstrated by bare (*Ced-K*) *White cedar* (*Cupressus Lusitanica*, Yucatan, Mexico) samples, flame retarded (*Ced-K-FR*) samples (***a***) and plasma-flame retarded wood (*Ced-18-FR; Ced-18-FR-A5-S*) samples (***b***) during air flow pyrolysis in the temperature interval up to 500 ^{0}C shown by *DSC* spectra (heating rate: 10 ^{0}C per minute).

CD - temperature area of protective carbon layer formation.

pyrolysis can be divided into *four stages*: moisture evolution (dehydration), *hemicellulose* decomposition, *cellulose* decomposition and *lignin* decomposition [10, 11].

The pyrolysis characteristics of bare *White cedar* wood are shown in Fig. 3 - the fifth pyrolysis stages or temperature regimes with their critical points (stage transitions): S1 - *desorption, dehydratation*; S2 - *smoldering, ignition*; S3 - *flaming*; S4 - *glowing, charing*; S5 - *slow extinction with ash forming*.

The pyrolysis characteristics of the new synthesized dried phosphor and nitrogen containing flame retardant (PhNFR) without surfactant and super spreader are shown in Fig. 4. The temperature area of *protective carbon layer formation* was found out between 158 and 286 ^{0}C, Fig. 5.

The *ignition point* (*IP*) of *White cedar wood* was found at 256 ^{0}C, Fig. 3.

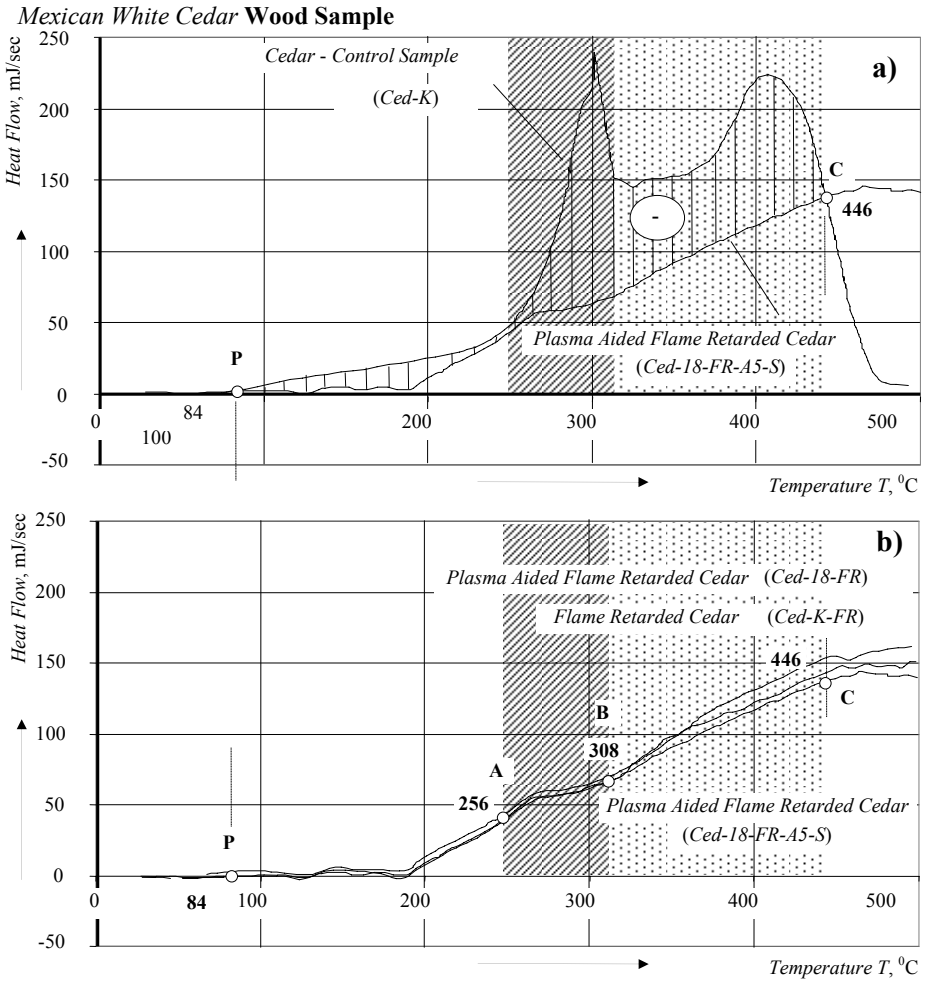

Fig. 6. Thermal *DSC*-analysis: flame retardency effect illustrated by the difference between heat flows demonstrated by bare (*Ced-K*) *White cedar* (*Cupressus Lusitanica*, Yucatan, Mexico) samples, flame retarded (*Ced-K-FR*) wood samples (***a***) and plasma-flame retarded wood (*Ced-18-FR; Ced-18-FR-A5-S*) samples (***b***) during air flow pyrolysis in the temperature interval up to 500 ^{0}C shown by *DSC* spectra (heating rate: 10 ^{0}C per minute).

PC - protective temperature area with suppressed wood ignition, flaming and glowing.

4. Conclusion

The application of thermal analysis (*TGA*, *DTA*, and *DSC*) allows evaluating the *White cedar wood* decomposition (pyrolysis) under the influence of heat by setting pyrolysis stage temperature ranges and hemi-cellulose, cellulose and lignin characteristic temperature peaks.

Thermal analysis helps reveal and illustrate the impact of the newly produced phosphor and nitrogen containing flame retardant on *White cedar wood* behaviour (pyrolysis). It significantly reduces the heat release within the range of 84÷446 (565) ^{0}C by suppressing the flaming and glowing combustion of wood and decreases considerably the mass loss. This flame-retardant chemicals shift the *White cedar wood* thermal degradation to *the low temperature pathway* of non-combustible gases and greater proportion of remaining wood as char residue - the transition to glowing combustion is already taking place and the remaining char residue is 54.5 wt. %

(against 20 wt. % for bare *White cedar*); at the temperature of 465 ^{0}C the remaining char residue is 43.9 wt. % (against 1.2 wt. % for bare *White cedar*), Fig. 5 and 7.

Thermal analysis enables studying the plasma aided capillary impregnation technology using water solution containing phosphorus flame retardant and its impact on *White cedar wood* plasma aided flame retardency. The experimental study of chemical, ion and capillary activity change of the *White cedar* wood surface using selected surfactant and spreader shows that it has no substantial contribution to the plasma aided flame retardency. The change of the impregnation solution ionic and capillary activity (*PhFRIS*) resulting from the anionic surfactant and silicon spreader application accelerates, increases the amount of the applied flame retardant and the depth of the capillary impregnation, but does not alter substantially the efficiency, neither in terms of heat release, nor in terms of mass losses, Fig. 5, 6 and 7.

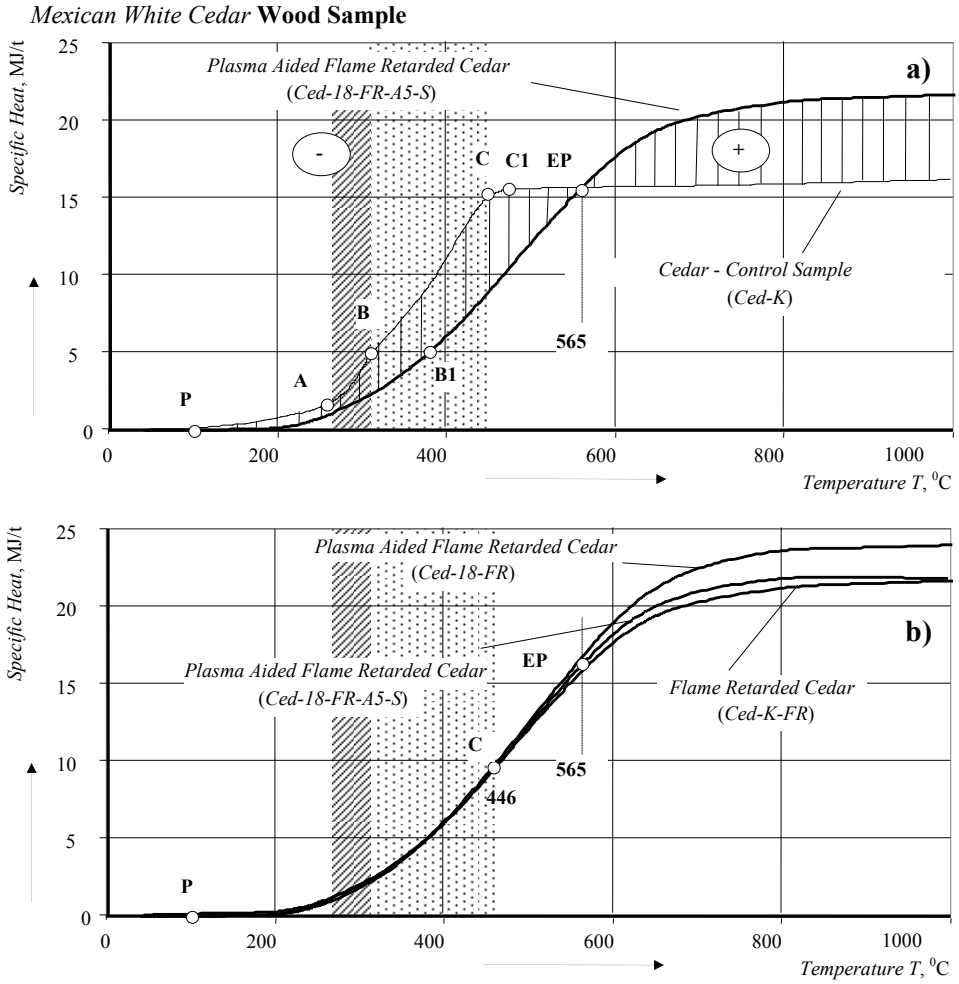

Fig. 7. Thermal analysis: ***integral flame retardency effect*** illustrated by the difference between released specific (per unit mass of sample) heat demonstrated by bare (*Ced-K*) *White cedar* (*Cupressus Lusitanica*, Yucatan, Mexico) samples, flame retarded (*Ced-K-FR*) samples (***a***) and plasma-flame retarded wood (*Ced-18-FR; Ced-18-FR-A5-S*) samples (***b***) during air flow pyrolysis in the temperature interval up to 1 000 ^{0}C takes by *TGA* and *DSC* spectra (heating rate: 10 ^{0}C per minute).

P-EP - protective temperature area with suppressed wood ignition, flaming, glowing and after glowing char degradation.

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