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ПЛАЗМЕНО ПОДПОМОГНАТА ОГНЕЗАЩИТА НА ДЪРВЕСИНА ОТ ТЦАЛАМ (LYSILOMA BAHAMENSIS) - I

Диляна Господинова, Ивайло Иванов, Петър Динев,
Люсиен Велева, Алехандро Гутьерес

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 (и функционализиране) на повърхността променя съществено електрическата, химичната и капилярната активност на порестата повърхност, което от своя страна определя подобряването на основни характеристики на импрегнационния процес. Термичният анализ (ТГА, ДТА и ДСК) е използван, за да се разкрие влиянието на нов забавител на горенето и на плазмено-химичното активиране на капилярната импрегнация върху огнезащитата на дървесина от Тцалам (*Lysiloma Bahamensis*).

Ключови думи: диелектричен бариерен разряд, плазмено подпомогната капилярна импрегнация, забавители на горенето, дървесина от Тцалам.

PLASMA AIDED FLAME RETARDATION OF TZALAM WOOD (LYSILOMA BAHAMENSIS) - I

Dilyana Gospodinova, Ivajlo Ivanov, Peter Dineff,
Lucien Veleva and Alejandro Gutierrez

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 pretreatment 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 (TGA, DTA and DSC) 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 Tzalam (*Lysiloma Bahamensis*) wood. This study has been developed as part of a large investigation on plasma-chemically activated wood surface and flame retardant treated wood.

Keywords: dielectric barrier discharge, plasma aided capillary impregnation, flame retardants, Tzalam 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 matrix to adsorb water is thus of critical importance for the water solution capillary impregnation of the wood.

The plasma-chemical surface pre-treatment modifies the ionic (or electrical) and chemical activity of the wood surface as well as its capillary activity. It improves such technological characteristics of the capillary impregnation process as penetration depth, solution spreading and adsorption speed, and adsorbed solution quantity per unit of surface area. 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].

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 as solution spreading and adsorption speed and quantity of flame retardant [3, 4].

Tzalam (Scientific name: *Lysiloma bahamensis*) is primarily the common name of Mexican wood (Calam, Caribbean, Mayan or Aztec Walnut), but it also grows into the tropical Americas (Belize) and the Caribbean. *Tzalam* is also known as *Cuban*, *False* or *Wild Tamarind*, *Abey*, *Frijolillo* and *Sabicu*. *Tzalam* is a hard wood of medium density. It is fairly fine-textured with a straight open grain and colours that range from light brown to chocolate, sometimes with streaks of red or brown. This wood is highly durable (service life of more than 25 years) and easy to work, finishes smoothly and takes a fairly high natural polish. Its applications include flooring, furniture and non-structural construction, such as panelling.

Tzalam wood is harder than softwoods. The dominant feature separating "hardwoods" from softwoods is the presence of vessels or pores. Hardwoods have a more complex structure than softwoods. The vessels may show considerable variation in size, shape of perforation plates, and structure of cell wall, Fig.1c.

Tzalam is largely used in non-structural constructions, flooring and panelling. But due to its relatively high density, fine-texture and surface inactivation it is difficult to apply flame retardants through capillary impregnation.

THE OBJECTIVE of this paper is 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 impregnation solution, both aiming to improve the *Tzalam* wood flame retardation.

Some experimental results of the investigation are presented here: alteration of the wood surface chemical composition or the surface functionalization as a result of cold plasma pre-treatment at atmospheric pressure and room temperature monitored

by some methods of commonly used thermal analysis (*thermogravimetric analysis, TGA; differential thermal analysis, DTA; and differential scanning calorimetry, DSC*); applying solution impregnation on bare or plasma pre-treated *Tzalam* wood with or without addition of a surfactant to the impregnating solution and the resulting change of wood thermal degradation depending on the flame retardation under different conditions monitored by *TGA, DTA, and DSC*.

2. Experimental

Tzalam hard wood (*Lysiloma bahamensis*), Yucatan, Mexico) with *average dried weight: 780 kg/m³; basic specific gravity: 63; Janka hardness: 6 230 N; rupture strength or modulus of rupture: 88.28 MPa; elastic strength or modulus of elasticity: 13.10 MPa; radial or R-shrinkage: 2.7 %; tangential or T-shrinkage: 7.2 %, and volumetric shrinkage: 9.5 %; T/R ratio: 2.7; and moisture content of 7.8 %* was used in this investigation, Fig.1.

Thermal analysis test samples with size of 5 x 30 x 150 mm were made from *Tzalam* heartwood.

On the basis of prior art, as well as on our own former experience in plasma aided impregnation of wood and wooden materials, [6, 7], an oxidative (nitrogen oxides, *NO_x*) surface plasma pre-treatment 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*).

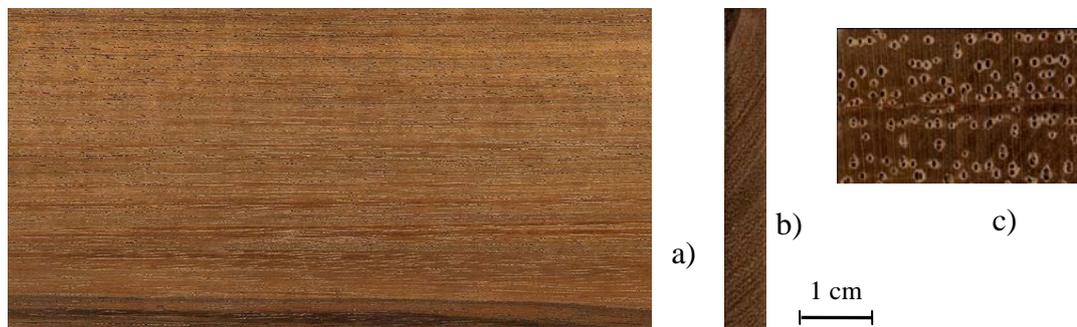


Fig.1. Flatsawn (a), quartersawn (b) surfaces of *Tzalam* wood sample, and an end grain view (c) of *Tzalam* (x 10).

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 two different - low frequency (50 Hz) and high frequency (10 kHz), voltage generators. The wood samples were disposed in operating volume and were treated for one minute (60 sec) under chosen frequencies and voltages.

A halogen-free, *phosphorus and nitrogen containing flame retardant* has been used in this investigation as a 30 wt. % water solution. 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/cm³) is based on a halogen free phosphorus and nitrogen containing flame retardant. The replacement of the halogen con-

taining flame retardants by halogen-free ones has been imposed by the toxicity of the halogens [8]. A new flame retardant product based on ortho-phosphorous acid, urea and ammonia has been produced and studied.

Wood inactivation is known as a surface phenomenon affecting just a thin outer layer of the wood. Inactivated wood surface does not have well enough capillary adsorption, which impedes the penetration of the impregnating solution containing phosphorous compound as a flame retardant. Plasma-chemical surface activation (functionalization) with an effective participation of ionic surfactants and silicone spreaders eliminates the *inactivation-impregnating* problem creating a protective flame retardant layer on the wood surface [5].

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. %, or 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. The capillary impregnation has been applied on bare (for comparison) or plasma pre-treated *Tzalam* wood samples at atmospheric pressure by spraying the corresponding flame retardant solution (390 ml/m²).

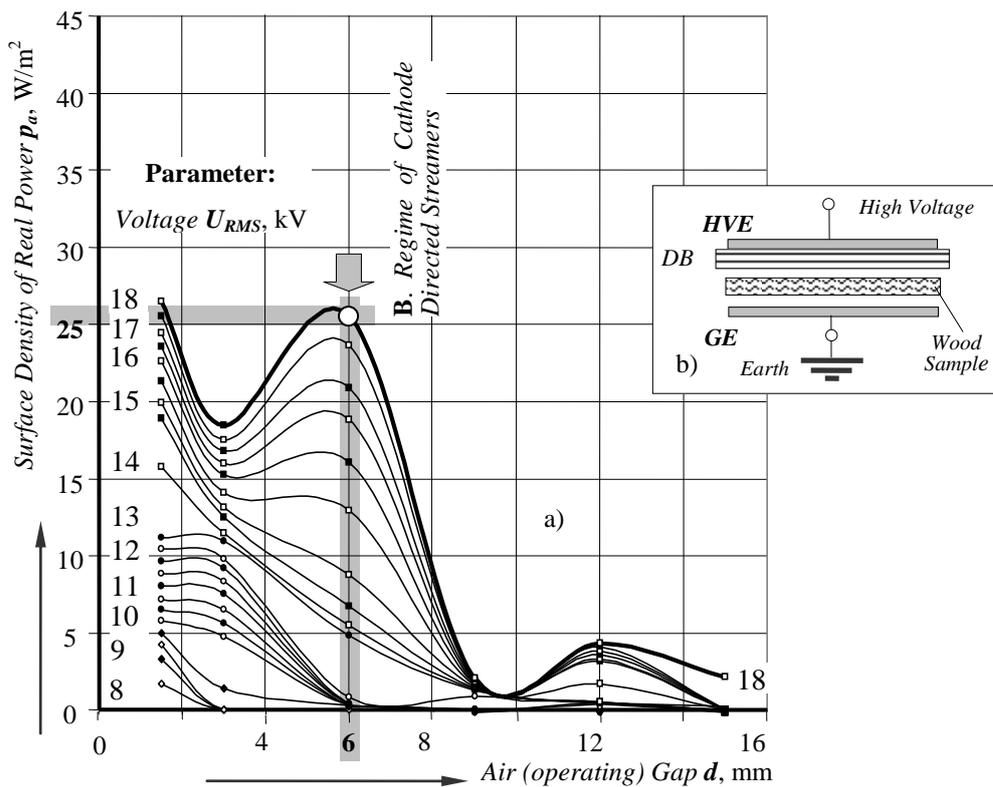


Fig.2. Dielectric barrier air discharge in asymmetric coplanar electrode system with one glass barrier (a), technological discharge characteristic " $p_a - U_{RMS}$ ", and regime of plasma pre-treatment at industrial frequency (b).

Thermal analysis – thermogravimetric analysis (*TGA*), differential scanning calorimetry (*DSC*), and differential thermal analysis (*DTA*), have been performed

in air at a heating rate of 10⁰C/min within the temperature range of 25÷1 000⁰C using *Perkins-Elmer* equipment.

3. Experimental results and discussion

The studied *plasma aided capillary impregnation* was based on both: plasma-chemical 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, 7].

The dielectric barrier discharge 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 of the flame retardant solution impregnation, have been directly monitored by the thermal behaviour of bare and flame protected *Tzalam* wood – by *TGA*, *DTA*, and *DSC*-analyzes.

3.1. Thermal degradation and temperature regimes of wood mass loss

Hemicellulose, *cellulose* and *lignin* are the three main components of wood biomass which in general cover respectively 20÷40, 40÷60, and 10÷25 wt. % for lignocellulosic biomass. Its pyrolysis can be divided into four stages: moisture evolution, hemicellulose decomposition, cellulose decomposition and lignin decomposition [5, 6, and 7].

As wood reaches elevated temperatures, the different chemical components undergo thermal degradation which affects the performance of wood. The extent of these changes depends on the achieved temperature level and the duration of exposure conditions. Chemical bonds begin to break at temperatures higher than 100⁰C and are manifested as carbohydrate and lignin weight losses of various types (wood pyrolysis) that increase with the temperature according to the pyrolysis models of *F. Browne*, 1958; *R. Miller* and *J. Bellan*, 1996, and *K. Bryden*, 1998).

Thermal degradation above 100⁰C can be divided into four stages or temperature regimes, [11]:

i) the first stage is between 100 and 200⁰C. Wood becomes dehydrated and generates water vapour and other non-combustible gases and liquids including CO₂, formic acid, acetic acid, and H₂O.

ii) the second stage is in the range from 200 to 300⁰C. Some wood components begin to undergo significant pyrolysis, in addition to the previously produced gases and liquids. Significant amounts of CO and high boiling point tar are given off.

The *hemicelluloses* and *lignin* components are pyrolyzed respectively within the ranges of 200÷300⁰C and 225÷450⁰C. Dehydration reactions around 200⁰C are responsible for pyrolysis of hemicellulose and lignin and result in a high char yield for wood.

The thermal degradation of *cellulose* can be accelerated in the presence of water, acids, and oxygen although cellulose remains mostly unpyrolyzed. As the temperature increases, the degree of polymerization of cellulose decreases further, free radicals appear, and carbonyl, carboxyl, and hydroperoxide groups are formed. Overall

pyrolysis reactions are endothermic due to decreasing dehydration and increasing CO formation from porous char reactions with water and CO₂ with temperature increase. During this “*low-temperature pathway*” of pyrolysis, exothermic reactions of exposed char and volatiles with atmospheric oxygen are manifested as *glowing combustion*.

iii) *the third stage* is from 300 to 450 °C because of the vigorous production of flammable volatiles. This begins with significant depolymerization of *cellulose* in the range of 300÷350 °C. Also, around 300 °C aliphatic side chains start splitting off from aromatic rings in the lignin. Finally, the carbon-carbon linkage between lignin structural units is cleaved from 370 to 400 °C. The lignin degradation reaction of this exothermic reaction is represented by peaks occurring between 225 °C and 450 °C. In this “*high-temperature pathway*,” pyrolysis of wood results in overall low char residues of around 25 % or less of original dry weight. Many fire retardants work by shifting wood degradation to the “*low-temperature pathway*,” which reduces volatiles available for *flaming combustion*.

iv) *the fourth stage* is above 450 °C, the remaining wood residue is char, which undergoes further degradation by being oxidized to CO₂, CO, and water. This is referred to as *afterglow*.

3.2. Flame-Retardency of Wood

Wood flame-retardancy delays ignition reduces heat release, and flame spread. As it is well known, many flame-retardant (*FR-*) chemicals shift the thermal degradation to the low temperature pathway of non-combustible gases and a greater proportion of char residue. The reactions are acid-catalyzed hydrolysis of the cellulose and hemicellulose. *FR-*chemicals dehydrate the wood and increase the condensation and cross-linking of the carbon skeleton. Other possible mechanisms for fire retardancy include formation of an insulating layer, increased dissipation via conduction of heat away from heat source, endothermic reactions to absorb heat, and release of radicals that inhibit flaming combustion [8].

For *interior applications* where leaching is not an issue, the following water-soluble inorganic salts are in use - monoammonium and diammonium phosphate, ammonium sulphate, zinc chloride, sodium tetraborate, and boric acid. These *FR-*chemicals are combined in formulations to develop effective fire performance (flaming, smouldering, and smoke) yet still retain acceptable hygroscopicity, strength, corrosivity, and other properties.

For leach-resistant system or for *exterior application*, a possible method is to polymerize the fire-retardant resins after impregnation into the wood. Such a treatment is the amino-resin system based on urea, melamine, dicyandiamide, and related compounds.

Mono-ammonium phosphate, one of the well-known *FR-*chemicals, is the most effective of the tested, increasing the char yield and thus promoting volatile loss through the *low-temperature pathway*. Cellulose reacts to the *FR-*chemicals in a similar manner to the wood, and lignin does not seem to be affected much by these chemicals. Thus, these *FR-*chemicals significantly reduce the flammable volatiles generated by the wood cellulose component. Potential *FR-*chemicals are often

initially tested using dynamic thermal analysis - thermogravimetry, differential thermal analysis, and differential scanning calorimetry [8, 9].

Table 1.
Pyrolysis characteristics of phosphor and nitrogen containing flame retardant

Powder Sample (after crystallization of phosphor containing FR)		PhFR
Stage Transitions		
Ignition Point (IP) - exuding non-flammable gases and vapours		70 °C
Burning Point (FP) - transition to flaming combustion		200 °C
Glowing Point (GP) - transition to glowing combustion		430 °C
After-glowing Point (CP) - transition to char degradation		720 °C
Extinction or Ash forming Point - transition to extinction or ash forming		870 °C
Heat Release (Exo), kJ/kg (J/g)		
Dehydratation Stage	59.897	0.2 %
Ignition Stage	1 452.432	4.6 %
Flaming Stage	2 948.116	9.4 %
Glowing Stage	7 440.514	23.8 %
After-glowing Stage	13 170.310	42.0 %
Extinction or Ash forming Stage (to 1 000 °C)	6 304.110	20.0 %
Total to 1 000 °C	31 375.380	100.0 %
Total to 335 °C	4 460.445	14.2 %
Total to 480 °C	11 900.960	37.9 %
Total to 725 °C	25 071.270	79.9 %
Mass Losses, mass. %		
Desorbtion of Gases, Dehydration Stage		2.3 %
Ignition Stage		20.6 %
Flaming Stage		17.4 %
Glowing Stage		30.2 %
After-glowing Stage		3.9 %
Extinction or Ash forming Stage		25.6 %
Total to 1 000 °C		100.0 %
Total to 335 °C		40.3 %
Total to 480 °C		70.5 %
Total to 725 °C		74.4 %

A new flame retardant product based on the ortho-phosphorous acid, urea and ammonia has been produced and studied.

3.3. Flame-retardency effect on heat release and mass losses

The pyrolysis characteristics of *Tzalam* were investigated using a thermogravimetric (TGA) analyzer with differential scanning calorimetry (DSC) detector and a pack bed, Table 2, Fig.3.

In thermal analysis, the pyrolysis of hemicellulose and cellulose occurs quickly, with main weight loss of *hemicellulose* at 220÷315°C and that of *cellulose* at 315÷400°C. However, *lignin* is more difficult to decompose and its mass loss happens in a temperature range from 160 to 900°C). Well known studies show that wood (or biomass) pyrolysis can be divided into four stages: moisture evolution (dehydration), *hemicellulose* decomposition, *cellulose* decomposition and *lignin* decomposition [10, 11].

From energy consumption viewpoint cellulose behaves differently from hemicellulose and lignin, in the course of pyrolysis.

The pyrolysis characteristics of bare *Tzalam* are shown in Table 1, Fig.5 and Fig.7 - the four pyrolysis stages or temperature regimes with their critical points (stage transitions) and the fifth stage of slow extinction with ash forming.

Table 2.
Pyrolysis Characteristics of bare *Tzalam* wood

Wood Sample - bare <i>Tzalam</i>		
Stage Transitions		
Ignition Point (IP) - exuding non-flammable gases and vapours		75 °C
Burning Point (BP) - transition to flaming combustion		230 °C
Glowing Point (GP) - transition to glowing combustion		335 °C
After-glowing Point (AGP) - transition to char decomposition		480 °C
Ash Forming Point (AFP)- transition to extinction and ash forming		725 °C
Heat Release (Exo), kJ/kg (J/g)		
Ignition Stage	841.383	5.5 %
Flaming Stage	4 545.213	29.5 %
Glowing Stage	8 873.511	57.6 %
After-glowing Stage	546.383	3.5 %
Extinction or Ash forming Stage	595.213	3.9 %
Total to 1 000 °C	15 401.702	100 %
Total to 335 °C	5 386.596	35.0 %
Total to 480 °C	14 260.107	92.6 %
Total to 725 °C	14 806.490	96.1 %
Mass Losses, mass %		
Desorbition of Gases, Dehydration Stage		6.9 %
Ignition Stage		5.3 %
Flaming Stage		50.1 %
Glowing Stage		32.0 %
After-glowing Stage		0.1 %
Extinction or Ash forming Stage - to 1 000 °C		0.1 %
Extinction Stage above 1 000 °C		5.5 %
Total to 1 000 °C		100.0 %
Mass Losses to 335 °C		62.3 %
Mass Losses to 480 °C		94.3 %
Mass Losses to 1 000 °C		94.5 %

All other wood samples and flame retardant chemical samples are discussed within the five pyrolysis stages thus defined. This allows an effective assessment: *first*, the effect of the newly produced and tested phosphor and nitrogen containing flame retardant impregnating solution (*PhFRIS*) on *Tzalam* wood; *second*, the impact of plasma aided flame retardant technology (surface plasma-chemical pre-treatment and functionalization; addition of anionic surfactant and silicon spreader to impregnating solution) on *Tzalam* flame retardency.

Only two of the studied options for plasma-aided flame retarded *Tzalam* pyrolysis characteristics are presented in a table form: *i* - *PhFRIS* capillary impregnation; *ii* - adjusted with both anionic surfactants (5 vol. %) and silicon spreader (0.1 vol. %). Plasma-aided capillary impregnation adjusted by anionic surfactant (5 vol. %) water solution is graphically presented on Fig.6 and Fig.8.

Table 3.
Pyrolysis characteristics of flame retarded *Tzalam* wood
(after surface plasma-chemical treatment)

Wood Sample - flame retarded <i>Tzalam</i> after surface plasma-chemical treatment		
Stage Transitions		
Ignition Point (IP) - exuding non-flammable gases and vapours	60 °C	
Burning Point (FP) - transition to flaming combustion	200 °C	
Glowing Point (GP) - transition to glowing combustion	425 °C	
After-Glowing Point (AGP) - transition to char decomposition	710 °C	
Extinction or Ash forming Point - transition to extinction and ash forming	880 °C	
Heat Release (Exo), kJ/kg (J/g)		
Ignition Stage	351.489	1.4 %
Flaming Stage	6881.915	27.9 %
Glowing Stage	14556.380	59.0 %
After-glowing Stage	2486.064	10.1 %
Extinction or Ash forming Stage (to 1 000 °C)	385.957	1.6 %
Total to 1 000 °C	24661.810	100.0 %
Total to 335 °C	3063.723	12.4 %
Total to 480 °C	10569.36	42.8 %
Total to 725 °C	22143.62	89.8 %
Mass Losses, mass. %		
Desorbtion of Gases, Dehydration stage	3.7 %	
Ignition Stage	15.1 %	
Flaming Stage	29.9 %	
Glowing Stage	34.3 %	
After-Glowing Stage	2.0 %	
Extinction or Ash forming Stage to 1 000 °C	2.0 %	
Extinction Stage above 1 000 °C	13.0 %	
Total to 1 000 °C	100.0 %	
Total Mass Losses to 335 °C	42.6 %	
Total Mass Losses to 480 °C	56.7 %	
Total Mass Losses to 725 °C	84.4 %	
Total Mass Losses to 1000 °C)	87.0 %	

The results shown on Fig.3÷Fig.8 allow the following conclusions from the thermal analysis:

i) Tzalam wood reveals the following characteristics (*TGA*, *DTA* and *DSC*):

- self-sustaining exothermic pyrolysis process and transition to flaming observed at temperatures over 200 °C;

- self-sustaining exothermic pyrolysis process and transition to glowing can be observed at temperatures over 430 °C;

- a characteristic peak, associated with *hemi-cellulose* pyrolysis occurs at a temperature of 280 °C (*DTA*), Fig. 4, but it is almost swallowed by the next peak at 304 °C, which can be associated mainly with the *cellulose* pyrolysis. A single peak is observed at 300 °C (*DSC*), Fig. 3, corresponding to the *hemi-cellulose* and *cellulose* pyrolysis. These experimental facts comply with the general notion, placing the *hemi-cellulose* pyrolysis peak in the temperature range from 220 to 315 °C, and that of the *cellulose* - in the range from 315 to 400 °C;

Table 4.
Pyrolysis characteristics of flame retarded *Tzalam* wood
(after surface plasma-chemical treatment with an anionic surfactant and spreader)

Wood Sample - <i>Tzalam</i> (Surface Plasma Treated+PhFRIS+Surfactant+Spreader)		
Stage Transitions		
Ignition Point (IP) - exuding non-flammable gases and vapours		70 °C
Burning Point (FP) - transition to flaming combustion		200 °C
Glowing Point (GP) - transition to glowing combustion		430 °C
After-glowing Point (CP) - transition to char degradation		720 °C
Extinction or Ash forming Point - transition to extinction or ash forming		870 °C
Heat Release (Exo), kJ/kg (J/g)		
Ignition Stage	411.857	1.7 %
Flaming Stage	7 150.714	30.0 %
Glowing Stage	14 381.250	60.4 %
After-glowing Stage	1 882.071	7.9 %
Extinction or Ash forming Stage (to 1 000 °C)	0.000	0.0 %
Total to 1 000 °C	23 825.893	100.0 %
Total to 335 °C	3 226.607	13.5 %
Total to 480 °C	10 611.110	44.5 %
Total to 725 °C	22 145.460	92.9 %
Mass Losses, mass. %		
Desorbition of Gases, Dehydration Stage		0.0 %
Ignition Stage		4.3 %
Flaming Stage		15.0 %
Glowing Stage		31.5 %
After-glowing Stage		36.9 %
Extinction or Ash forming Stage		12.3 %
Total to 1 000 °C		100.0 %
Total to 335 °C		43.6 %
Total to 480 °C		57.1 %
Total to 725 °C		86.4 %
Total to 1 000 °C		90.1 %

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ПЛАЗМЕНО ПОДПОМОГНАТА ОГНЕЗАЩИТА НА ДЪРВЕСИНА ОТ ТЦАЛАМ (LYSILOMA BAHAMENSIS) - II

Диляна Господинова, Ивайло Иванов, Петър Динев,
Люсиен Велева, Алехандро Гутierrez

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 (и функционализиране) на повърхността променя съществено електрическата, химичната и капилярната активност на порестата повърхност, което от своя страна определя подобряването на основни характеристики на импрегнационния процес. Термичният анализ (ТГА, ДТА и ДСК) е използван, за да се разкрие влиянието на нов забавител на горенето и на плазмено-химичното активиране на капилярната импрегнация върху огнезащитата на дървесина от Тцалам (*Lysiloma Bahamensis*).

Ключови думи: диелектричен бариерен разряд, плазмено подпомогната капилярна импрегнация, забавители на горенето, дървесина от Тцалам.

PLASMA AIDED FLAME RETARDATION OF TZALAM WOOD (LYSILOMA BAHAMENSIS) - II

Dilyana Gospodinova, Ivajlo Ivanov, Peter Dineff,
Lucien Veleva and Alejandro Gutierrez

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 (TGA, DTA and DSC) 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 Tzalam (*Lysiloma Bahamensis*) wood. This study has been developed as part of a large investigation on plasma-chemically activated wood surface and flame retardant treated wood.

Keywords: dielectric barrier discharge, plasma aided capillary impregnation, flame retardants, Tzalam wood.

- a characteristic peak, associated with lignin degradation exothermic reaction, is represented by peaks at 390 °C (*DSC*), Fig.3, and at 423 °C (*DTA*), Fig.4. Generally, the peaks of lignin degradation reaction occur between 225 and 450 °C;

- during the transition to glowing combustion (pyrolysis), 37.7 wt. % of the *Tzalam* wood is solid - the remaining wood residue is char, which undergoes further degradation by being oxidized to CO₂, CO, and water during the afterglow stage;

- the remaining wood residue as char above 480°C (after-glowing degradation of char) is only 5.7 wt. %

ii) the examined phosphor and nitrogen containing flame retardant (*FR-chemical*), applied as an impregnation solution (*PhFRIS*), displays the following characteristic features during the *Tzalam* wood flame retardancy:

- this flame-retardant chemicals shift the *Tzalam* 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 at a temperature of 411 °C (against 329 °C for bare *Tzalam*) and the remaining char residue is 52 wt. % (against 37.7 wt. % for bare *Tzalam*);

- some feasible mechanisms for fire retardancy include: *acid-catalyzed* (phosphoric acid) *hydrolysis* of *cellulose* and *hemi-cellulose* as reactions above 106 °C - lignin does not seem to be much affected by this *FR-chemical*; dehydration of *Tzalam* wood by *FR-chemical*; condensation enlargement and cross-linking of the carbon skeleton; insulating layer formation, increased dissipation via heat conduction away from the heat source, limited access of oxygen deep in it, and limited release of combustible gases out of it, endothermic reactions to absorb heat (between 106 and 235 °C, Fig.5);

- effective suppression of flaming and glowing combustion within the temperature range from 65 to 428 (432) °C, Fig.5;

iii) 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.6 and Fig.8.

4. Conclusion

The application of thermal analysis (*TGA*, *DTA*, and *DSC*) allows evaluating the *Tzalam 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 *Tzalam* wood behaviour (pyrolysis).

It significantly reduces the heat release within the range of 65÷430 °C by suppressing the flaming and glowing combustion of wood and decreases considerably the mass loss.

Thermal analysis enables studying the plasma aided capillary impregnation technology using water solution containing phosphorus flame retardant and its impact on *Tzalam* wood plasma aided flame retardancy.

The experimental study of chemical, ion and capillary activity change of the *Tzalam* wood surface using selected surfactant and spreader shows that it has no substantial contribution to the plasma aided flame retardancy.

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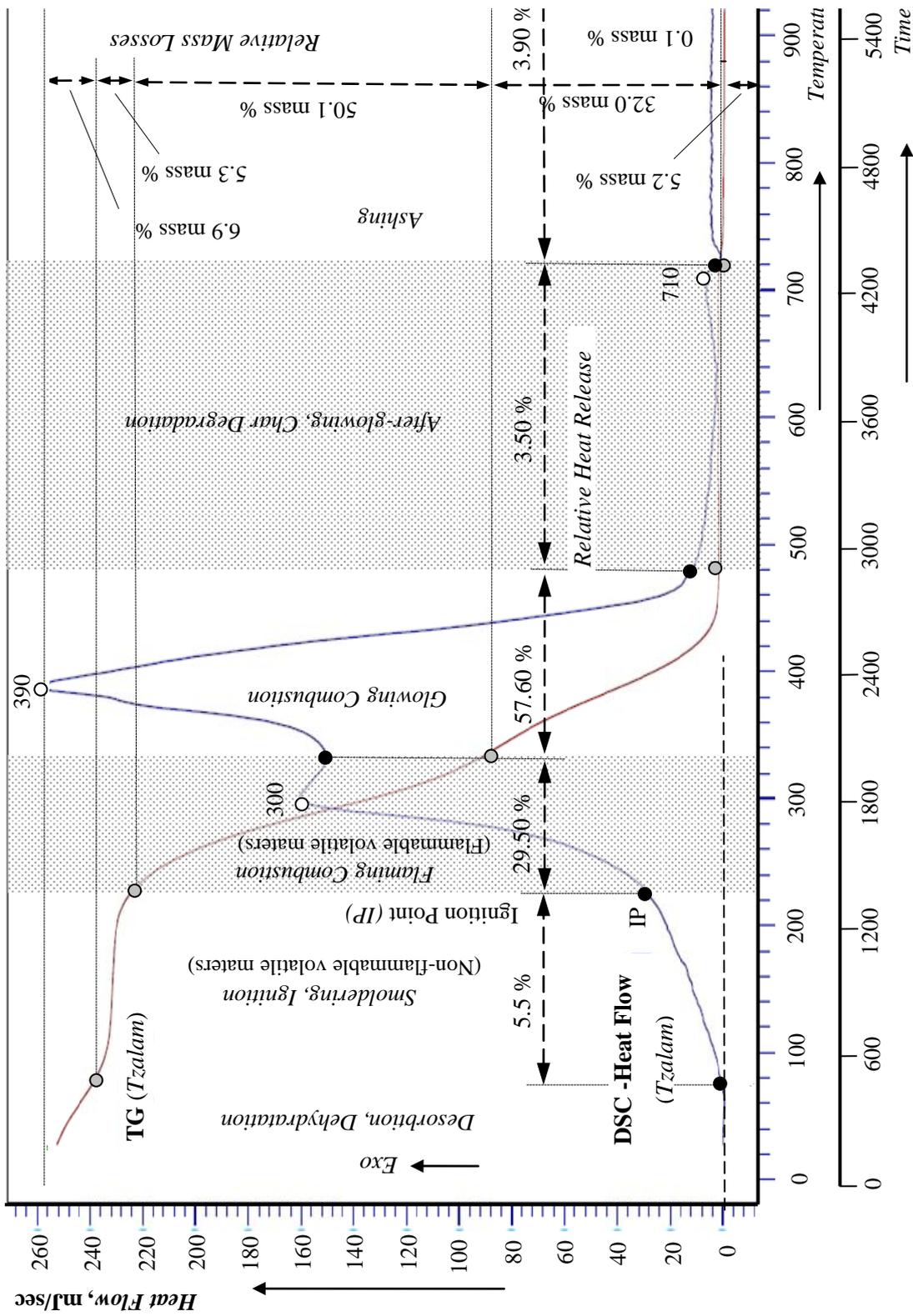


Fig.3. Thermal analysis - DSC and TGA spectra of bare *Tzalam* wood (*Lysiloma bahamensis*, Yucatan, Mexico) in air (heating rate - 10 °C per minute): *Tzalam* wood pyrolysis stages identification.

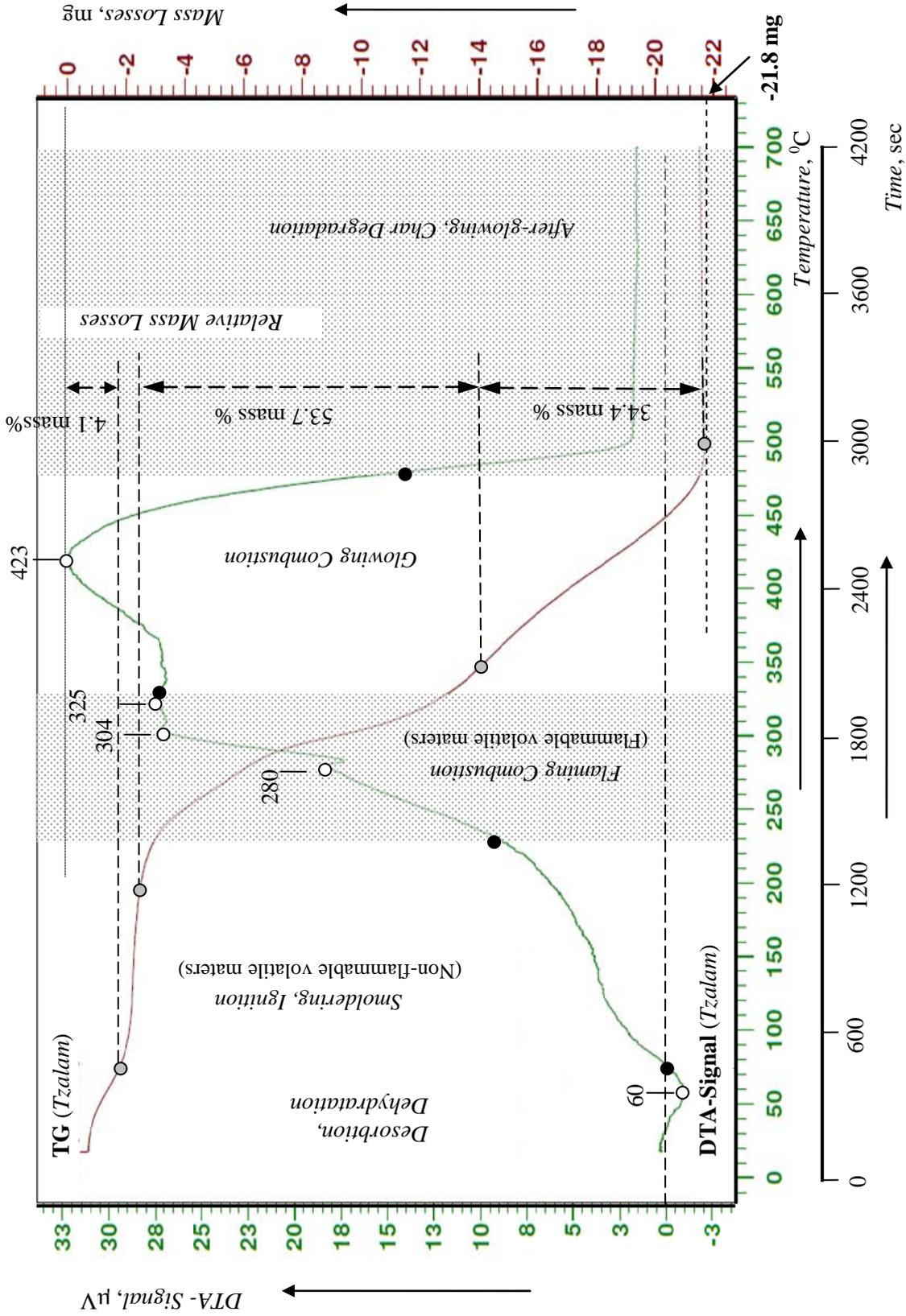


Fig.4. Thermal analysis - TGA and DTA spectra of bare *Tzalam* wood (*Lysiloma bahamensis*, Yucatan, Mexico) in air (heating rate - 10 °C per minute): *Tzalam* wood pyrolysis stages identification.

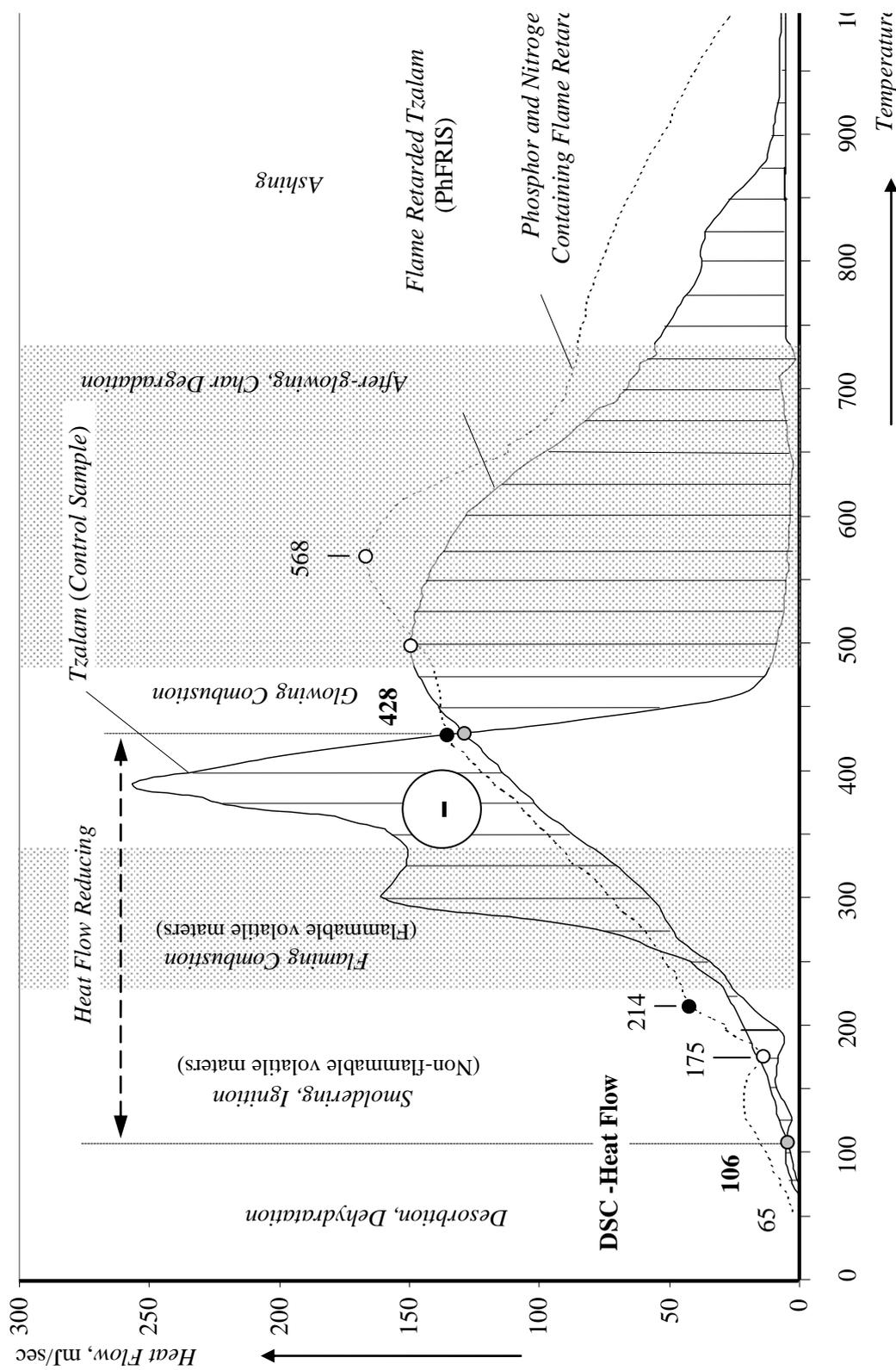


Fig.5. Thermal analysis - flame retardancy effect illustrated by a difference between heat flows released in the course of bare and flame retardant treated *Tzalam* wood (*Lysiloma bahamensis*, Yucatan, Mexico) pyrolysis in the temperature interval between 65 and 428 °C by DSC spectra (heating rate - 10 °C per minute). The DSC-spectrum of the phosphor and nitrogen containing flame retardant used is shown with a dashed line.

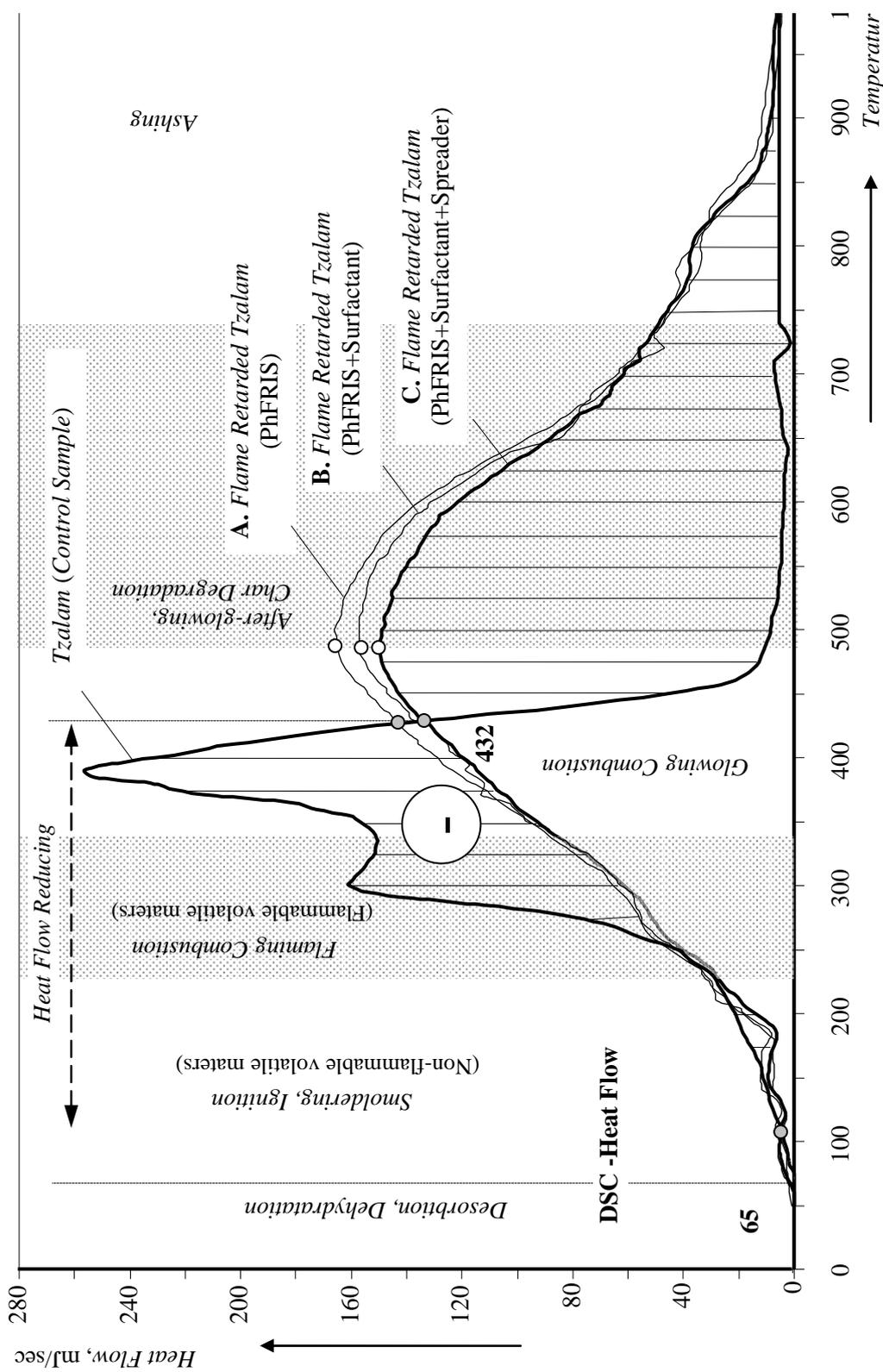


Fig.6. Thermal analysis - flame retardancy effect illustrated by a difference between heat flows released in the course of bare and various flame retardant treated *Tzalam* wood (*Lysiloma bahamensis*, Yucatan, Mexico) pyrolysis in the temperature interval between 65 and 432 °C by DSC-spectra (heating rate - 10 °C per minute): **A** - flame retarded wood by capillary *FRIS*-impregnation; **B** - flame retarded wood by plasma-aided (industrial frequency at 18 kV (*RMS*) capillary impregnation with 5 vol. % of anionic surfactant; **C** - flame retarded wood by plasma-aided capillary impregnation with anionic surfactant, 5 vol. %, and silicon spreader, 0.1 vol. % }

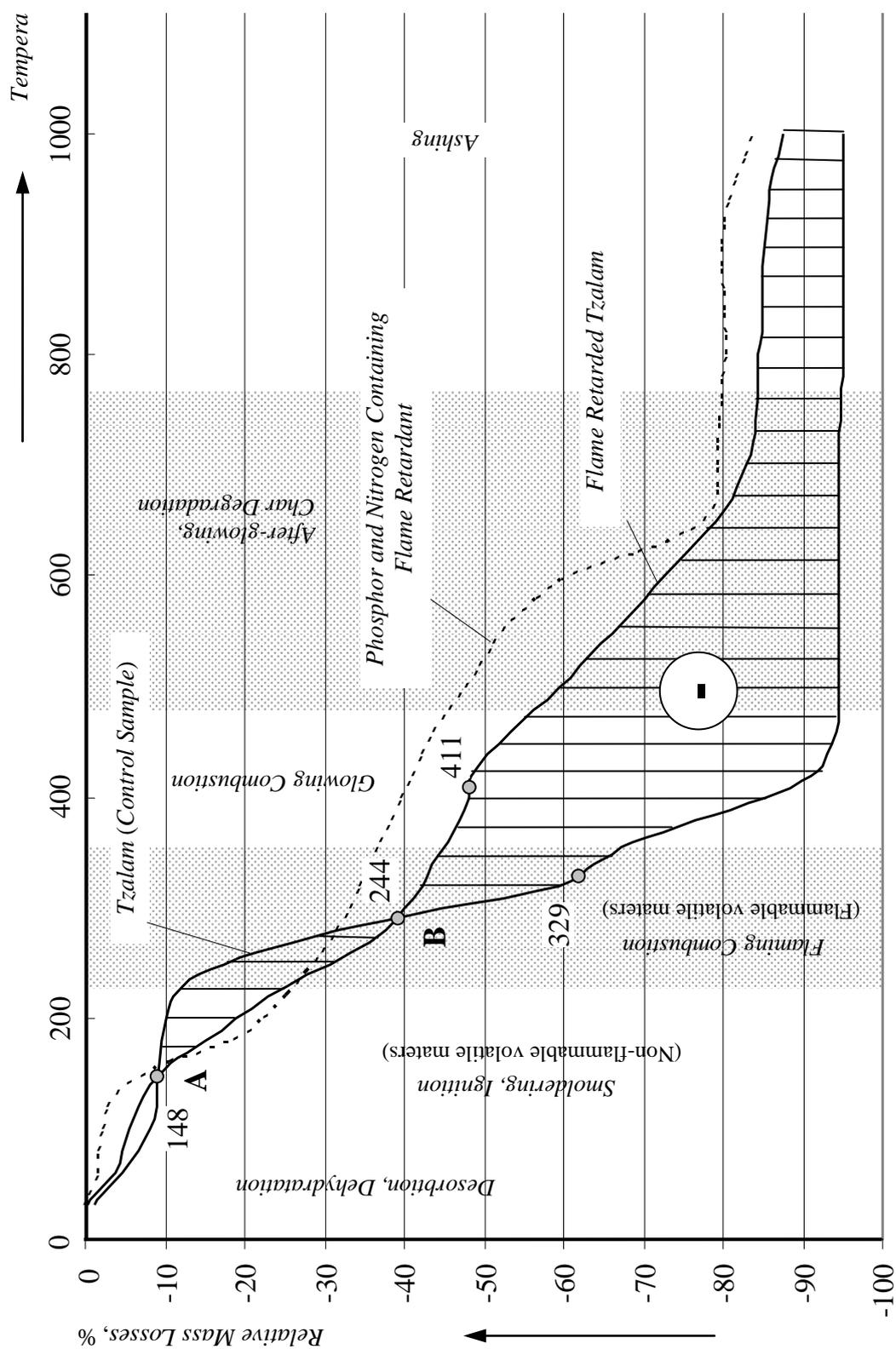


Fig.7. Thermal analysis - flame retardancy effect illustrated by a difference between relative mass losses in the course of bare and flame retardant treated *Tzalam* wood (*Lysiloma bahamensis*, Yucatan, Mexico) pyrolysis above 244 °C by TGA-spectra (heating rate - 10 °C per minute). The TGA-spectrum of phosphor and nitrogen containing flame retardant water solution used (*PhFRIS*) is shown (as a dashed line).

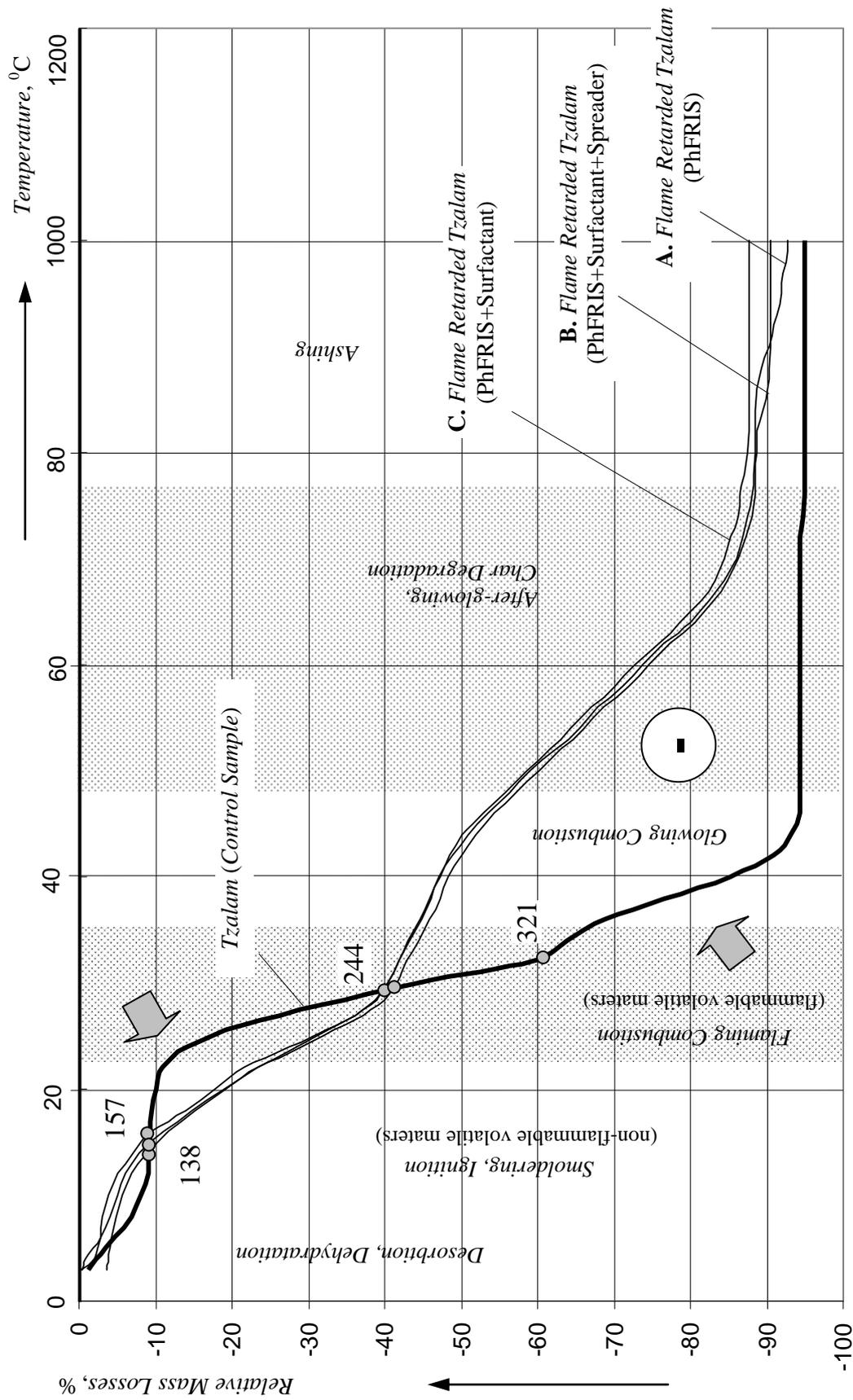


Fig.8. Thermal analysis - flame retardancy effect illustrated by a difference between relative mass losses in the course of bare and various flame retardant treated *Tzalam* wood (*Lysiloma bahamensis*, Yucatan, Mexico) pyrolysis above 244 °C by TGA-spectra (heating rate - 10 °C per minute): **A** - flame retarded wood by capillary *PhFRIS* impregnation; **B** - flame retarded wood by plasma-aided capillary impregnation with anionic surfactant, 5 vol. %; **C** - flame retarded wood by plasma-aided capillary impregnation with anionic surfactant, 5 vol. %, and spreader, 0.1 vol. %.

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