

# PLASMA-AIDED FLAME RETARDATION OF MAHOGANY CAOBA (SWIETENIA MACROPHYLLA) WOOD

Assoc. Prof. M.Sc. Gospodinova D. Ph.D.<sup>1</sup>, M.Sc. Ivanov I.<sup>1</sup>, Prof. M.Sc. Dineff P. Ph.D.<sup>1</sup>, Prof. M.Sc. Veleva L. Ph.D.<sup>2</sup>  
 Faculty of Electrical Engineering - Technical University of Sofia, Bulgaria<sup>1</sup>  
 CINVESTAV - Merida, Ycatan, Mexico<sup>2</sup>

**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 plasma-aided flame retardation of Caoba or Mahogany (*Swietenia macrophylla*) wood. This study has been developed as part of a large research on plasma-chemically activated wood surface and flame retardant treated tropical wood.

**Keywords:** DIELECTRIC BARRIER DISCHARGE SURFACE TREATMENT, PLASMA-AIDED CAPILLARY IMPREGNATION, FLAME RETARDATION OF WOOD AND WOODEN PRODUCTS, THERMAL ANALYSIS.

## 1. Introduction

This study has been developed as part of a large research on plasma-chemically activated wood surface and flame retardant treated tropical wood.

The plasma aided flame retardation of wood, and wood products has been developed as a result of a new plasma-aided process of capillary impregnation that comprises a surface plasma pre-treatment for alteration of the chemical activity of wood surface as well as its electrical (ionic) and capillary activities, and in general for improvement the technological characteristics of the capillary impregnation process. A technological 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. The cold plasma pre-treatment by non-equilibrium DBD of wood, like *White pine* (Bulgaria), *Tzalam* (Mexico) and *Douglas fir*, (Canada), improves technological characteristics such as a solution spreading and adsorption speed, as well as a specific amount of the adsorbed flame retardant. In this way, the plasma pre-treatment of wood and wooden products improves its flame retardation [1, 4]. [1, 2].

*Mahogany Caoba* tree grows up in the Atlantic Coast from Mexico through Panama and the Amazon region of Peru, Bolivia and Brazil. It was used by the Maya to make dugout canoes. In the Spanish territories this tree was called *caoba*.

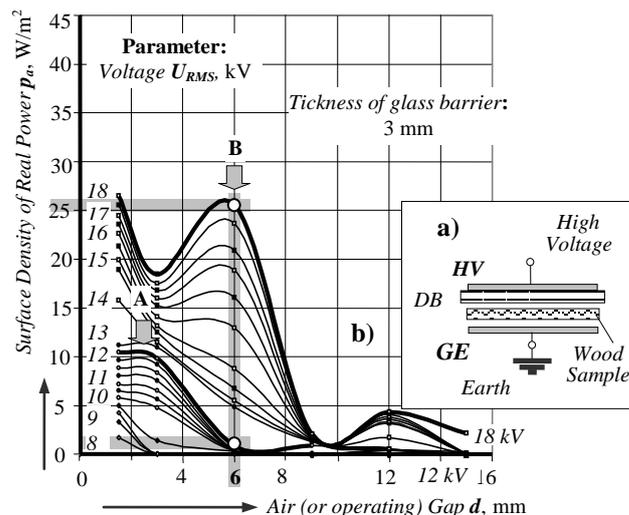
*Mahogany* has a straight, fine and even grain, and is relatively free of voids and pockets. Its reddish-brown color darkens over time, and displays a reddish sheen when polished. This soft wood has excellent workability, and is very durable. Historically, the tree's girth allowed for wide boards from traditional mahogany species. These properties make it a favorable wood for crafting cabinets and furniture. *Mahogany* is still widely used for fine furniture, veneer, furring, ceilings of houses and crafts. It also resists wood rot, making it attractive in boat construction. It is also often used for musical instruments. But due to its fine-texture and surface inactivation it is difficult to apply flame retardants through capillary impregnation. The plasma-chemical surface pre-treatment by dielectric barrier air discharge at atmospheric pressure (DBD) was specify as new good way to *Mahogany* wood surface functionalization and activation [5].

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 impregnation solution, both aiming to improve the *Mahogany* 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 surfactants 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 Investigation

*Mahogany Caoba* soft wood (*Swietenia macrophylla*, Yucatan, Mexico) with average dried weight: 420 kg/m<sup>3</sup>; *Janka hardness*: 3.3 kN; *maximum stress in compression parallel*: 44.5 MPa; *stress in compression perpendicular*: 6.4 MPa; *maximum shear stress in parallel*: 9.7 MPa; *modulus of rupture in bending*: 83.3 MPa; *radial or R - shrinkage*: 4.1 %; *tangential or T - shrinkage*: 7.2 %, and *volumetric shrinkage*: 9.5 %; *T/R ratio*: 1.75; and *moisture content* of 7.8 % was used in this investigation, Fig. 1.



**Fig. 1.** Plasma-chemical surface pre-treatment of wood sample by non-equilibrium dielectric barrier air discharge at atmospheric pressure in asymmetric coplanar system with one glass barrier (a), technological regime of cathode directed streamers (b).

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) or 25 kV (PV), Fig. 1.

A halogen-free, **phosphorus and nitrogen containing flame retardant** as a 30 wt. % aqueous solution has been used in this investigation. The impregnating flame retardant aqueous solution (PhFRIS, dry substance of 30 wt. %; phosphorus content of about 13 wt. %, pH = 7÷8 and density of 1.15 g/cm<sup>3</sup>) was based on a halogen free phosphorus and nitrogen containing flame retardant. The replacement of the halogen containing 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.

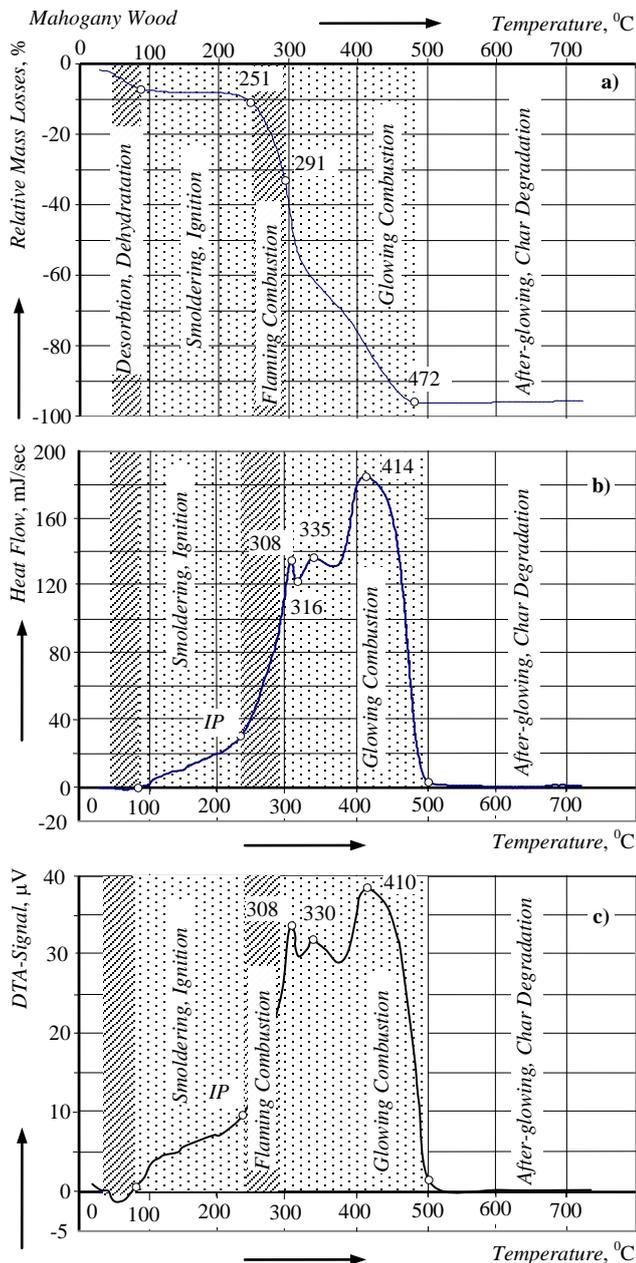
Germany) in quantity of 0.1 vol. %, as well as their combinations, have been used to control the ion activity of the flame retardant impregnation aqueous solution. The capillary impregnation has been applied on bare (for comparison) or plasma pre-treated *Mahogany* wood samples at atmospheric pressure by spraying the corresponding flame retardant solution (390 ml/m<sup>2</sup>).

**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 °C/min within the temperature range of 25÷1000 °C using *Perkins-Elmer* equipment.

### 3. Results and Discussion

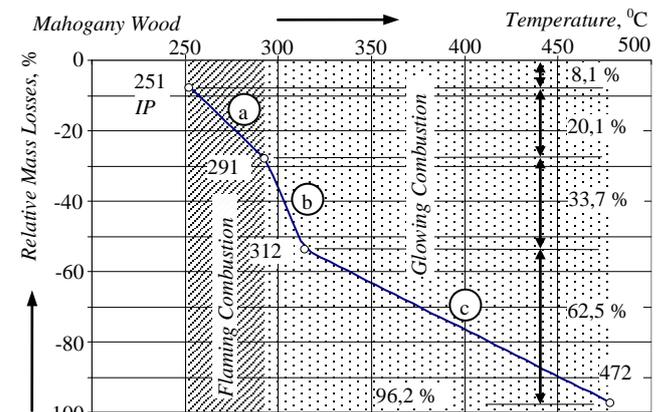
The studied *plasma-aided capillary impregnation* of *Mahogany* wood was based on both: plasma-chemical pre-treatment of the wood surface, Fig. 1, and flame-retardant impregnation treatment by a new aqueous solution with ion activity optimization. It was expected that increased wood capillary activity and increased solution adsorption speed and capacity would allow good enough flame retardant performance of porous wood surface [1, 2, 7].

The DBD surface plasma-chemical activation effects, 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 *Mahogany* wood – by TGA, DTA, and DSC-analyses.



**Fig. 2.** Thermal analysis - TGA (a), DSC (b), and DTA (c) spectra of bare *Mahogany* (*Swietenia macrophylla*, Yucatan, Mexico) wood in air (heating rate - 10 °C per minute): *Mahogany* wood pyrolysis stages and characteristic peaks identification.

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,



**Fig. 3.** Temperature regimes of mass losses after obtained kinetic statistic models (linear regression) of bare *Mahogany* wood pyrolysis: **a** -  $ML = -0.5007 T + 117,612$ ;  $R^2=0.9961$ ; **b** -  $ML = -1.2352 T + 331.603$ ;  $R^2=0.9970$ ; **c** -  $ML = -0.2655 T + 29.124$ ;  $R^2=0.9947$ .

**ML** - relative mass losses in %; **T** - temperature in degree of Celsius;  $R^2$  - coefficient of determination equation.

It is well known that *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. Chemical bonds begin to break at temperatures higher than 100 °C 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).

The results on *thermal degradation* of bare *Mahogany* wood above 100 °C shown Fig. 2, 3, and 4 allow the following conclusions:

**A.** *Mahogany Caoba* wood reveals the following characteristics (TGA, DTA and DSC analysis):

i) self-sustaining exothermic pyrolysis process and transition to flaming was observed at temperatures over 250 °C;

ii) self-sustaining exothermic pyrolysis process and transition to glowing was observed at temperatures over 290 °C. The identification of the individual stages of development of pyrolysis is accomplished by a new method based on the representation of the process from a kinetic point of view by a mathematical model representing a polygon of straight broken lines (linear regression), Fig. 3.

The various modes of pyrolysis are successfully presented by linear regression of the type, Fig. 3:

$$ML = \mathbf{B} T + \mathbf{A} = \mathbf{k} \mathbf{B} t + \mathbf{A} = \mathbf{D} t + \mathbf{A} \quad (1)$$

where ML is mass losses, mg; T - temperature, °C; t - time, sek,  $T = k t$ ,  $k = 10 \text{ }^\circ\text{C}/\text{min} = 1/6 \text{ }^\circ\text{C}/\text{sek}$ .

iii) a characteristic peak, associated with *hemi-cellulose* pyrolysis occurs at a temperature of 280±290 °C (DTA), Fig. 2b and c, but it is almost swallowed by the next peak at 308 °C, which can be associated mainly with the *cellulose* pyrolysis. A single peak was observed at 308 °C (DSC), Fig. 2b and c, 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;

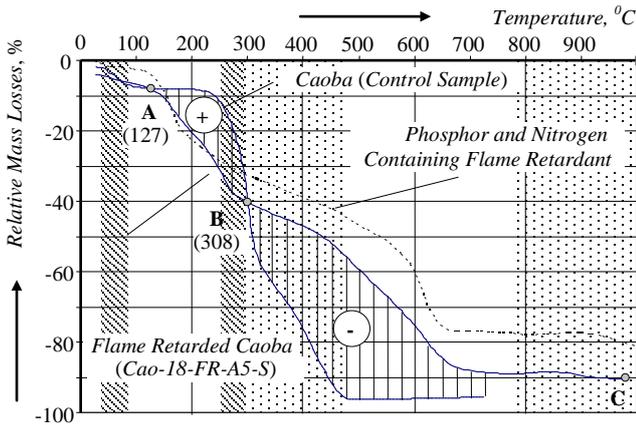
iv) characteristic peak, associated with *lignin* degradation exothermic reaction, was represented by peaks at 414 °C (DSC), Fig. 3, and at 423 °C (DTA), Fig. 2b and c. Generally, the peaks of *lignin* degradation reaction occur between 225 and 450 °C;

v) during the transition to glowing combustion (pyrolysis), 72.8 wt. % of the *Mahogany* wood was solid;

vi) remaining wood residue after glowing degradation or after 472 °C was char which undergoes further degradation by being oxidized to CO<sub>2</sub>, CO, and water during the afterglow stage. The remaining wood residue above 472 °C was 3.8 wt. %, Fig. 2a and 3.

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

i) this flame-retardant chemicals shift the *Mahogany* 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 418 °C (against 291 °C for bare *Mahogany*) and the remaining char residue is 54 wt. % (against 43 wt. % for bare *Mahogany*), Fig. 2a and 4;



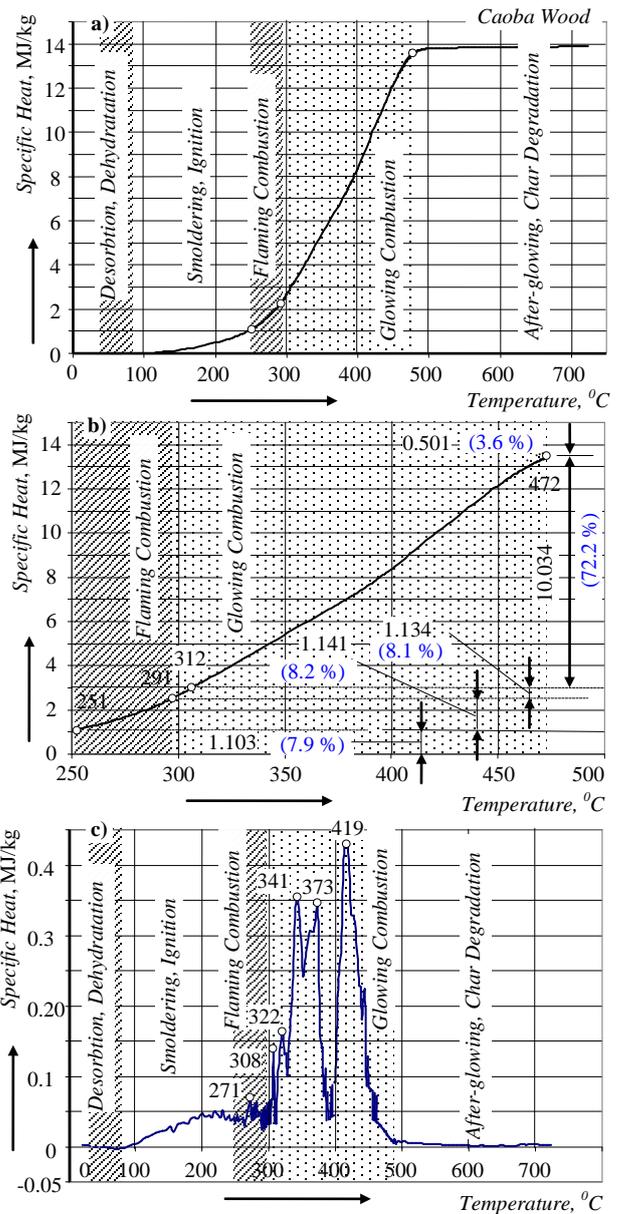
**Fig. 4.** Thermal analysis - TGA spectra of bare and flame retarded samples of *Mahogany* (*Swietenia macrophylla*, Yucatan, Mexico) wood in air: flame retardancy effect obtained by plasma aided capillary impregnation treatment with flame retardant (phosphor and nitrogen) containing aqueous solution (30 mass %).

**AB** - protective char layer production after flame retardant activation at about 125 °C; **BC** - flame retardancy effect of relative mass losses decrease after obtaining a protective char layer at about 300 °C.

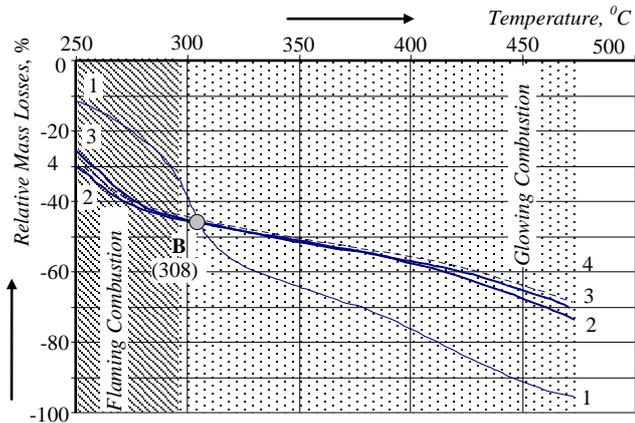
ii) some feasible mechanisms for fire retardancy include: *acid-catalyzed* (phosphoric acid) *hydrolysis* of *cellulose* and *hemi-cellulose* as reactions above 106 °C - *lignin* does not seem to be much affected by this FR-chemical; dehydration of *Mahogany* wood by FR-chemical; condensation enlargement 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 100 and 251 °C, Fig. 2b);

iii) the effective suppression of flaming and glowing combustion within the temperature range from 65 to 472 °C, Fig. 5;

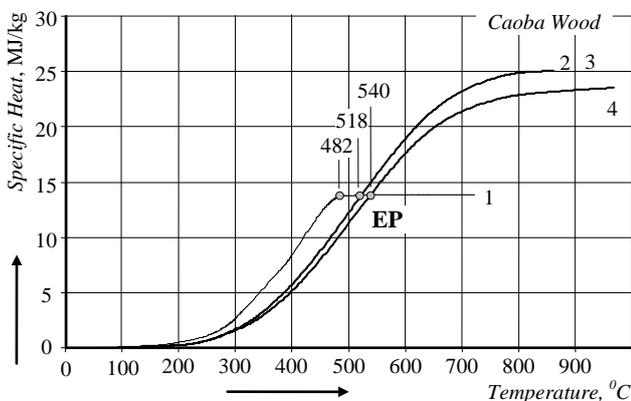
iv) the change of ionic and capillary activity resulting from the anionic surfactant and silicon spreader application in the impregnation solution (PhFRIS) accelerates, increases the amount of the applied flame retardant and the depth of the capillary impregnation, but does not alter substantially the efficiency, neither in terms of heat release and heat flow, nor in terms of mass losses, Fig. 7, 8 and 6.



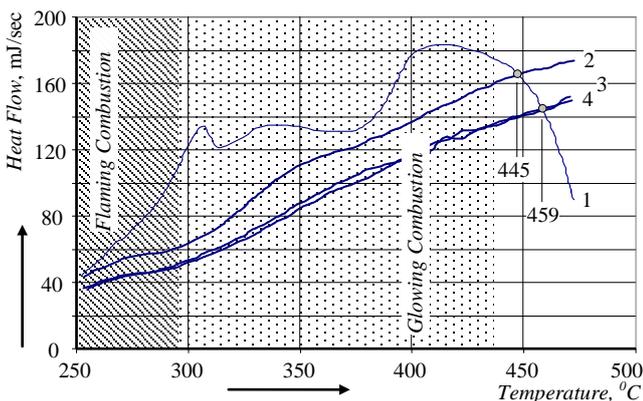
**Fig. 5.** Differential Scanning Analysis in air: integral (a, b) and differential (c) specific heat spectra of bare *Mahogany* (*Swietenia macrophylla*, Yucatan, Mexico) wood - *Mahogany* wood pyrolysis stages and characteristic peaks identification.



**Fig. 6.** Thermal analysis - TGA spectra of bare and flame retarded samples of Mahogany (*Swietenia macrophylla*, Yucatan, Mexico) wood in air: 1 - bare Mahogany wood sample: Cao-K; 2 - flame retarded Mahogany wood sample: Cao-K-FR; 3 - plasma aided flame retarded Mahogany wood sample: Cao-18-FR; 4 - plasma aided flame retarded Mahogany wood sample: Cao-18-FR-A5-S.



**Fig. 7.** DSC - thermal analysis: integral specific heat spectra of bare (1) and flame retarded (2, 3, and 4) samples of Mahogany (*Swietenia macrophylla*, Yucatan, Mexico) wood: 1 - bare Mahogany wood sample: Cao-K; 2 - flame retarded Mahogany wood sample: Cao-K-FR; 3, 4 - plasma aided flame retarded Mahogany wood sample: Cao-18-FR; Cao-18-FR-A5-S.



**Fig. 8.** DSC - thermal analysis: heat flow effect of plasma aided flame retardancy (3 and 4) of Mahogany (*Swietenia macrophylla*, Yucatan, Mexico) wood: 1 - bare Mahogany wood sample: Cao-K; 2 - flame retarded Mahogany wood sample: Cao-K-FR; 3 - plasma aided flame retarded Mahogany wood sample: Cao-18-FR; 4 - plasma aided flame retarded Mahogany wood sample: Cao-18-FR-A5-S.

A new interesting information is obtained from DSC - thermal analysis, after switching from the data on heat flow to energy (heat) and its differential and integral distribution, Fig. 5: *i* - the differential distribution of the heat generated repeats the characteristic peaks of the distribution of heat flow and DTA-signal, Fig.2 b and c, but shifted to the right toward higher

temperature areas; *ii* - the integral distribution of the heat generated (exothermic), Fig. 7, clearly reveals the delaying effect of the flame retardant chemicals used in relation to the heat generated up to the temperature range 482÷540 °C; *iii* - after this interval of suppression, however, follows a release of much larger amounts of heat, which is determined by the thermal degradation of the protective char layer; *iv* - the release of heat from bare Mahogany wood sample ends at about 500 °C, i.e. the entire heat release goes for growth of the fire before reaching the flash point (600 °C) and full fire development; *v* - flame-retarded Mahogany wood releases significantly less amount of heat - up to about 4 MJ/kg, which is one of the effects of flame retardancy; *vi* - plasma-aided flame retardancy (curve 4) shifts to the right the point of alignment (540 °C) and reduces substantially the heat, in relation to the cases where surfactants and spreaders are not used, Fig. 7 (curve 2 and 3).

## Conclusion

The application of thermal analysis (TGA, DTA, and DSC) allows evaluating the Mahogany wood pyrolysis under heat influence by setting pyrolysis stage temperature ranges and hemicellulose, cellulose and lignin characteristic temperature peaks. Thermal analysis helps define and illustrate the impact of the newly produced phosphor and nitrogen containing flame retardant on Mahogany wood behaviour. It significantly reduces the heat release within the range of 65÷540 °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 aqueous solution containing phosphorus flame retardant and its impact on Mahogany wood plasma-aided flame retardancy. The created new approaches for processing of the data from TGA and DSC-analysis allow revealing more clearly the effect of flame-retardant chemicals and of plasma-aided flame retardant capillary impregnation technology.

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