Thermal Behavior Criteria of Flame Retarded Wood Obtained by Simultaneous Thermal Analysis:

III. THERMAL BEHAVIOR CRITERIA OF PLASMA-AIDED FLAME RETARDANCY

Peter Dineff, Ivaylo Ivanov, Dilyana Gospodinova
Dept. of Electrical Apparatus
Technical University - Sofia
Sofia, Bulgaria
dineff_pd@abv.bg

Lucien Veleva (Muleshkova)
Center for Research and Advanced Studies
National Polytechnic Institute
Merida, Yucatan, Mexico
veleva@mda.cinvestav.mx

***Abstract* — the plasma-aided flame retardation of wood and wooden products has been 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. Simultaneous thermal analysis has been used to reveal the impact of plasma-aided capillary impregnation on flame retardation of wood. This study has been developed as part of a large investigation on the impact of plasma activated (functionalized and ion activated) wood surface on wood flame retardancy.**

***Keywords* — dielectric barrier discharge, flame retardancy, plasma-aided capillary impregnation, simultaneous thermal analysis, specific heat flux, thermal behaviour criteria**

I. INTRODUCTION

The plasma-chemical wood surface pre-treatment substantially alters its ionic, chemical and capillary activity, thus improving some capillary impregnation process basic characteristics, such as penetration depth, solution spreading and adsorption speed, adsorbed solution capacity. The plasma-aided flame retardation of wood and wooden products has been developed as a result of plasma-aided process of capillary impregnation [2 and 3].

The pyrolysis and combustion changes or the difference between flame retardancy and plasma-aided flame retardancy have been examined in a new way by simultaneous thermal method (*STA*) and new integral criteria, which can differentiate between a flaming and controlled by flame retardancy (and plasma-aided flame retardancy) glowing (or smoldering) wood combustion [4 and 5].

The objective of this paper was to study the difference in thermal behavior (pyrolysis and combustion) between classic flame retardancy, obtained by capillary impregnation with phosphor and nitrogen containing flame retardant and plasma-aided flame retardancy by simultaneous thermal method (*STA*) and new integral criteria. Plasma-aided flame retardancy was realized through atmospheric dielectric barrier discharge in air.

The authors gratefully acknowledge the financial support of the Technical University of Sofia for the Research Project 132PD0051-01 (2013÷2014).

978-1-4799-5817-7/14/$31.00 ©2014 IEEE

II. THEORETICAL AND EXPERIMENTAL INVESTIGATION

A. New thermal analysis approach to plasma-aided flame retardancy

A new thermal analysis approach to distinguish between the flame retardancy and plasma-aided flame retardancy of wood was discussed. This technique is based on the simultaneous thermogravimetric and differential scanning calorimetric analysis (*TGA-DSC*) or on mass losses and heat flux released temperature spectra in flaming and glowing wood pyrolysis and combustion. Wood and cellulosic materials decompose on heating by two alternative pathways in different conditions - low and high temperature pathway [1 and 3].

The low temperature pathway, which dominates at temperatures below 300 ^{0}C, involves reduction in the degree of polymerization by bond scission; elimination of water;

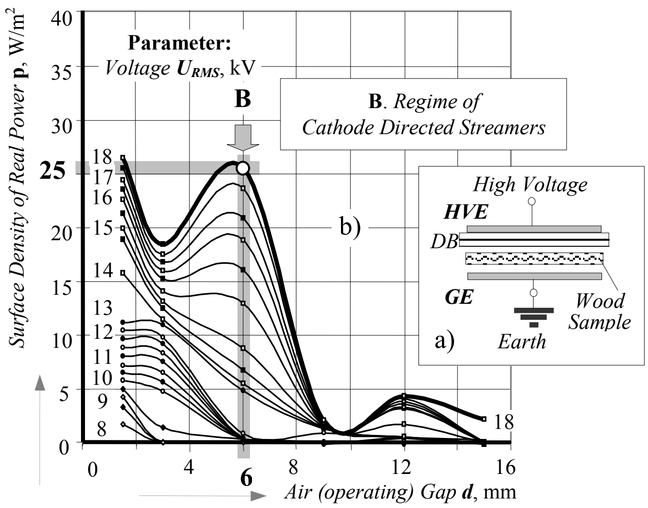

Fig. 1. Atmospheric dielectric barrier air discharge (*DBD*) in asymmetric coplanar two-electrode system (*a*) with an assymmetrically located dielectric barrier (alkali glass); technological discharge characteristic and selection of the *DBD*-mode (*b*) of plasma pre-treatment at industrial frequency (50 Hz) and 18 kV (rms)

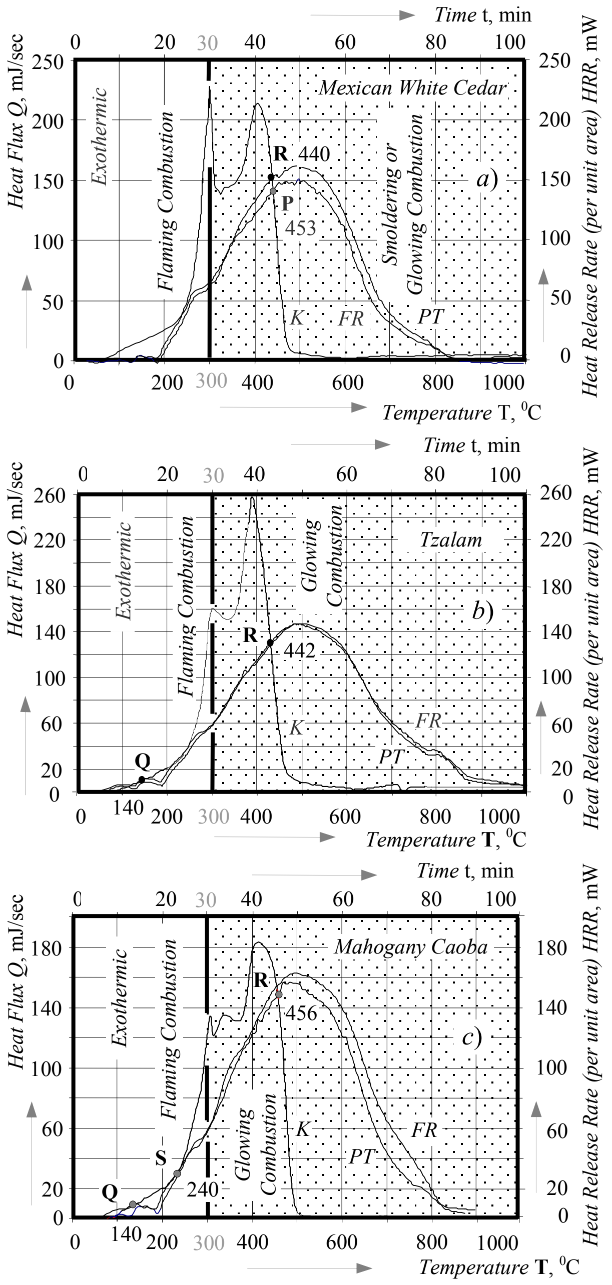

Fig. 2. Results of simultaneous thermal analysis (*STA*) - *DSC*-spectra of bare (*K*), flame retarded (*FR*) and plasma-aided flame retarded (*PT*) wood samples in air (linear heating with rate: 10 °C per minute; initial sample mass: 14.2 mg) - wood pyrolysis and combustion stages identification: ***a*** - Mexican White Cedar (*Cupressus Lusitanica*); ***b*** - Tzalam (*Lysiloma bahamensis*); ***c*** - Mahogany Caoba (*Swietenia macrophylla*)

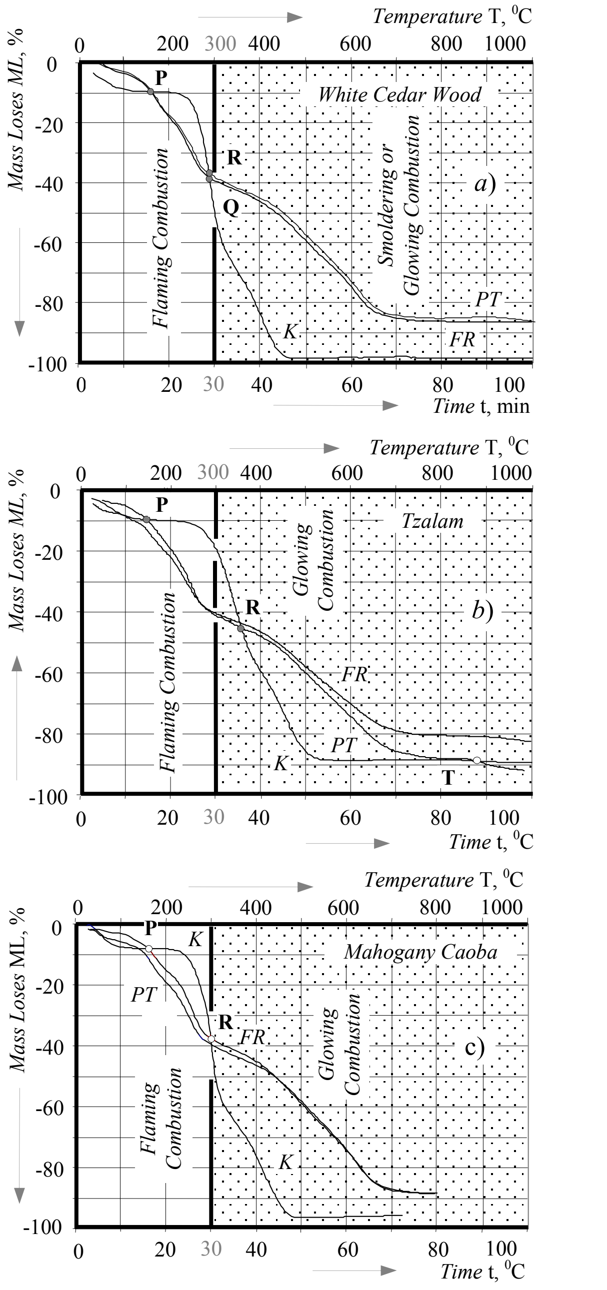

Fig. 3. Results of simultaneous thermal analysis (*STA*) - *TGA*-spectra of bare (*K*), flame retarded (*FR*) and plasma-aided flame retarded (*PT*) wood samples in air (linear heating with rate: 10 °C per minute; initial sample mass: 14.2 mg) - wood pyrolysis and combustion stages identification: ***a*** - Mexican White Cedar (*Cupressus Lusitanica*); ***b*** - Tzalam (*Lysiloma bahamensis*); ***c*** - Mahogany Caoba (*Swietenia macrophylla*)

formation of free radicals, carbonyl, carboxyl, and hydroperoxide groups; evolution of gases - CO and CO_2; and, finally, production of a highly reactive carbonaceous char. Oxidation of the combustible volatiles gives flaming combustion [1].

Flame retardancy and plasma-aided flame retardancy suppress the flaming and provide a flameless form of combustion in a different way [2 and 3].

B. Integral pyrolysis and combustion behavior criteria

The apparatus used for this study was a Perkin Elmer 6000 simultaneous (*TGA-DSC*) thermoanalyzer. This paper describes a new simultaneous technique to differentiate between flame retardancy and plasma-aided flame retardancy and further describes the use of simultaneous *TGA-DSC* technique to study the flammability changes occurring in wood under plasma

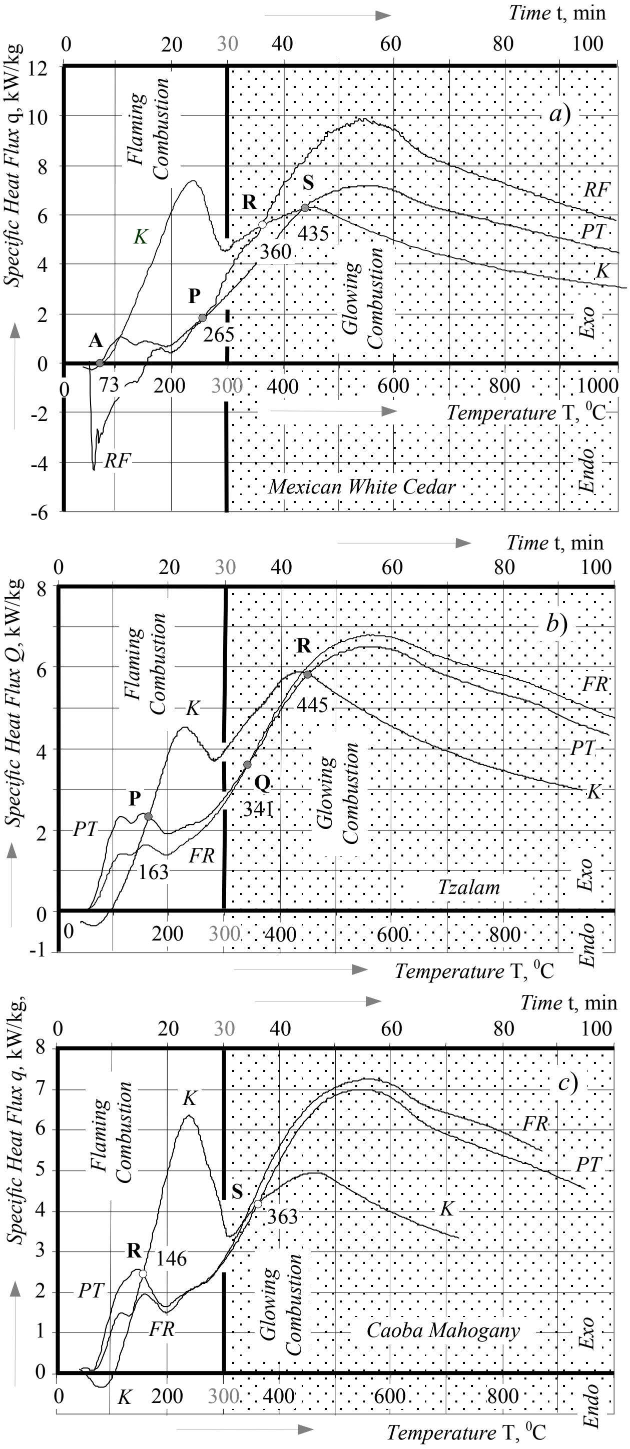

Fig. 4. New approach and criterion of pyrolysis and combustion behavior established on simultaneous thermal analysis (*STA*) - specific heat flux spectra (per unit area and mass losses) of bare (*K*), flame retarded (*FR*) and plasma-aided flame retarded (*PT*) wood samples: ***a*** - Mexican White Cedar (*Cupressus Lusitanica*); ***b*** - Tzalam (*Lysiloma bahamensis*); ***c*** - Mahogany Caoba (*Swietenia macrophylla*)

pre-treatment and *phosphor and nitrogen containing flame retardant* (*PhN-FR*), in particular the suspected decrease in the flammability of flame retarded wood exposed to

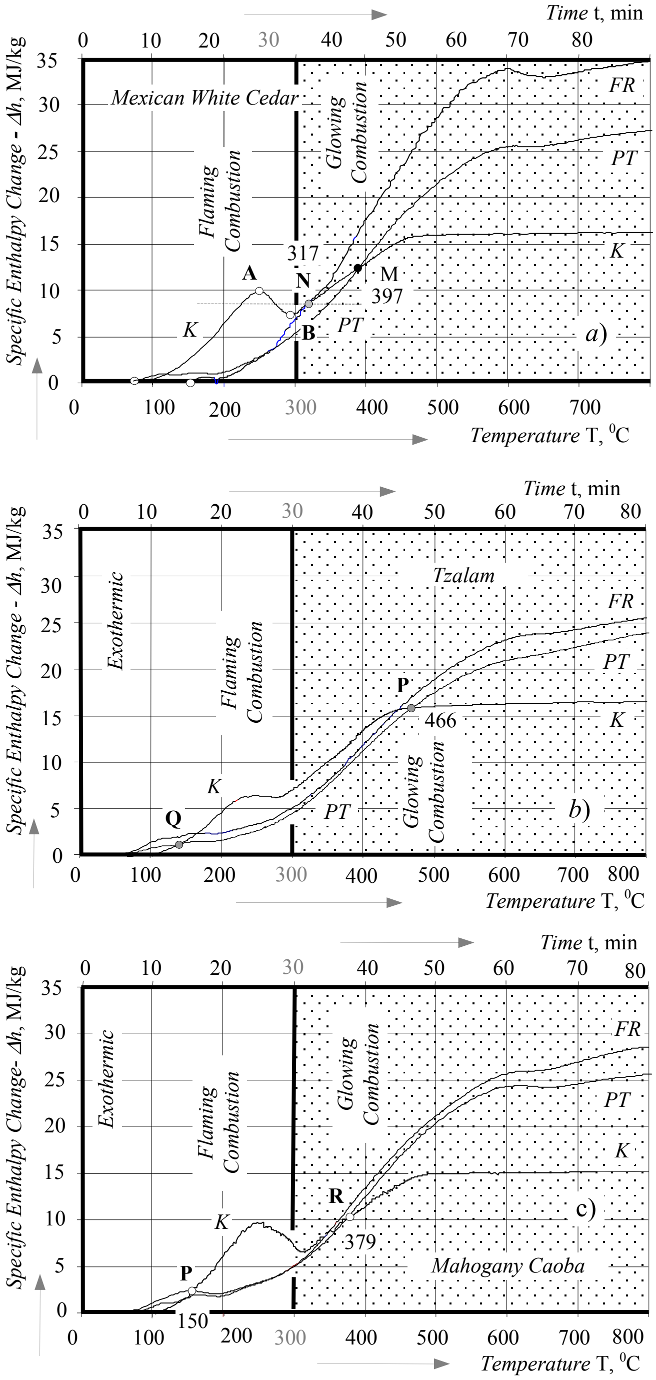

Fig. 5. New approach and criterion of pyrolysis and combustion behavior established on simultaneous thermal analysis (*STA*) - specific enthalpy change spectra (per unit mass losses) of bare (*K*), flame retarded (*FR*) and plasma-aided flame retarded (*PT*) wood samples: ***a*** - Mexican White Cedar (*Cupressus Lusitanica*); ***b*** - Tzalam (*Lysiloma bahamensis*); ***c*** - Mahogany Caoba (*Swietenia macrophylla*)

plasma-chemical surface pre-treatment with an *atmospheric dielectric barrier discharge* (*ADBD*) in air at ambient temperature, [2, 3].

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 pre-treatment has been applied on the test samples for 60 sec in a non-equilibrium cold plasma of dielectric barrier air discharge (*DBD*) in air at atmospheric pressure, industrial frequency (50 Hz) and 18.0 kV (*rms*) or 25.4 kV (*peak value*).

The *DBD*-plasma system consisted of coplanar shaped rectangular electrodes with a glass barrier (3 mm thick) closely arranged to the grounded electrode, with 6 mm operating distance between the high voltage electrode and the glass 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 a minute (60 sec) under chosen operational regime, Fig. 1a.

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 [5].

Three species of tropical wood (heartwood) from Mexico's Rainforest, particularly in Yucatán, were studied: Mexican white cedar (*Cupressus Lusitanica*), Tzalam or Caribbean walnut (*Lysiloma bahamensis*), and Mahogany caoba (*Swietenia macrophylla*).

III. Results and Discusion

The application of thermal analysis (*TGA* and *DSC*) allows evaluating the bare wood samples decomposition (pyrolysis) under the influence of heat by setting pyrolysis stage temperature ranges and hemi-cellulose, cellulose and lignin characteristic temperature peaks Fig. 2 and 3.

In *DSC* and *TGA*-spectra the observed results allow us to state three essential conclusions. Firstly, the heat flux (*Q*) and mass losses (*ML*) temperature spectra bring to light the pyrolysis stage temperature ranges of bare wood samples and characteristic flaming and glowing (pyrolysis and combustion) peaks Fig.2 and 3.

Secondly, a thermal analysis approach based on two criteria that vary differently can not distinguish generally in a good way the flame retardancy behavior (*FR*) and the plasma-aided flame retardancy behavior (*PT*).

Thirdly, the characteristic peaks of flaming for bare wood samples are arranged at the same temperature (300 ^{0}C) in heat flux spectra. There are not characteristic peaks at this temperature with flame retardancy (*FR*) and plasma-aided flame retardancy (*PT*). The flame combustion mechanism was suppressed - there is only a glow combustion mechanism controlled by the used flame retardant Fig. 2.

The used phosphor and nitrogen containing flame retardant suppresses flame combustion and heat release up to higher temperature, as follows - for Mexican white cedar up to 435 ^{0}C, for Tzalam - 445 ^{0}C and for Mahogany caoba - 363 ^{0}C Fig. 2.

The heat flux (*Q*) spectrum at constant pressure, Fig. 2, was used to calculate by integrating the corresponding enthalpy changes. For an exothermic reaction at constant pressure, the system's change in enthalpy equals the energy released in the pyrolysis and the combustion [4].

This study, [4 and 5], has also established both new general criteria for distinguishing flame retardancy from plasma-aided flame retardancy: the specific heat flux (*q* or *HRR* - heat release rate per unit area and mass of wood sample), Fig. 4, and the specific (per unit mass) enthalpy change ($-\Delta h$) Fig. 5:

The result specific heat flux and specific enthalpy change temperature spectra give us new more reliable information:

1. The characteristic peaks of flaming for bare wood was transferred to the substantially lower temperatures: for Mexican white cedar to 246 ^{0}C, for Tzalam - 254 ^{0}C and for Mahogany caoba - 250 ^{0}C. The pyrolysis or combustion mechanism was changed from flaming to glowing (smoldering) at about 300 ^{0}C Fig. 4 and 5.

2. The area of suppressed flame combustion and heat release of plasma-aided flame retarded wood extends to the lower temperatures as compared with those obtained by the analysis on the heat flux (*Q*), Fig. 2 and 4 - for Mexican white cedar up to 397 ^{0}C, for Tzalam - 466 ^{0}C and for Mahogany caoba - 379 ^{0}C Fig. 4 and 5.

3. The specific enthalpy change ($-\Delta h$) temperature spectrum is an integral characteristic and the specific heat (*q*) flux temperature spectrum is a differential characteristic of wood pyrolysis and combustion process.

IV. Conclusion

Simultaneous *TGA-DSC* technique measures both heat flux and mass losses in a wood sample as a function of temperature or time in a controlled (air) atmosphere. Simultaneous measurement of these two material properties not only improves productivity but also simplifies interpretation of the results by new integral criteria such as *the specific enthalpy change* and *specific heat flux* and their temperature or time spectra. The complimentary information obtained allows differentiation between thermal effects of flame retardancy and plasma-aided flame retardancy of wood.

References

[1] H. Yang, R. Yan, H. Chen, D. Ho Lee, and C. Zheng, "Characteristics of hemicellulose, cellulose and lignin pyrolysis", Fuel, vol. 86, 2007, pp. 1781÷1788.

[2] P. Dineff, L. Kostova, "Method of plasma-chemical modification", H05H 1/24, International patent publication No.: WO Patent 2006/ 133524 A2; International patent application No.: PCT/BG2006/ 000012; Priority date: 14.06.2005; Publication date: 21.12. 2006.

[3] P. Dineff, D. Gospodinova, L. Kostova, T. Vladkova, and E. Chen, "Plasma-aided surface technology for modification of materials referred to fire protection", Problems of atomic science and technology, vol. 6; Series plasma physics (14), 2008, pp. 198÷200.

[4] P. Dineff, I. Ivanov, D. Gospodinova, and L. Veleva, "Thermal behavior criteria of flame retarded wood obtained by simultaneous thermal analysis: I. New thermal behavior criteria of wood", XVIII-th International Symposium on electrical apparatus and technologies "SIELA'2014", May 29÷31, 2014, Bourgas, Bulgaria; Proceedings of papers (in press).

[5] P. Dineff, I. Ivanov, D. Gospodinova, and L. Veleva, "Thermal behavior criteria of flame retarded wood obtained by simultaneous thermal analysis: II. Flame retardancy criteria of wood", XVIII-th International Symposium on electrical apparatus and technologies "SIELA'2014", May 29÷31, 2014, Bourgas, Bulgaria; Proceedings of papers (in press).