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

II. FLAME RETARDANCY CRITERIA OF WOOD

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***Abstract* — The flame retardation of wood and wooden products has been developed by creating new phosphor and nitrogen containing flame retardant for capillary impregnation improving some impregnation process basic characteristics, such as penetration depth, solution spreading and adsorption speed, adsorbed solution capacity. Simultaneous thermal analysis (STA) has been used to reveal the impact of this flame retardant on flame retardation of wood. Three tropical wood species (heartwood) from Mexico's Rainforest, particularly in Yucatán, were studied. This study has been developed as part of a large investigation on plasma activated (functionalized and ion activated) wood surface and flame retardant treated wood.**

Keywords — capillary impregnation, flame retardancy, plasma-aided capillary impregnation, simultaneous thermal analysis, specific enthalpy change, thermal behaviour criteria

I. INTRODUCTION

The flaming pyrolysis and combustion suppression by flame retardancy with a new phosphor and nitrogen containing flame retardant (*PhN-FR*) have been examined in a new way including simultaneous thermal (*TGA-DSC*) method and new criteria, which can differentiate between a flaming and controlled by flame retardancy glowing (or smoldering) wood combustion.

II. THEORETICAL AND EXPERIMENTAL INVESTIGATION

A. Simultaneous thermal analysysis

The S*imultaneous Thermal Analysis* (*STA*) technique consists of recording the mass loses (*ML*) and the heat flux (*Q*) evolved in flaming and glowing thermal destruction of wood sample during the increase in temperature from ambient temperature until 1 000 ^{0}C with a 10 ^{0}C/min heating rate. This hyphenated technique is based on the simultaneous carry out of thermogravimetric and differential scanning calorimetric analysis (*TGA-DSC*). The results of a *STA* experiment are: a curve of heat flux, or heat release rate per unit area, and a curve of mass losses versus temperature or versus time.

It is well known that lignin and hemicellulose play an important role on the thermal degradation of wood at the temperature below 300 ^{0}C. This is the *low temperature pathway*, which involves reduction in the degree of polymerization by bond scission; elimination of water; formation of free radicals, carbonyl, carboxyl, and hydroperoxide groups; evolution of *CO* and CO_2; and production of a highly reactive carbonaceous char.

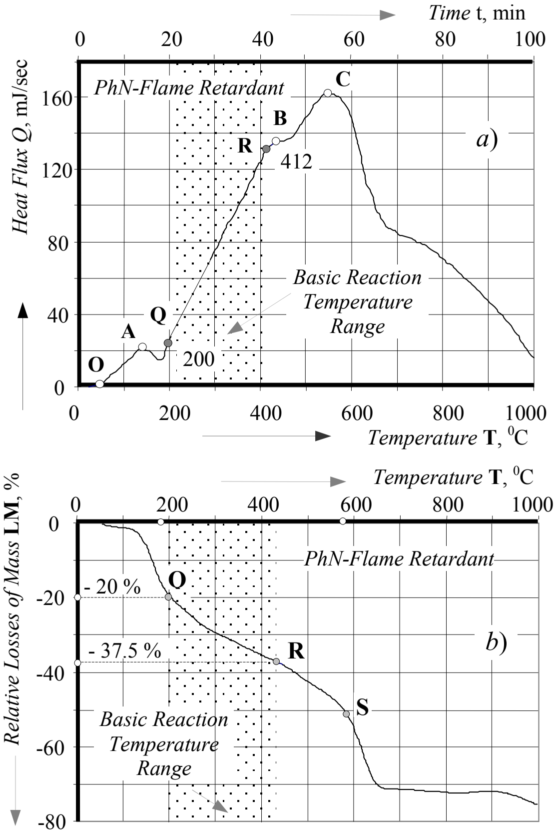

Fig. 1. Results of simultaneous thermal analysis (*STA*) - *DSC*- (***a***) and *TGA*- (***b***) spectra of used phosphor and nitrrogen comtaining flame retardant (*PhN-FR*) in air (linear heating with rate: 10 ^{0}C per minute; initial sample mass: 14.2 mg) - *QR* is a basic reaction temperature range which produces orthophosphoric acid.

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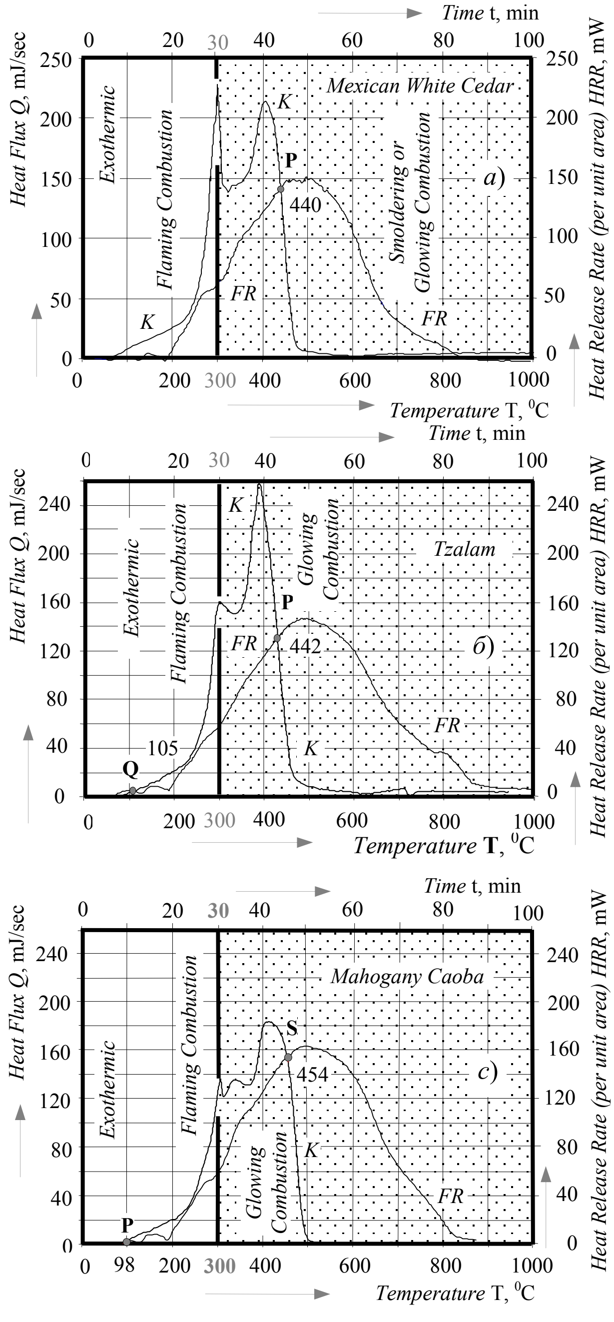

Fig. 2. Results of simultaneous thermal analysis (*STA*) - *DSC*-spectra of bare (*K*) and flame retarded (*FR*) wood samples in air (linear heating with rate: 10 ^{0}C per minute; initial sample mass: 14.2 mg) - wood pyrolysis and combustion stages identification: ***a*** - Mexican White Cedar (*Cupressus Lusitanica*); ***b*** - Tzalam (*Lysiloma bahamensis*); ***c*** - Mahogany Caoba (*Swietenia macrophylla*)

Oxidation of the combustible volatiles gives flaming combustion. Flaming combustion could be retarded by inorganic materials that suppress the formation of the combustible volatiles through dehydration and charring of the substrate. A new aqueous fire retardant composition (*PhN-RF*) for wood and cellulosic material on the basis of urea - $CO(NH_2)_2$, and orthophosphoric acid - H_3PO_4, was used as source of inorganic acid groups such as phosphoric acid, monoammonium phosphate or diammonium phosphate, [1].

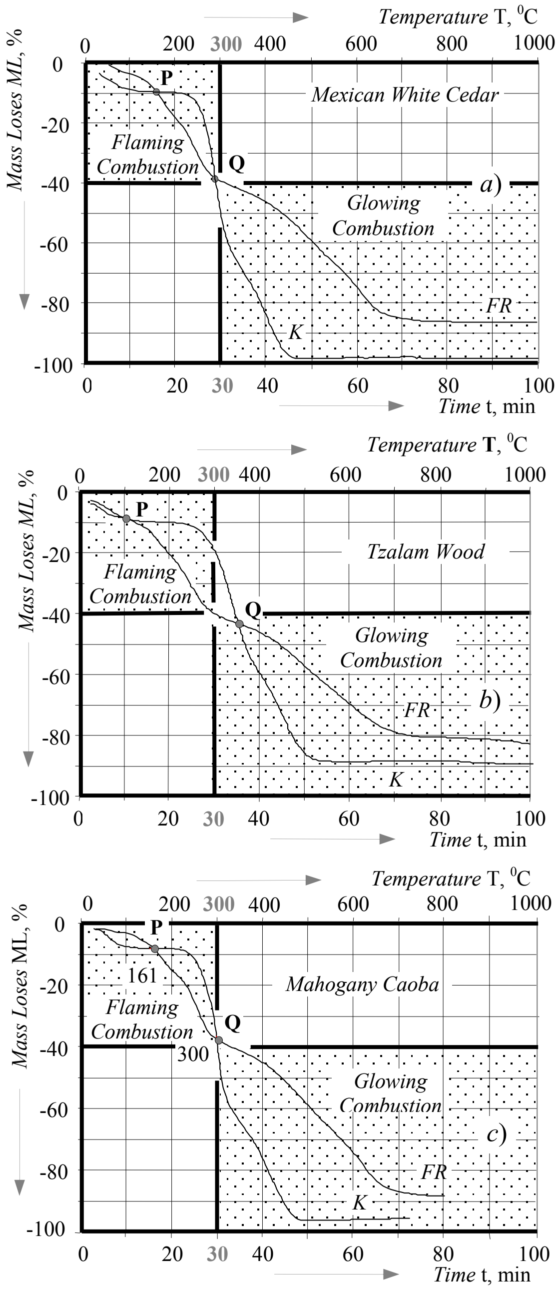

Fig. 3. Results of simultaneous thermal analysis (*STA*) - *TGA*-spectra of bare (*K*) and flame retarded (*FR*) wood samples in air (linear heating with rate: 10 ^{0}C per minute; initial sample mass: 14.2 mg) - wood pyrolysis and combustion stages identification: ***a*** - Mexican White Cedar (*Cupressus Lusitanica*); ***b*** - Tzalam (*Lysiloma bahamensis*); ***c*** - Mahogany Caoba (*Swietenia macrophylla*)

The objective of this paper was to study the thermal behavior (pyrolysis and combustion) of flame retarded woods, obtained by capillary impregnation with phosphor and nitrogen containing flame retardant by simultaneous thermal method (*STA*) and new criteria. Flame retardancy suppresses the flaming combustion and provides a flameless form of combustion in a different way [2, 3].

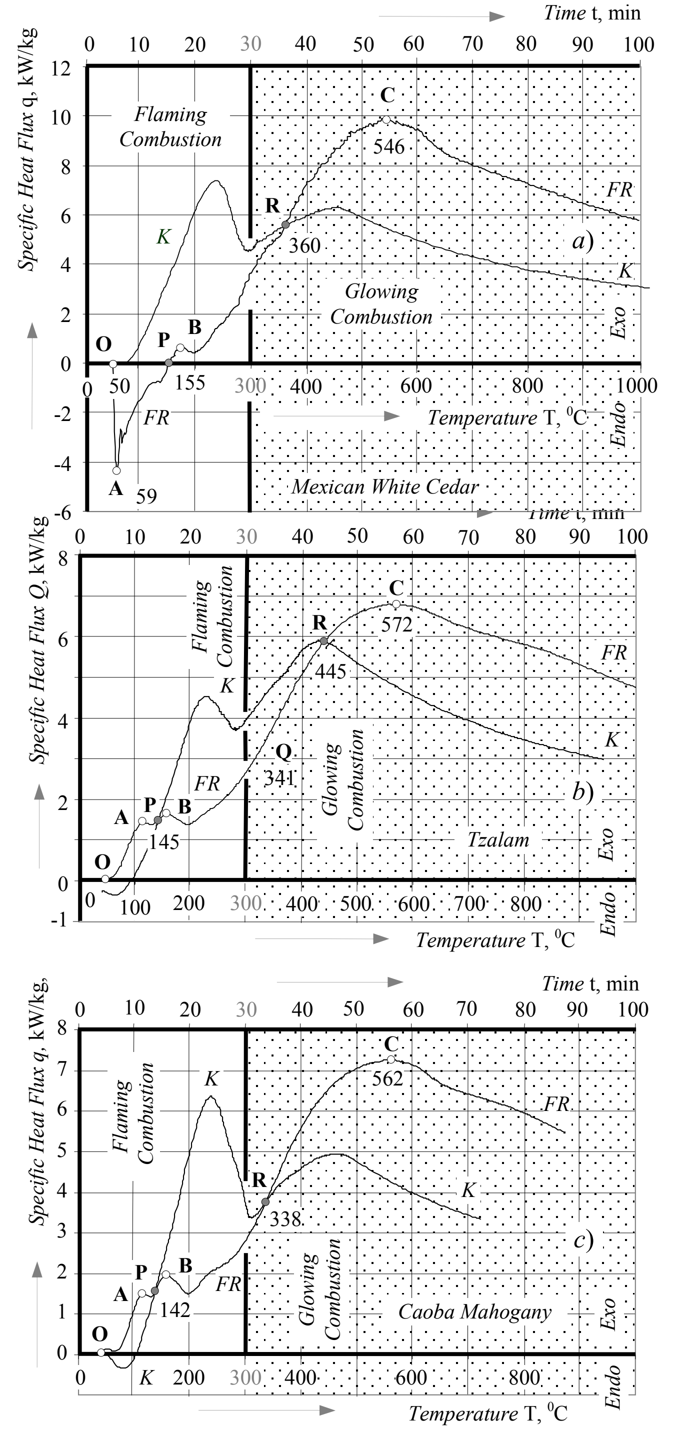

Fig. 4. New approach and criterion of pyrolysis and combustion behavior established on simultaneous thermal analysis (*STA*) - specific heat flux spectra *q* (per unit area and mass losses) of bare (*K*) and flame retarded (*FR*) wood samples: ***a*** - Mexican White Cedar (*Cupressus Lusitanica*); ***b***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

The apparatus used for this study was a Perkin Elmer simultaneous *TGA-DSC* thermoanalyzer. Three tropical wood species (heartwood) from the Mexico's Rainforest, particularly in Yucatán, were studied: the Mexican white cedar (*Cupressus Lusitanica*), the Tzalam or Caribbean walnut (*Lysiloma bahamensis*), and Mahogany caoba (*Swietenia macrophylla*).

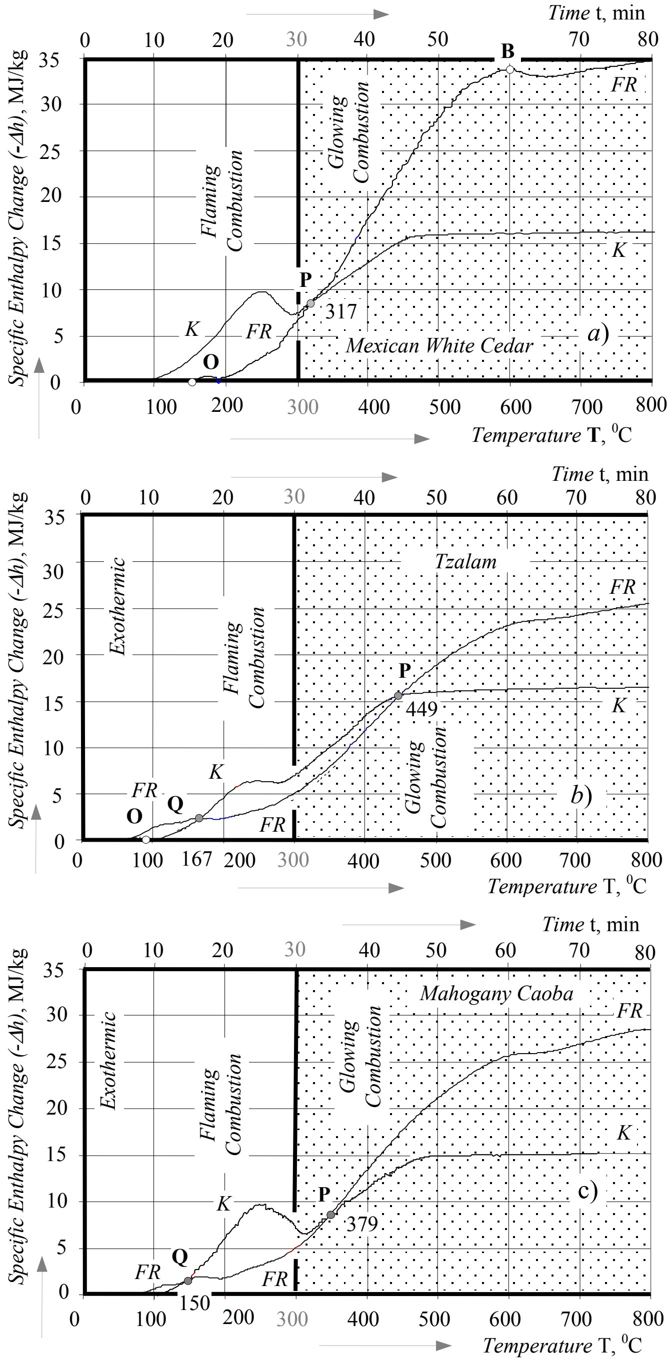

Fig. 5. New approach and criterion of pyrolysis and combustion behavior established on simultaneous thermal analysis (*STA*) - specific enthalpy change spectra (*-Δh*) (per unit mass losses) of bare (*K*) and flame retarded (*FR*) wood samples: ***a*** - Mexican White Cedar (*Cupressus Lusitanica*);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

A halogen-free, *phosphorus and nitrogen containing flame retardant* product (*PhNFR*) based on ortho-phosphorous acid, urea and ammonia has been produced and studied in this study as a 30 wt. % water solution. The basic reaction temperature range of *PhN-FR* which produces orthophosphoric acid is shown by *STA* - temperature spectra Fig. 1.

B. Flame retardancy behavior criteria

This paper describes a new simultaneous thermoanalytical technique based on *STA* (*TGA* and *DSC*) analysis for revealing the mechanism of flame combustion and its suppression by the used flame retardant. Since the *DSC* is at constant pressure, the heat flow (*Q*) curve, Fig. 2, can be used to calculate by integrating the corresponding enthalpy changes ($-\Delta H$), and the two new criteria - specific heat flux (*q*) and enthalpy change ($-\Delta h$) Fig. 4 and 5 [4].

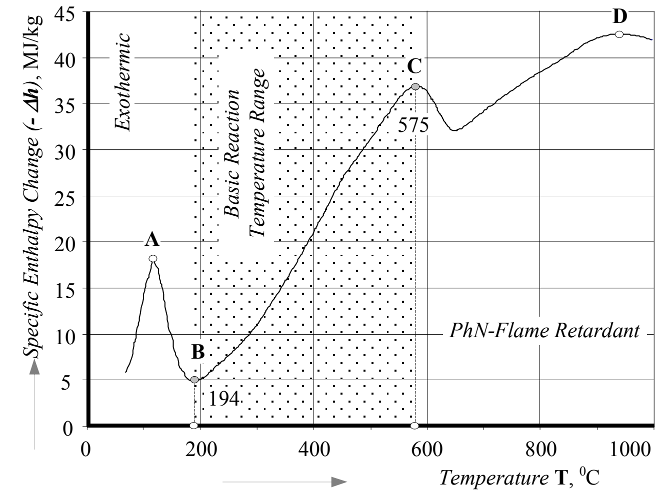

Fig. 6 New approach and criterion of thermal destruction of phosphor and nitrogen containing flame retardant (*PhN-FR*) established by simultaneous thermal analysis (*STA*) - specific enthalpy change ($-\Delta h$) temperature spectra (per unit area and mass losses)

This study has also established two thermal behavior criteria - *the specific heat flux* (heat release rate per unit area and mass), Fig. 4, and the *specific enthalpy change* (per unit mass), Fig. 5 to illustrate the suppression of low temperature pathway and the absence of flaming. Phosphorus and nitrogen containing flame retardant was activated at temperature about 194 ^{0}C, Fig. 1 and 6, and provides controlled production of a highly reactive carbonaceous char as barrier topcoat. Oxidation of the chemically reactive char gives controlled by flame retardancy glowing (or smoldering) combustion - flameless form of combustion, Fig. 4 and 5.

III. RESULTS AND DISCUSION

The mechanisms of the thermal decomposition and flaming suppression, the rates of combustion and heat release, and the favorable condition of carbonaceous char formation have been investigated by simultaneous thermal analysis to provide appropriate description flame retarded wood combustion and fire prevention.

The application of simultaneous thermal analysis (*TGA* and *DSC*) allows evaluating the bare and flame retarded wood samples decomposition (pyrolysis) under the influence of heat by setting pyrolysis stage temperature ranges and characteristic temperature peaks Fig. 4 and 5.

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].

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 317 ^{0}C, for Tzalam - 449 ^{0}C and for Mahogany caoba - 379 ^{0}C Fig. 5.

Simultaneous thermal analysis approach based on these two criteria that vary differently with temperature can successfully distinguish generally the bare wood thermal behavior (*K*) and flame retardancy behavior (*FR*). This approach was applied in the same way in the study of thermal destruction of used flame retardants Fig. 6.

This study has also established both new general criteria for revealing the effect of 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.

IV. CONCLUSION AND PERSPECTIVES

Simultaneous TGA-DSC technique measures both heat flux *Q* and mass losses *ML* in a wood sample as a function of temperature or time in a controlled atmosphere (air). Simultaneous measurement of these two properties simplifies interpretation of the results by new integral criteria such as *specific heat flux* (*q*) and *specific enthalpy change* ($-\Delta h$). The information allows both *flaming combustion suppressing mechanism* and *effect of flame retardant controlled glowing combustion* of retarded woods.

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