

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

I. NEW THERMAL BEHAVIOR CRITERIA OF WOOD

Ivaylo Ivanov, Dilyana Gospodinova,
Peter Dineff
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
Mérida, Yucatán, Mexico
veleva@mda.cinvestav.mx

Abstract — Simultaneous Thermal Analysis (STA) unifies the application of thermogravimetry (TGA) and differential scanning calorimetry (DSC) to one and the same sample in a single instrument, under perfectly identical conditions. The results obtained by STA were used in a new way, to reveal the influence of plasma-aided flame retardancy on thermal behavior and flammability of wood. New integral criteria of thermal behavior such as specific enthalpy change, kJ/kg, and specific heat flux, kW/kg or kJ/(kg sec), have been developed by investigating three different species of Mexican wood (Yucatan) - Mexican white cedar (*Cupressus Lusitanica*); Caoba mahogany (*Swietenia macrophylla*); and Tzalam (*Lysiloma bahamensis*).

Keywords — capillary impregnation, Caoba mahogany, enthalpy change, flame retardancy, Mexican white cedar, plasma-aided flame retardation, simultaneous thermal (TGA-DSC) analysis, thermal behaviour criteria, Tzalam

I. INTRODUCTION

Simultaneous Thermal Analysis (STA) generally refers to the simultaneous application of thermogravimetry (TGA) and differential scanning calorimetry (DSC) to one and the same sample in a single instrument. The test conditions are perfectly identical for the TGA and DSC signals - same atmosphere, gas flow rate, vapor pressure, heating rate, thermal contact, radiation effects, etc. Simultaneous thermal measurement offers more information than separate measurements with two different systems. STA measures both heat flow and mass losses (e.g. thermal degradation) in a wood sample as a function of temperature or time in a controlled atmosphere. Simultaneous measurement of these two properties not only improves productivity but also simplifies interpretation of the results [1, 2].

On the basis of prior art, as well as on our own experience in plasma-aided impregnation of flame retarded wood, [3 and 4], the flammability changes of three species of rainforest wood (Mexico, Yucatán) have been examined in a new way, including simultaneous TGA-DSC method and new thermal behavior criteria, which can distinguish successfully flaming from glowing combustion (burning) stage.

This study has been developed as part of a large

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

investigation on the impact of plasma activated (functionalized and ion activated) wood surface on wood flame retardancy obtained by capillary impregnation [3, 4].

II. THEORETICAL AND EXPERIMENTAL INVESTIGATION

A. New thermal analysis approach

Cellulosic materials decompose on heating by two alternative pathways. The first (low temperature) pathway, which dominates at temperatures below 300 °C, 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 CO₂; and, finally, production of a highly reactive carbonaceous char.

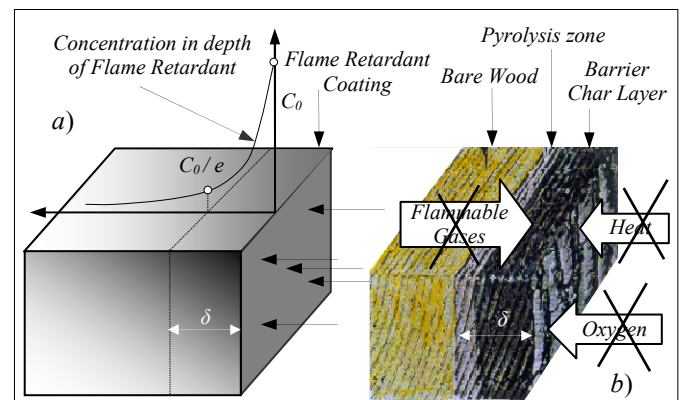


Fig. 1 General schematic of a flame retardant coating produced by capillary impregnation (a) and its thermal behavior - formation of glassy char barrier inhibiting the “pyrolysis” process breaking down and release of flammable gases which is necessary to feed flames (b)

The second (high temperature) pathway, which takes over at temperatures above 300 °C, involves cleavage of molecules by transglycosylation, fission, and disproportionation reactions to provide a mixture of anhydro sugars and lower molecular weight volatile products. Oxidation of the combustible volatiles gives flaming combustion and oxidation of the reactive char gives glowing combustion - flameless form of combustion [3].

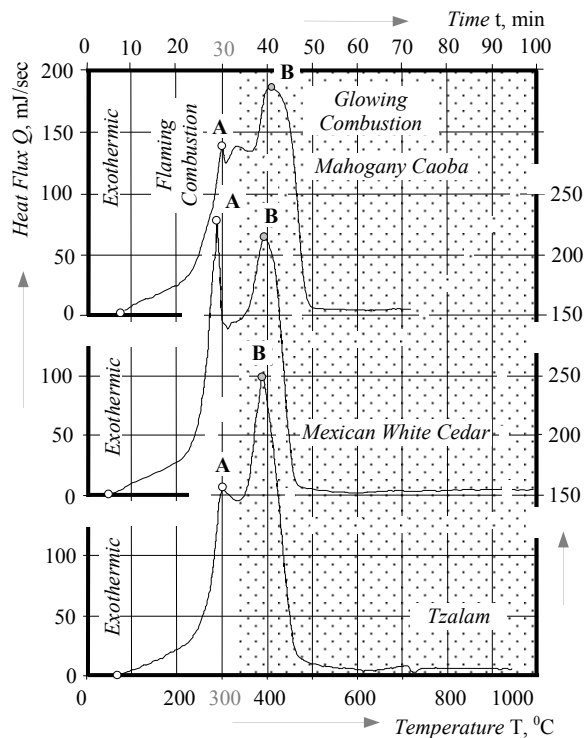


Fig. 2 Results of simultaneous thermal analysis (STA) - DSC-thermal spectra of three species of rainforest (Yucatán, Mexico) wood (heart) samples in air (linear heating with rate: 10 °C per minute; initial sample mass: 14.2 mg) - wood pyrolysis and combustion stages identification: peak *A* - flaming pyrolysis and combustion; *B* - glowing or smoldering pyrolysis and combustion

In the presence of a heat source, phosphorus flame retardants release phosphoric acid which causes the material to char and form a thick glassy layer δ of carbon. This carbonated char stops the decomposition (degradation) process (pyrolysis) and prevents the release of flammable gases, essentially cutting off fuel to the flame. It also provides a barrier between the material and the heat source and the oxygen from air. Flame retardants containing phosphorus interrupt the combustion process by promoting “charring” Fig. 1 [4].

A new thermal analysis approach to distinguish between the flaming and glowing combustion stage was discussed. This technique is based on the simultaneous thermogravimetric and differential scanning calorimetric analysis or on the mass losses of the sample and the heat evolved in flaming and glowing combustion, Fig. 2 and 3.

The enthalpy (H) is the preferred expression of system energy changes in many chemical and physical measurements, because it simplifies certain descriptions of energy transfer. Enthalpy change (ΔH) accounts for energy transferred to the environment at constant pressure through heating. The change ΔH is positive ($+\Delta H$) in endothermic reactions, and negative ($-\Delta H$) in heat-releasing exothermic processes.

For processes under constant pressure ($dp = 0$), ΔH is equal to the change in the internal energy of the system, plus the work that the system has done on its surroundings - this means that the change $\pm\Delta H$ under such conditions is the heat absorbed (or released) by the material sample through a chemical

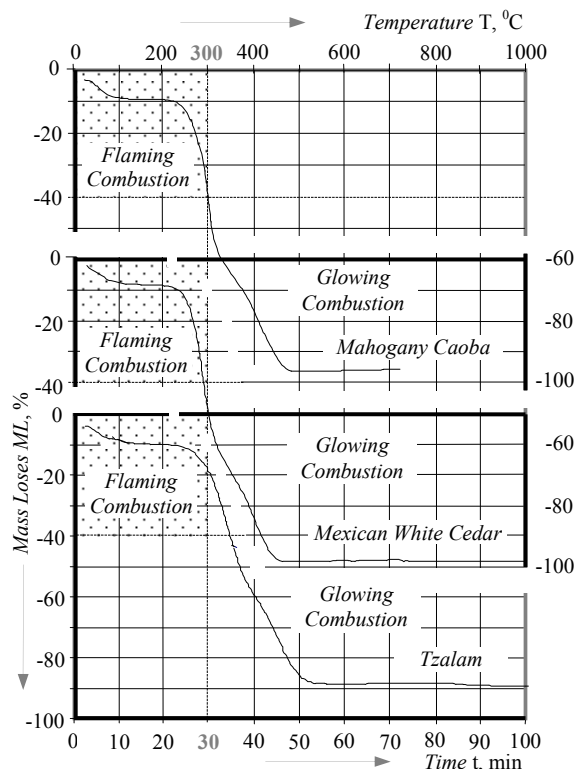


Fig. 3 Results of simultaneous thermal analysis (STA) - TGA-thermal spectra of three species of bare (heart) wood samples in air (linear heating with rate: 10 °C per minute; initial sample mass: 14.2 mg) - wood pyrolysis and combustion stages identification: flaming pyrolysis and combustion, glowing or smoldering pyrolysis and combustion

reaction or by external heat transfer. The specific enthalpy change ($-\Delta h$) is defined as $-\Delta h = -\Delta H/m$ where m is the mass losses of wood sample.

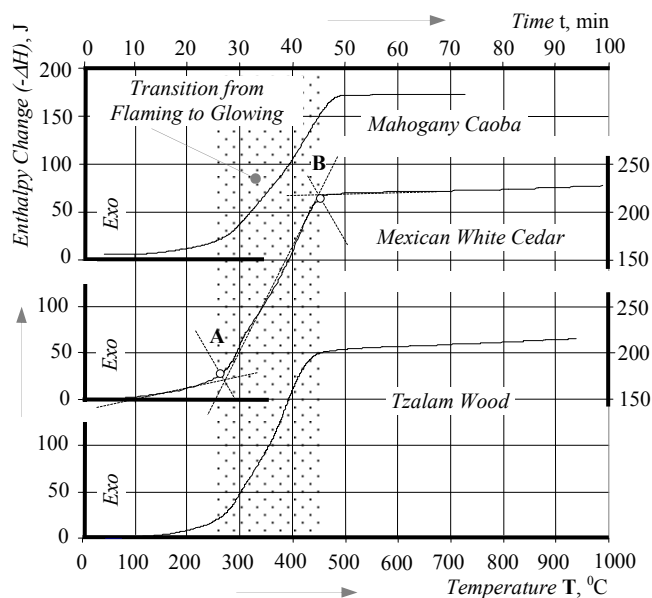


Fig. 4 Results of the data processing from STA (DSC-) analysis - enthalpy change ($-\Delta H$) as function of temperature or time (integral curve) of three species of rainforest heart wood samples: *AB* - transition from flaming to glowing in the case of White cedar pyrolysis and combustion

The SI unit for specific enthalpy change is joule per kilogram (J/kg).

STA-technique is an experimental technique which allows determining the specific enthalpy change of wood during thermal analysis (pyrolysis and combustion). The apparatus used for this study was a Perkin Elmer simultaneous TGA-DSC thermoanalyzer.

B. Thermal behavior criteria of wood

This paper describes a new approach to differentiate between flaming and glowing combustion based on flammability changes occurring in three species of rainforest wood under environmental conditions. Since the DSC was conducted at constant pressure, the heat flux (Q) curve, Fig. 2, can be used to calculate the enthalpy changes ($-\Delta H$) by integrating, Fig. 4.

This study has also established two new criteria to distinguish flaming from glowing combustion stage: an integral criterion - the specific (per unit mass) enthalpy change ($-\Delta h$), MJ/kg, Fig. 7, 8, 9 and 10, and a differential criterion - the specific (heat release rate per unit area and mass of wood sample) heat flux (q), kJ/(kg sec) Fig. 5.

The specific enthalpy ($-\Delta h_f$) corresponding to the flaming combustion peak (OAB) can be assessed from the area of triangle ΔOAD , in MJ/kg: *Caoba mahogany* - 5.622, Fig. 6; *Mexican white cedar* - 6.325; *Tzalam* - 4.784.

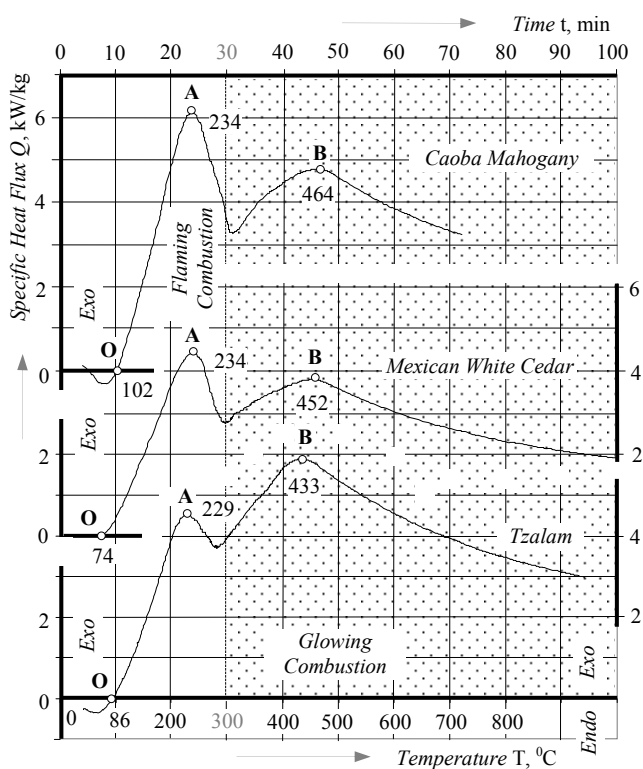


Fig. 5 New approach and criterion of thermal behavior established on simultaneous thermal analysis (STA) - specific heat flux thermal spectra q (per unit area and mass losses) of three species of bare wood samples: peak A - flaming pyrolysis and combustion; B - glowing or smoldering pyrolysis and combustion

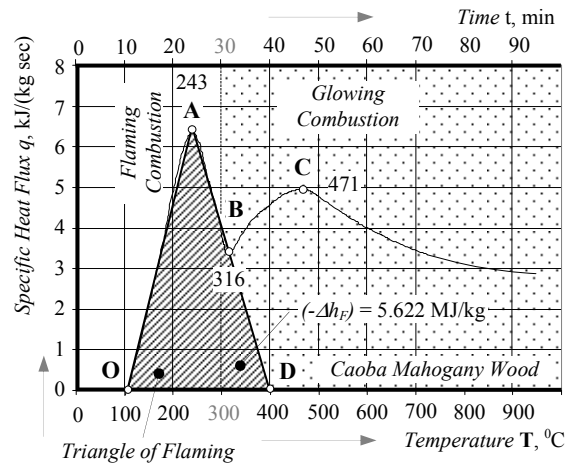


Fig. 6 Definition and assessment of specific enthalpy change ($-\Delta h_f = 5.622$ MJ/kg) of flame pyrolysis and combustion of Mexican white cedar (*Cupressus Lusitanica*) heart wood sample by the triangle of flaming (ΔADO)

The transition area of flaming to glowing pyrolysis and combustion stage (MN) was defined and determined by a temperature interval: *Caoba mahogany* from 220 to 342 °C, Fig. 8; *Mexican white cedar* - from 218 to 314 °C; *Tzalam* - from 243 to 286 °C. The average specific enthalpy change ($-\Delta h_f$) of this transition is, in MJ/kg: *Caoba mahogany* - 7.818; *Mexican white cedar* - 8.372; *Tzalam* - 6.387.

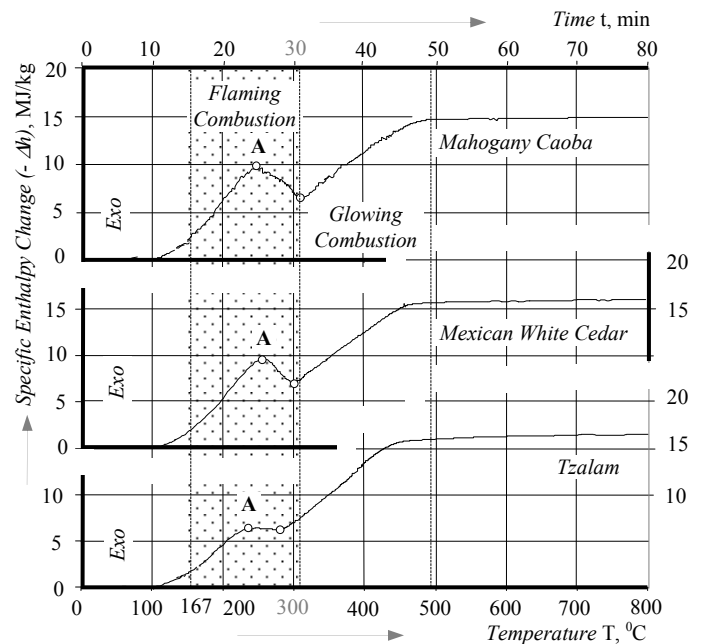


Fig. 7 New approach and criterion of thermal behavior established on simultaneous thermal analysis (STA) - specific (per unit area and mass losses) enthalpy change ($-\Delta h$) of three species of rainforest heart wood samples as function of temperature and time

III. RESULTS AND DISCUSSION

Tzalam has a very high mean density compared with the two other species, in kg/m^3 : *Tzalam* - 780; *Caoba mahogany* - 650; *Mexican white cedar* - 470. The high density of the

Tzalam wood indicates that the cell walls are thick. The size of the pores is then reduced, and the diffusion of the steam diminishes consequently. The first stage of the *Tzalam* degradation seems to be due to the superposition of the beginning of the lignin decomposition, the evaporation of the constitution water and the xylan degradation of the hemicellulose. The different temperature ranges of transition area, Fig. 5, 7 and 8, can be explained by the distinct percentages of the mass of the wall constituents and the physical structures of the wood for each species.

The range of mass losses belonging to transition area, Fig. 10, is relatively large, but it is restricted from 40 to 50 %. The transition from flaming to glowing combustion takes place at about 8 MJ/kg.

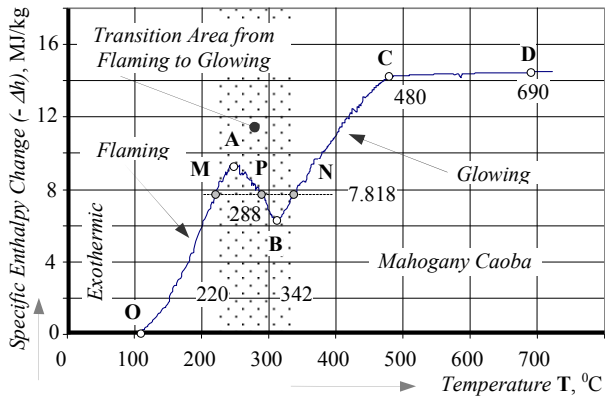


Fig. 8 Definition of a transition area from flaming to glowing pyrolysis and combustion (*MN*) by the amendment of specific enthalpy change ($-\Delta h$) in the temperature interval from 220 to 342 °C on the example of Mahogany caoba (*Swietenia macrophylla*) heart wood sample: the average specific enthalpy change of the transition is 7.818 MJ/kg

The two mechanisms of wood combustion - flaming and glowing, can be illustrated by a specific temperature range of enthalpy variation, and accordingly represented by linear models, Fig. 9.

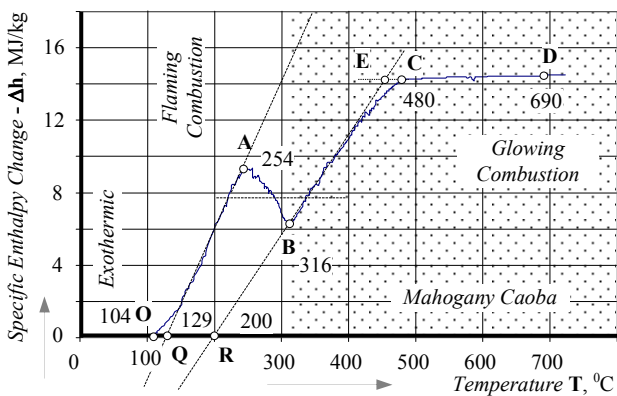


Fig. 9 Two mechanisms of pyrolysis and combustion illustrated by the specific enthalpy change ($-\Delta h$) as function of the temperature: linear model of flaming (*QA*) - $-\Delta h = 74.1758 T - 9568.6813$; and linear model of glowing (*BE*) - $-\Delta h = 55.7766 T - 11155.3268$, on the example of Mahogany caoba (*Swietenia macrophylla*) heart wood sample

The application of simultaneous thermal analysis (*TGA* and *DSC*) allows evaluating the wood samples decomposition

(pyrolysis) under the heat influence by setting pyrolysis stages, temperature ranges and wood characteristic temperature peaks Fig. 5, 6, 7, 8 and 9.

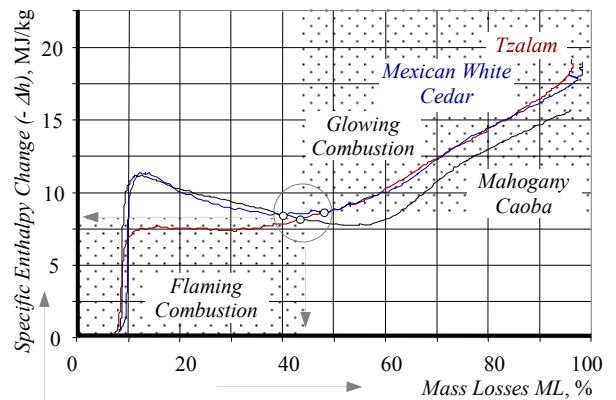


Fig. 10 Specific enthalpy change ($-\Delta h$) as function of mass losses (*ML*) for three species of rainforest heart wood - available flaming and glowing pyrolysis and combustion stages

Then the degradation process of the three woods can be summarized. After the departure of the free water, the degradation of the main constituents of woods begins at about 100 °C and presents two stages in general. The xylan of the hemicellulose degrades firstly and the products of its decomposition may activate the degradation of one part of the lignin - at the temperatures above 250 °C the larger part of the wood sample is broken down into volatile products.

The degradation consists of two stages: the observed first peak on the specific heat flux thermograms between 200 and 250 °C is due to the superposition of the lignin and the hemicellulose degradations. For the temperatures higher than 300°C, the deterioration of the cellulose overlaps with the decomposition of the lignin and stabilizes over 320 °C - there is a second peak between 433 and 464 °C Fig. 5.

IV. CONCLUSION AND PERSPECTIVES

Simultaneous thermal analysis approach based on two criteria - specific enthalpy change ($-\Delta h$) and specific heat flux (*q*) can distinguish generally in a good way the flaming and glowing pyrolysis and combustion stages.

REFERENCES

- [1] P. Le Parlouër, "Simultaneous TG-DSC: a new technique for thermal analysis", *Thermochimica Acta*, vol. 121, 1987, pp. 307+322.
- [2] J. Redfern, "Polymer studies by simultaneous thermal analysis techniques", *Polymer International*, vol. 26, 1991, issue 1, pp. 51+58.
- [3] 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.
- [4] 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.
- [5] 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.