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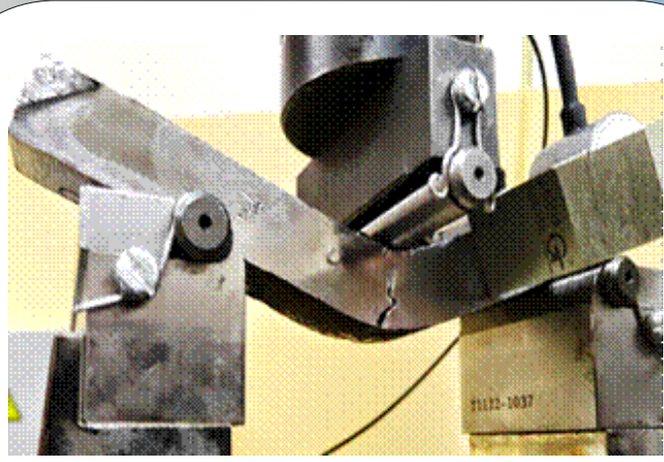

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C O N T E N T S

SIMULTANEOUS THERMAL ANALYSIS ON PLASMA-AIDED CAPILLARY IMPREGNATION FOR EUROPEAN WHITE PINE FLAME RETARDATION IMPROVEMENT

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Abstract: *Simultaneous Thermal Analysis (STA, TGA and DSC) unifies the simultaneous application of thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) to one and the same wood sample in a single instrument, under perfectly identical conditions - same atmosphere, gas flow rate, pressure, heating rate, thermal contact, etc. New thermal analysis approaches for integral distinguishing between the flaming and glowing combustion of wood were discussed. The results obtained by STA were used in a new way in order to reveal the influence of plasma-aided capillary impregnation on thermal decomposition and glowing of wood controlled by oxygen and nitrogen containing flame retardant. New integral criterion of thermal behavior and decomposition such as specific enthalpy change has been developed by investigating samples of European White Pine (Pinus Sylvestris, Bulgaria) wood. This study has been developed also as part of a large investigation on plasma-chemically activated (polarized, functionalized) wood surface and its capillary impregnation with nitrogen- and phosphor flame retardant containing water solution.*

Keywords: DIELECTRIC BARRIER DISCHARGE, FLAME RETARDANT, FLAME RETARDATION, PLASMA-AIDED CAPILLARY IMPREGNATION, SIMULTANEOUS (TGA÷DSC) THERMAL ANALYSIS, PINUS SYLVESTRIS WOOD.

1. Introduction

In order to enhance the utilization of wood and its inherent properties, a long range research and development, called *Non-equilibrium Air Plasma Surface Activation of Wood and Cellulosic Products*, has been formulated (*P. Dineff*, 2004). This concept was focused on achieving a basic understanding of wood and those surface properties that are not fully exploited in conventional wood manufacturing systems to date. The strategy was to activate these inherent properties and thus add economic value to completed wood products. In order to achieve this, a better knowledge of the fundamental behavior of wood surface was required, together with new applied plasma-aided processing technology and the development of necessary plasma-manufacturing systems, [2÷5].

The plasma-aided flame retardation of wood (*P. Dineff*, 2005), cellulosic and wooden products has been developed as a result of a new *plasma-aided process of capillary impregnation* that comprises: *i* - surface plasma pre-treatment for alteration of chemical, electrical (ionic) and capillary activities of wood surface as well as its surface energy; *ii* - modification of ionic activity and surface tension of flame retardant (*FR*) containing water solution by non-organic (anionic) and siloxane surfactants (*surface-active agents*), and in general for improvement of the characteristics of capillary impregnation process such as solution spreading and wicking speed, as well as the amount of the adsorbed flame retardant. In this way, the plasma pre-treatment of wood improves the flame retardation of wood, [1].

Simultaneous Thermal Analysis (*STA*, *TGA* and *DSC*) unifies the application of *thermal gravimetric analysis* (*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* (*-Δh*), kJ/kg, and *specific heat flux* (*q*), kW/kg or kJ/(kg sec), have been developed. This analysis distinguishes in a good way the flaming and glowing (or charing) pyrolysis and combustion stages, [2÷5].

The application of *STA* allows evaluating the wood pyrolysis under heat influence by setting pyrolysis stage, temperature ranges and characteristic temperature peaks. Thermal analysis helps define and illustrate the impact of the used surfactants on *flame retardancy of wood*. The influence of surfactants on the flame pyrolysis and combustion resistivity refers to some of the unique behavior of wood, [2, 3 and 4].

Wood samples from *European White Pine* (*Pinus Sylvestris*, Bulgaria) wood have been used in this study, since it represents an economic interest as a basic structural building material used in Bulgaria. Moreover, an industrial approbation of plasma-aided flame retardation of European white pine was implemented effectively in the period 2005÷2010, [1], within a project funded by the National Science Fund at the Ministry of Education and Science of Bulgaria.

The objective of this paper was to study the effect of air plasma surface pre-treatment on *European White Pine* (*EWP*) aiming to improve the wood flame retardation by simultaneous thermal analysis.

2. Experimental Investigation

An original method and technological plasma system (plasma device and applicators) have been created to produce cold non-equilibrium air plasma through *dielectric barrier discharge* (*DBD*) at atmospheric pressure and room temperature and out of the production line, [5].

Anionic phosphate surfactant ("*Aniticrystallin A*", Chimatech, Ltd., Bulgaria) in quantity of 5 vol. %, and *siloxane surfactant* (super spreader: Y-17113, *Momentive Performance Materials* GmbH & Co. KG, Germany) in quantity of 0.1 vol. % have been used to control the ion activity of the *FR*-impregnation solution and its surface tension. The used anionic surfactants (*-A5, or -5*), alone and in combination with siloxane surfactant (*-A5-S or -5S*), lowers the surface tension of the impregnating solution and thus allowing it to wet and penetrate solids. Sessile drop technique (CRÜSS Drop shape analyzer DA 30) was used for these measurements, [2÷5].

The use of both surfactants in the *FR*-water solution leads to significant reduction of surface tension (less than 10 mN/m) and good wetting and chemical affinity. Regardless of the *open time* between plasma pre-treatment and capillary impregnation - two or twenty-four hours, the introduction of surfactants provides good wetting and wicking, and good chemical affinity, [2÷5].

The studied flame retardancy of white pine wood was based on both: plasma-chemical pre-treatment of the wooden surface to increase its surface energy, and *PhN-FR*-solution modification by an ionic surfactant and combination of different surfactants. It was expected that the increased wood capillary activity, *FR*-solution sorption speed and capacity, and a better quality *FR*-coating, would allow good enough flame retardancy on porous wood surface, [5].

3. Results and Discussion

Based on previous experience in the field of plasma-aided capillary impregnation 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 atmospheric dielectric barrier air discharge (*ADBD*) at industrial (50 Hz) and increased frequency (30 kHz), and at 15 kV (*RMS*) or 25 kV (*PV*) voltage, [2 ÷ 4].

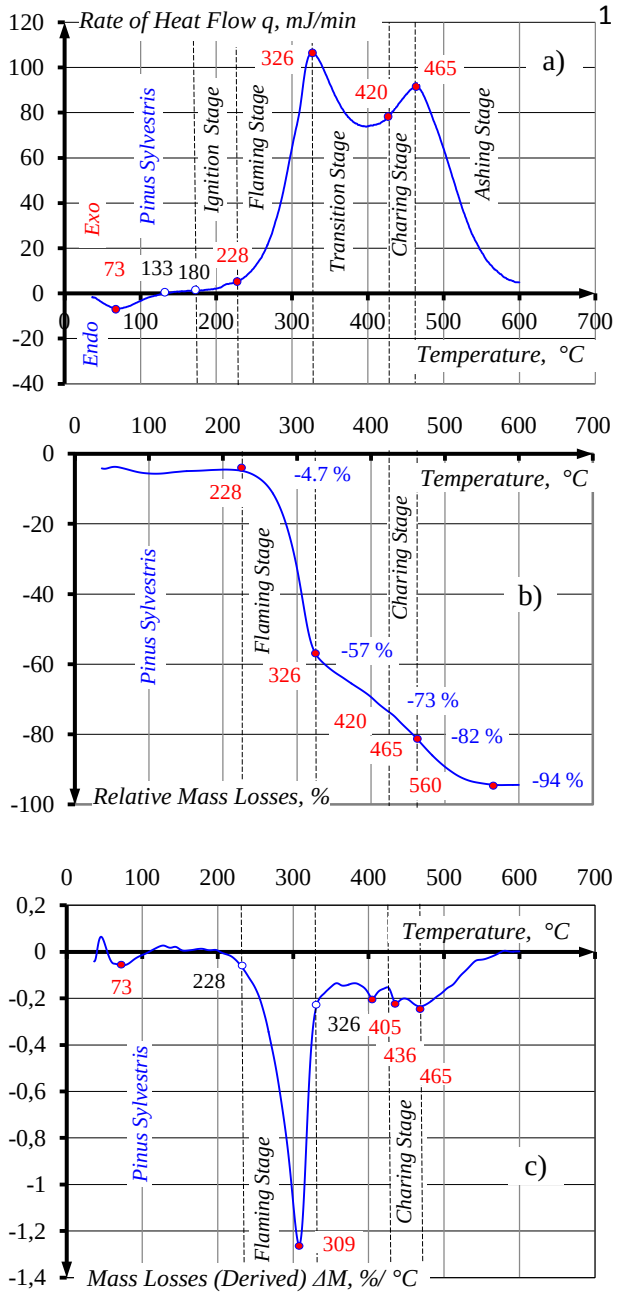

Fig. 1. *Thermal analysis - DTA, TGA and DSC-spectra of bare White pine wood (Pinus Sylvestrus, Bulgaria) samples in air (heating rate: 10 ^{0}C per minute): wood pyrolysis stages identification - Ignition, Flaming, Transition flaming to charing, Charing, and Ashing stages by:* ***a*** *- DSC-spectrum;* ***b*** *- TGA-spectrum;* ***c*** *- DTA-spectrum.*

Some experimental results considered using a new criterion of thermal behavior (pyrolysis and combustion), [4], *specific enthalpy* (*-Δh*) – per unit mass losses, are presented here as a result of both non-equilibrium air plasma pre-treatment at atmospheric pressure and room temperature and capillary impregnation by a new phosphor and nitrogen containing surfactant modified water solution monitored by simultaneous (synchronous) thermal analysis (*STA*, or *TGA* and *DSC*) of commonly used *thermal gravimetric analysis* (*TGA*) and *differential scanning calorimetry* (*DSC*).

There is a possible way to detect the influence of the anionic surfactant (*FR5*) or that of the combination of surfactants (*FR5S*) on wood flame retardancy by comparing the flaming resistivity of the modified by surfactants containing solution (*FR5* and *FR5S*) wood with that of the surfactant-free or basic *FR*-solution (*FR*).

3.1. *Thermal analysis of bare wood*

The results from the thermal analysis – rate of heat flow, relative mass losses, and derived mass losses are presented on Fig. 1. Based on the results of synchronously recorded thermograms, Fig. 1a и 1b, the spectrum of specific enthalpy was built, which connects the lost mass from the wood sample with the heat released in the course of the study, Fig. 2.

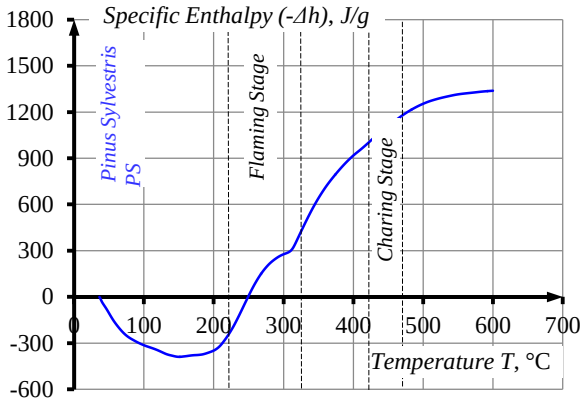

Fig. 2. *Criterion of wood pyrolysis and combustion behavior established by simultaneous thermal analysis (STA) of bare European white pine (Pinus Sylvestris, Bulgaria) sample - specific enthalpy (-Δh) spectra (per unit mass losses).*

The typical maximums and stages of ignition and combustion for White pine wood are presented on Fig. 1: ignition stage; flaming stage including the transition to self-sustaining flaming combustion (burning) and pirolysis; transition stage from flaming to charing; and ashing stage. The flaming stage ends at 326 ^{0}C, the wood sample has already lost 57 % from its mass. It can be assumed that the combustion process is completed at 560 ^{0}C, where the wood sample has lost 94 % from its mass, Fig. 1a and b.

The derivatogram, Fig. 1c, shows a very well-formed peak at 309 ^{0}C, which corresponds to the flaming stage (268÷326 ^{0}C) and characterizes the processes of wood pirolysis and combustion.

The hypothesis that connects the mass losses directly with the released heat, reveals three typical stages of thermal behavior: *the first* one is the stage of heat absorption and mass losses (to about 249 ^{0}C); *the second* (to 310 ^{0}C) and *the third* – stages of more intense heat release and corresponding mass losses, Fig. 2.

Thus at the end of the second stage the specific enthalpy (*-Δh*) reaches 300 J/g, while at the end of the third stage it exceeds this value many times (1340 J/g).

3.2. *Plasma-aided flame retardancy*

Considered was the thermal behavior of wood sample (*PT*) resulting from the plasma-aided impregnation with the base *FR*-solution after *DBD*-treatment at 50 Hz, Fig. 3. The consideration is carried out in relation to two possible options of flame retardation – with the base *FR*-water solution (*FR*) and with a modified by anionic surfactant base solution (*FR5*). It's only natural to compare all of this as change in wood thermal behavior with the bare wood, while the impregnation is carried out with the same amount of *FR*-solution for all investigated wood samples.

The wood sample *PT*, resulting from the plasma-aided capillary impregnation, shows the highest resistance to combustion in the three main stages of combustion and pirolysis – flaming, transition from flaming to charing, and charing, Fig. 3.

The minimum mass loss, Fig. 3b, gives significant advantage of this approach: at the end of the flaming stage the wood sample loses 38 % of its weight (54.7 % for bare wood sample), and at 600 ^{0}C it has lost only 65% (95 % for bare wood sample), Fig. 3b.

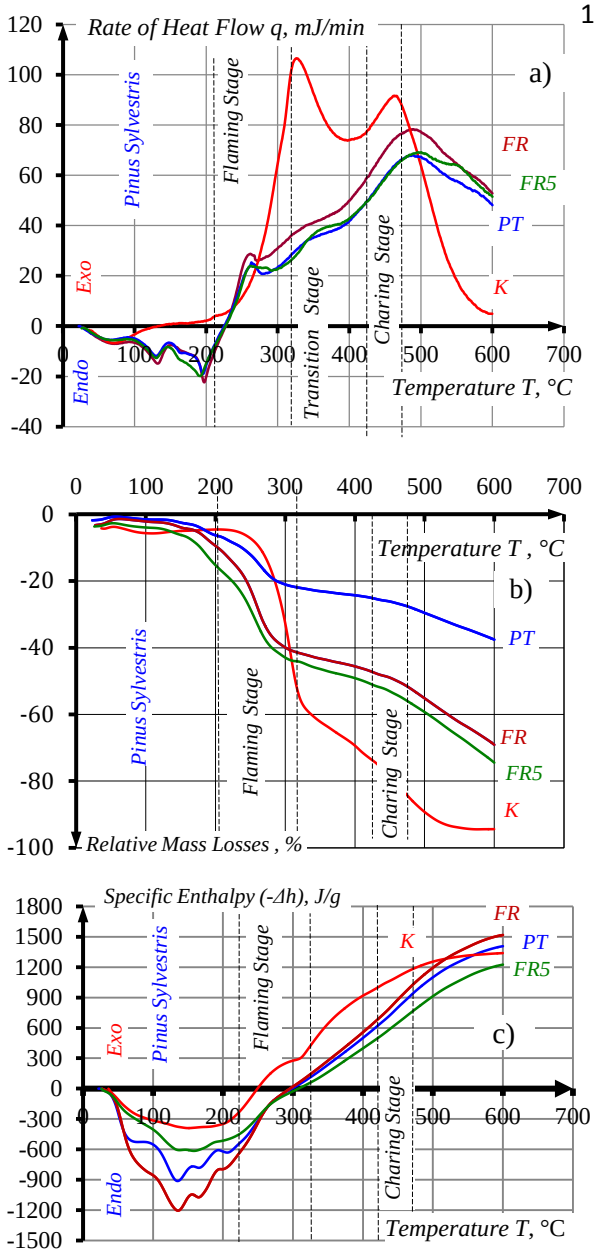

Fig. 3. *Criteria of wood pyrolysis and combustion behavior of European white pine (Pinus Sylvestris) bare wood sample (K); flame retarded wood sample (FR); plasma-aided flame retarded sample (PT); FR-sample with FR-solution modified (5 vol. %) with anionic surfactant (FR5) established by simultaneous thermal analysis (STA):* ***a*** *– DSC-spectra;* ***b*** *– TGA-spectra;* ***c*** *– STA (DSC÷TGA)-spectra.*

However one should take into account that the perceived advantage of plasma-aided flame retardancy can be used practically only in the implementation of the technology „*in line*“,where the impregnation process follows immediately after the plasma-chemical surface pre-treatment.

3.2. Surfactant-aided flame retardancy

The use of surfactants underlies the developed by us technological approach towards providing better pyrolysis and combustion resistivity of wood and wooden products under conditions of “*in situ*” applications – outside the production line. The selected species and combination of surfactants, as well as the concentrations used are based on our own preliminary studies, [1, 2, 3, and 4]. The results from the conducted study reveal the impact of the used surfactants, but it can not be said definitively that they improve the pyrolysis and combustion resistivity of European white pine wood, Fig.4.

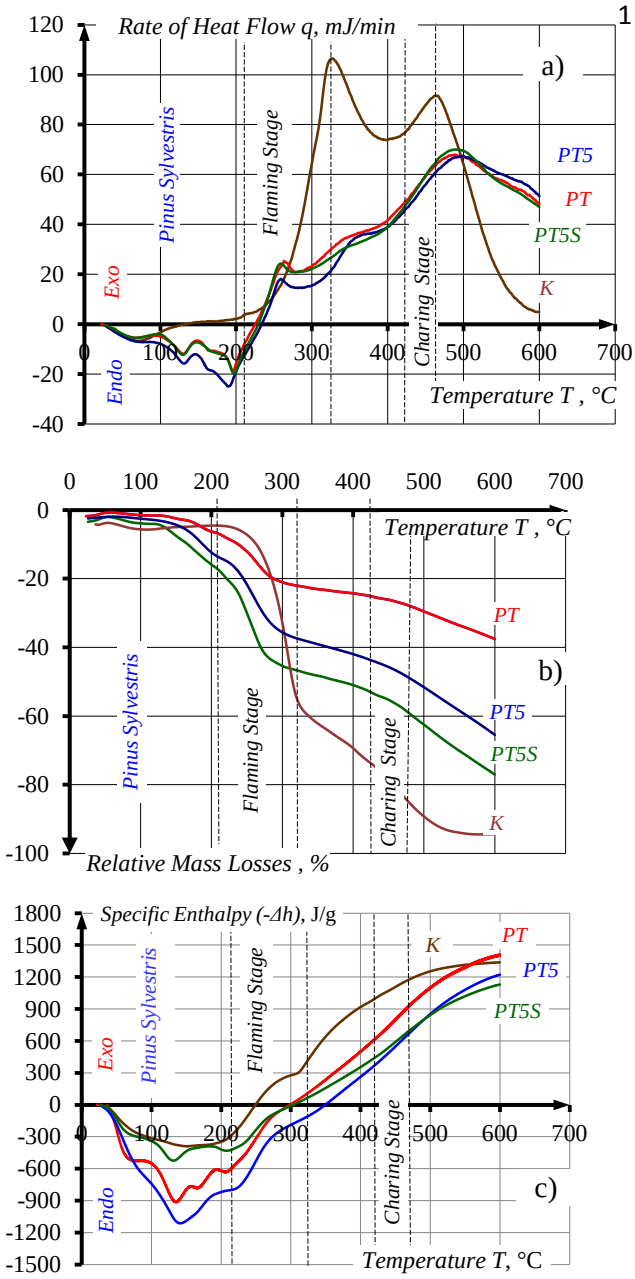

Fig. 4. *Criteria of wood pyrolysis and combustion behavior of White pine bare wood (Pinus Sylvestris) sample (K); plasma-aided flame retarded sample (PT); PT-sample with FR-solution modified (5 vol. %) with anionic surfactant (PT5); PT-sample with FR-solution modified with anionic surfactant and siloxane surfactant (0.1 %) (PT5S) established by simultaneous thermal analysis (STA):* ***a*** *– DSC-spectra;* ***b*** *– TGA-spectra;* ***c*** *– STA (DSC÷TGA)-spectra.*

Using surfactants significantly increases mass loss compared to the obtained by plasma-aided flame retardancy, but nevertheless the positive effect on bare wood sample remains, Fig. 4.

However we should not forget the initial conditions of this study – it was held with the same amount of *FR*- additive. The use of surfactants permits the introduction of a much larger (more than three times) quantity of the active *FR*- substance. For each particular case of plasma aided impregnation it can be found the right surfactant and an effective amount of it.

3.2. High frequency plasma-aided flame retardancy

Additional comparative study was performed at two different frequency of plasma (*DBD*-) chemical surface pre-treatment – 50 Hz and 30 kHz

The results of the study, Fig.5, illustrate the advantage of the technology used at industrial frequency (50 Hz). This advantage, however, is measured by a few more percent (up to 10 %), which has no essential importance from a technological point of view.

Conclusion

The application of *STA* (*TGA* and *DSC*) allows evaluating the wood pyrolysis under heat influence by setting pyrolysis stage, temperature ranges and characteristic temperature peaks. Thermal analysis helps define and illustrate the impact of the used surfactants on *flame retardancy of wood*.

The study results illustrate the potential of the plasma-aided flame retardancy technology to increase the combustion and pyrolysis resistivity of *European white pine*. The use of plasma aided finishing without surfactants can be apply effectively only at zero open time or when the impregnation process follows immediately the plasma-surface treatment, i.e. in production line ("*in line*").

The using of some surfactants limits though slightly the effectiveness of plasma-aided flame retardancy. This fact has been established at the same amount of active *FR*-additive. The surfactant application however allows the introduction of more than three times larger amount of the solution and the active substance. Thus, the efficiency of surfactant application was determined by the ability to use larger amounts of the *FR*-additives.

References

[1] Dineff P., L. Kostova. *Method for Plasma Chemical Surface Modification*. H05H 1/24, Bulgarian Patent Publication No.: BG 66022 B1; International Patent Publication No.: WO Patent 2006/133524 A2; Priority Date: 14.06.2005 (BG No. 109189), Publication Date: 21.12. **2006**.

[2] Ivanov, I., D. Gospodinova, P. Dineff, L. Veleva, *Thermal Behavior Criteria of Flame Retarded Wood Obtained by Simultaneous Thermal Analysis: I. New Thermal Behavior Criteria of Wood*, 18th International Symposium on Electrical Apparatus and Technologies, SIELA 2014, 29÷31 May, **2014,** Bourgas, Proceedings, pp. 81÷84, ISBN 978-1-4799-5816-0, IEEE Catalog Number CFP1428Z-PRT; INSPEC Accession Number: 14525476, DOI: 10.1109/SIELA.2014.6871862.

[3] Ivanov, I., D. Gospodinova, P. Dineff, L. Veleva, *Thermal Behavior Criteria of Flame Retarded Wood Obtained by Simultaneous Thermal Analysis: II. Flame Retardancy Criteria of Wood*, 18th International Symposium on Electrical Apparatus and Technologies, SIELA 2014, 29-31 May, **2014,** Bourgas, Proceedings, pp. 85÷88, ISBN 978-1-4799-5816-0, IEEE Catalog Number CFP1428Z-PRT; INSPEC Accession Number: 14516377, DOI: 10.1109/SIELA.2014.6871863.

[4] Dineff P., I. Ivanov, D. Gospodinova, L. Veleva, *Thermal Behavior Criteria of Flame Retarded Wood Obtained by Simultaneous Thermal Analysis: III. Thermal Behavior Criteria of Plasma-Aided Flame Retardancy*, 18th International Symposium on Electrical Apparatus and Technologies, SIELA 2014, 29-31 May, **2014,** Bourgas, Proceedings, pp. 33 - 36, ISBN 978-1-4799-5816-0, IEEE Catalog Number CFP1428Z-PRT; INSPEC Accession Number: 14516381, DOI: 10.1109/SIELA. 2014.6871850.

[5] Ivanov, I., D. Gospodinova, P. Dineff, and L. Veleva (Muleshkova). *Simultaneous Thermal Analysis Investigation on Plasma-Aided Flame Retardancy of Wood*. International virtual journal "Machines, Technologies, Materials", **2014**, Year VIII, Issue 10, pp. 9÷12, ISSN 1313-0226. XI. INTERNATIONAL CONGRESS "MACHINES, TECHNOLOGIES MATERIALS", **2014**, September 17÷20, Varna, Bulgaria: paper 44.

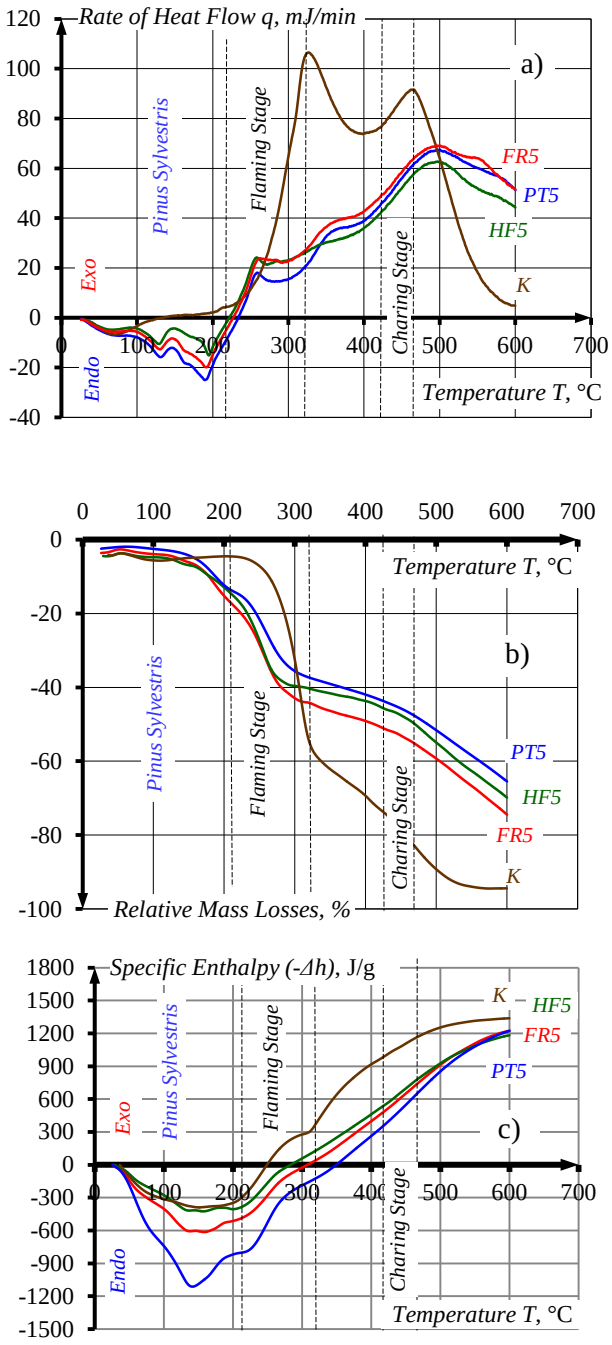

Fig. 5. *Criteria of wood pyrolysis and combustion behavior of White pine bare wood (Pinus Sylvestris) sample (K); flame retarded wood sample with FR-solution modified (5 vol. %) with anionic surfactant (FR5); plasma-aided (50 Hz; 15 kV RMS) flame retarded sample (PT5) with FR-solution modified with anionic surfactant (5 vol. %); plasma-aided (30 kHz; 20 kV RMS) flame retarded sample with FR-solution modified (5 vol. %) with anionic surfactant (HF5) established by simultaneous thermal analysis (STA):* ***a*** *– DSC-spectra;* ***b*** *– TGA-spectra;* ***c*** *– STA (DSC÷TGA)-spectra.*