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NEW ATTEMPT AT PLASMA AIDED FLAME RETARDATION IN WOOD AND CELLULOSIC FIBROUS MATERIALS

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Introduction

The plasma aided flame retardation has been conceived and developed as a result of a new plasma aided process: the plasma aided capillary impregnation of water solution, which evolved as a fire protection process for wood, wooden products and cellulosic fibrous materials using original phosphorous and nitrogen flame retardants (*PhNFR*), manufactured by *Interiorprotect, Ltd.* (*Sofia, Bulgaria*) under the trade name of *CSE-96*. The plasma-chemical surface pre-treatment of wood modifies the chemical activity of its surface as well as the capillary activity of wood and improves such technological characteristics of the capillary impregnation process as the penetration depth, speed of solution spreading and adsorption, and specific quantity of adsorbed solution per unit of area. This allows using the plasma aided retardation as a finishing process and applying it in situ, [1, and 2].

This study was developed as part of an investigation of the thermal degradation analysis of flame retarded wood (*FR* wood), wooden products, and cellulosic fibrous materials. The study was focused on well-known thermal methods of analysis of degradation of wood, cellulose, hemicellulose, and lignin.

The methods included thermogravimetric analysis (*TGA*), differential thermal analysis (*DTA*), and differential scanning calorimetry (*DSC*). These thermal methods were used for evaluation of the influence of *FR* and plasma *FR* wood treatment on pyrolysis. Thermal analyses gave basic information on the mechanism of pyrolysis and combustion as well as data on the effect of *FR* wood treatment and modification. However, the correlation between results of thermal analyses and real fires has not been established yet, [2].

Wood cell wall is thought to be a composite material made of cellulose microfibrils embedded in a water-reactive matrix of hemicellulose and lignin. The ability of the matrix to adsorb water is thus of critical importance in the water solution capillary impregnation of wood (*N. Barber* 1968; *I. Cave* 1972). It is known that machining and heat treatments reduce wood hygroscopicity and chemical activity by modifying this water-reactive matrix (*E. Obataya* et al. 2000; *E. Obataya* and *B. Tomita* 2002) in different ways. Cold plasma pre-treatment redresses the wood surface balance, chemical and capillary activities, and as result of all changes increases the impregnation ability of wood and wooden materials (*P. Dineff* and *D. Gospodinova* 2005), [1, 2].

A discussion of the general thermal degradation process for natural wood and FR wood is followed by use of this method to analyze the thermal degradation of various kinds of *FR* woods including plasma aided flame retarded wood.

Experimental

The plasma aided flame retardation process involves three tools which are used for exerting direct impact on the thermal degradation of flame retarded wood: *the first one* consists in impregnating natural pine wood (*Pinus sylvestis*) with a 30-percent water solution of *PhNFR* (*CSE-96*) – sample *CSE*; *the second one* consists in adding 5 vol. % of anionic surfactant (AS5) to the impregnating solution *CSE-96* – sample *AS5*; *the third one* consists in performing cold plasma surface pre-treatment for 60 s in the plasma of dielectric barrier discharge (10 kHz) burning in air at atmospheric

pressure and room temperature – sample *HF*. The thermal degradation of all RF wood samples is compared with the basic sample made of natural pine wood (*Pinus sylvestris*). The thermal destruction of the *PhNFR* used, which contains about 13.5 mass % (as P_2O_5) is investigated separately.

Experimental conditions for all runs were as follows: thermogravimetric (*TG*), derivative thermogravimetric (*DTG*), and differential calorimetric (*DSC*) analyses were completed by *Perkin-Elmer*'s equipment in air; the heating rate was 10 ^{0}C/min and a heating range from 26 ÷36 ^{0}C to 600 ^{0}C was used; sample size usually was about 3.0 mg. All runs were done at least twice.

Results and Discussion

The thermal destruction of *PhNFR* starts intensively with a mass loss at about 143 ^{0}C (2 mass %) and rapidly attains its maximum at 190 ^{0}C (*DTG*), whereas in the range 26÷ 232 ^{0}C, i. e. before the flash point of 268.6 ^{0}C, its mass decreases with 30 mass %. This process is conducted with active heat absorption up to 356.5 ^{0}C, the general endothermic effect being 1236.8 J/g J/g. The exothermic effect from the destruction of *FR* after this temperature remains about two times lower, namely 528.0J/g, Fig. 1.

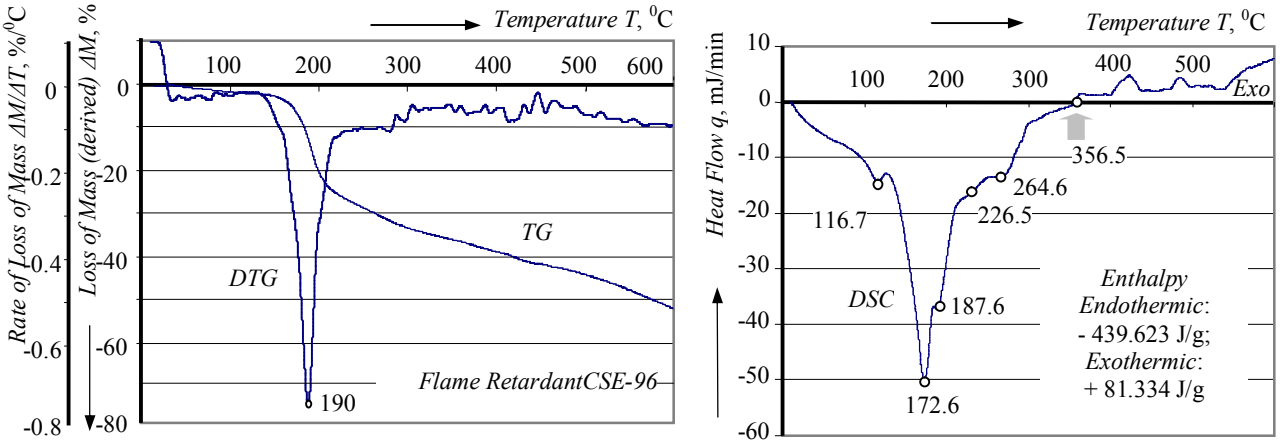

Fig. 1. *TG/DTG* and *DSC* - thermograms of phosphor and nitrogen containing flame retardant (*PhNFR*).

The thermograms from the thermogravimetric (*TGA*) and differential thermal analysis (*DTA*) (a), and differential scanning calorimetry (*DSC*) of all *FR*-wood materials investigated and those of a natural wood sample are represented in a common coordinate system, Fig. 2, the characteristic peaks and enthalpy for the characteristic areas of thermal degradation – the endothermic area of dehydratation, desorbtion of gases, and thermal destruction of *PhNFR*; and the exothermic areas corresponding to flaming and glowing with char formation - being given systematically in Table 1 and Table 2. A comparison between the two basic cases – plasma aided flame retarded wood (*HF*) и natural wood (*K*) – is represented separately, the characteristic points – ignition, burning, and flash points, the characteristic peaks of flaming *L* and glowing *N* – being shown on the curve of the basic relationship (*K*), Fig. 3. Combining the anionic active phosphor and nitrogen *FR*-water solution with cold plasma aided capillary impregnation creates new *FR*-wood products

Table 1

Peak	Pine sample (K)		CSE impregnation (CSE)		Surfactant aided impregnation (AS5)		Plasma aided impregnation (HF)	
	Temperature	Heat flow	Temperature	Heat flow	Temperature	Heat flow	Temperature	Heat flow
	^{0}C	mJ/min	^{0}C	mJ/min	^{0}C	mJ/min	^{0}C	mJ/min
A	76.7	- 6.710	74.7	- 7.026	70.1	- 5.638	68.2	- 4.788
B			132.2	-14.886	130.4	- 12.672	129.0	- 10.486
C			197.3	- 22.342	191.9	- 19.850	195.0	- 15.073
IP	132.5		227.38		227.0		221.9	
L			261.8	28.743	262.4	23.918	258.1	24.202
M	331.8	106.502	344.1	40.5010	369.2	39.500	349.0	30.2539
N	468,8	91.623	489.6	78.290	500.6	69.124	497.4	62.736

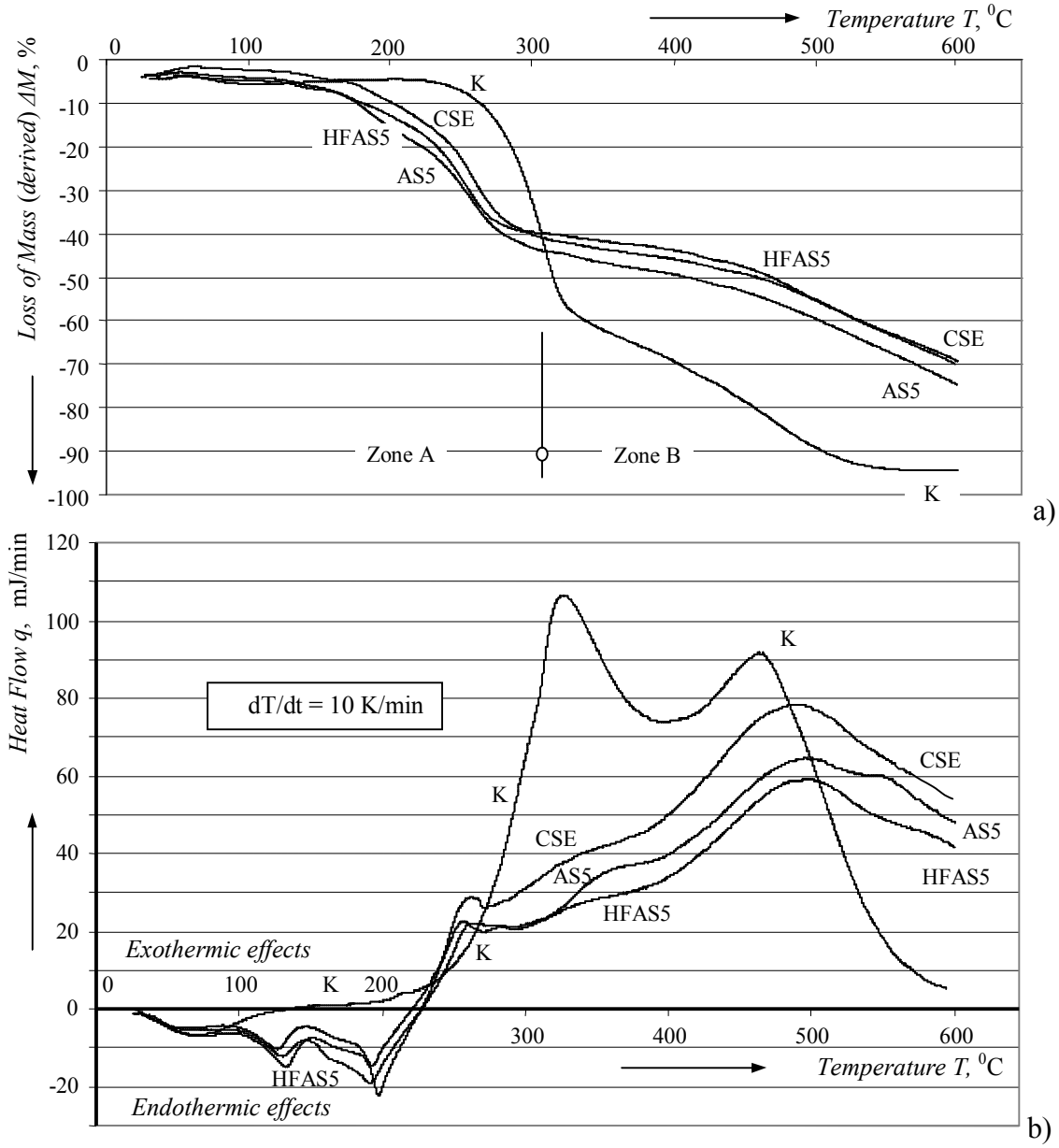

Fig. 2. TG/DTG and DSC thermograms of natural basic pine (*K*) wood (*Pinus sylvestris*) and different kind of FR wood: *CSE* – capillary impregnation with *CSE-96 FR*-solution; *AS5* - capillary impregnation with *CSE-96 FR*-solution improved by 5 vol. % of anionic surfactant "*Antikristalin*" (*Interiorportect*, Ltd., Bulgaria); *HF* – cold plasma aided capillary impregnation with anionic surfactant corrected *FR* water solution *CSE-96*.

with increased thermal degradation stability and reduced enthalpy of burning – 8.122 kJ/g versus 19.526 kJ/g (a reduction of 42 %), Table 2. In addition, the endothermic effect of *PhNFR* (peaks *B* and *C*) displaces substantially the ignition point from 132.5 ^{0}C to 221.9 ^{0}C, Fig. 3. The heat flow of peak *L* (flaming) remains very low (24.202 versus 106.502 mJ/min) and almost equal to the heat flow of the flash point of natural pine wood, Table 1.

Acknowledgement

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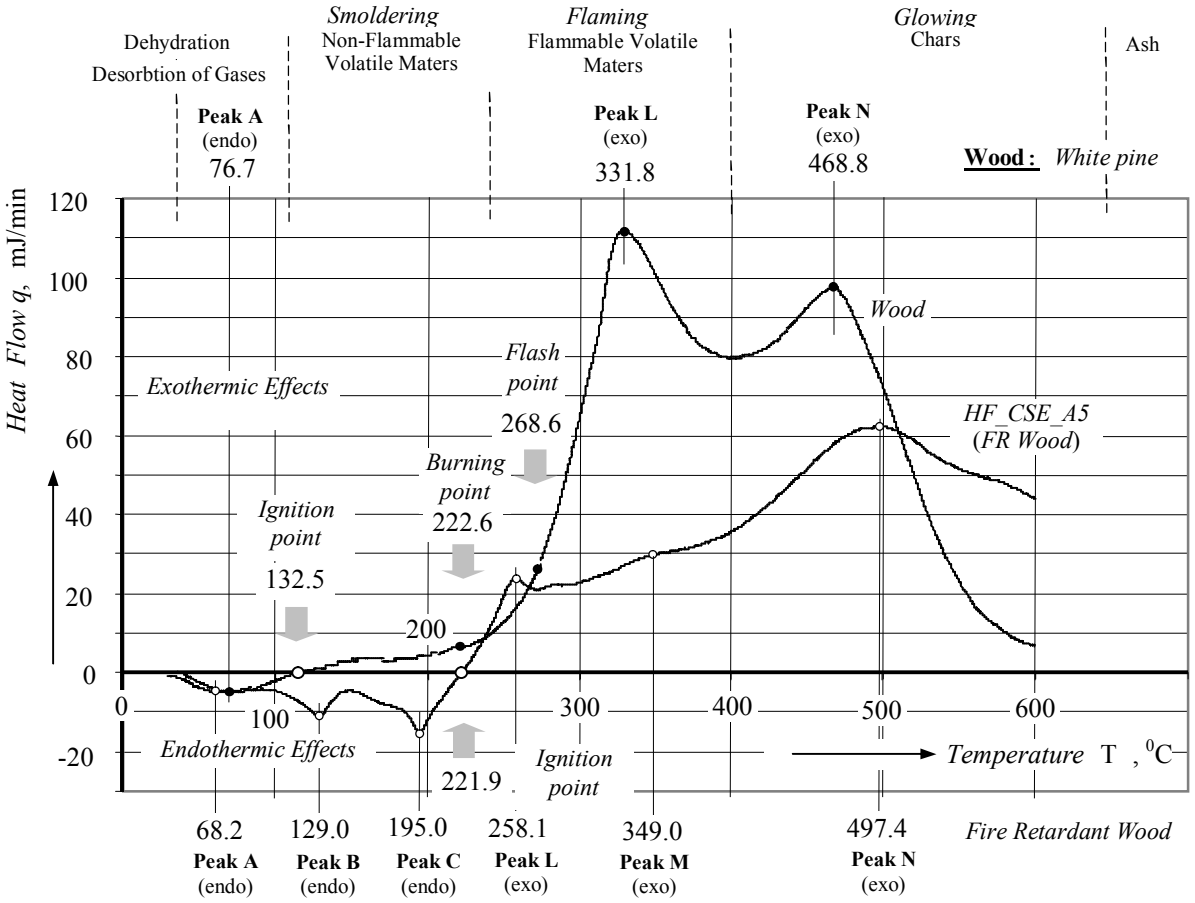

Fig. 3. Parallel between the *DSC* - thermograms of natural basic pine wood (*Pinus sylvestrum*) and *FR* pine wood treated by plasma aided impregnation

Table 2

Thermal effects	Pine sample (*K*)		CSE impregnation (*CSE*)		Surfactant aided impregnation (*AS5*)		Plasma aided impregnation (*HF*AS5)	
	Temperature ^{0}C	Enthalpy kJ/g	Temperature ^{0}C	Enthalpy kJ/g	Temperature ^{0}C	Enthalpy kJ/g	Temperature ^{0}C	Enthalpy kJ/g
Endo thermal	36.2 / 132.5	- 5.516	27.4 / 227.4	- 1.020	26.0 / 227.0	- 1.572	28.8 / 221.9	- 1.427
IP	132.5		227.4		227.0		221.9	
Exo thermal	132.5 / 331.8	1.709	227.4 / 277.0	0.840	227.0 / 297.1	1.022	221.9 / 269.2	0.645
Exo thermal	331.8 / 600.0	17.816	277.0 / 600.0	9.671	297.1 / 600.0	8.717	269.2 / 600.0	7.477
Exo thermal	132.5 / 600.0	19.525	277.0 / 600.0	10.512	227.0 / 600.0	9.739	221.9 / 600.0	8.122

References

[1] P. D. Dineff and L. G. Kostova, Method of Plasma-Chemical Modification. Patent WO2006/133524 A3.
[2] V. Repellin and R. Guyonnet, Evaluation of Heat-Treated Wood Swelling by Differential Scanning Calorimetry in Relation to Chemical Composition, Holzforschung, Vol. 59, pp. 28÷34, 2005.