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Testing the retardancy effect of various inorganic chemicals on smoldering combustion of *Pinus halepensis* needles

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Abstract

The fire retarding performance of 28 different inorganic chemical substances was tested by measuring the relative particle fire hazard properties of *Pinus halepensis* needles treated with these chemicals. The tests were performed using a new method, based on a specifically designed apparatus for monitoring the forest species temperature, under precisely controlled temperature and static air atmosphere conditions. The relative ignition and smoldering combustion properties determined were: the ignition delay time, the combustion rate, the heat content and the mass residue of forest samples. The key elements for the effectiveness of fire retardants were the delay of ignition and the reduction of heat and combustion rate. The chemicals examined were: Cu, Fe, Al_2O_3, Fe_2O_3, $SiO_2{\cdot}H_2O$, $NaHCO_3$, KI, KBr, KCl, NaCl, $CaCO_3$, $MnSO_4{\cdot}5H_2O$, $CuSO_4{\cdot}5H_2O$, $MgCl_2{\cdot}6H_2O$, $Na_2B_4O_7{\cdot}10H_2O$, Na_2HPO_4, Na_2CO_3, Na_2SiO_3, $ZnSO_4{\cdot}7H_2O$, $Zn_3(PO_4)_2{\cdot}2H_2O$, NH_4Br, NH_4Cl, NH_4HCO_3, $(NH_4)_2CO_3$, $NH_4H_2PO_4$ (MAP), $(NH_4)_2SO_4$ (AS), $(NH_4)_2HPO_4$ (DAP) and a commercial retardant containing both DAP and AS. Among them the best performance was exhibited by ammoniac phosphates, followed by ammoniac sulfates and silica.

Keywords: Inorganic chemical retardants; *Pinus halepensis* needles; Relative particle foliar flammability; Smoldering combustion

1. Introduction

Wildfires burn thousands of hectares all over the word each year and fire retardant studies of forest species are very important to forest fire management.

The burning of forest fuels can be simplified by considering three consecutive steps. First is the heating step, followed by the pyrolysis, an endothermic phenomenon, which breaks down the forest matter into low molecular mass gases (volatiles), tars, carbonaceous char and mineral ash. The main chemical events during pyrolysis are often described in the literature [1–5].

The last step is the combustion which is an exothermic process. The combustion of volatiles is known as gas-phase combustion (or flame-combustion) and takes place if the volatiles–air mixture is of the right composition and the temperature ranges between 400 and 500 °C. The combustion of char, without a flame, is known as glowing or smoldering combustion. Smoldering combustion usually is distinguished from glowing combustion in that combustion of the volatile pyrolysis products is not essential to propagate smoldering, and it may proceed in materials (i.e. wood) that have not undergone prior conversion to char residue. This solid-phase combustion takes place around 200 °C, with two peaks in intensity reported at 360 and 520 °C, until only ash residue remains [1].

Ignition is the transition between the pyrolysis and combustion stage, and fire spreading can be considered as a series of ignitions. There are two types of ignition: the piloted, which occurs in the presence of an ignition source (i.e., spark or flame) and the unpiloted (or spontaneous) ignition. Spontaneous ignition occurs when the convective or radiative energy from a fire or other heated objects is not readily dissipated by the wood sample, leading normally to smoldering combustion. It should be pointed out that both heat transfer modes are important in forest fires. On calm days heat transfer to unburned fuel in advance of fire will be dominated by thermal radiation. With wind speed above 10 m s^{-1} the convection heat transfer begins to dominate [6].

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Fire retardants can be used to influence the above described burning process. Depending on their nature, fire retardants can act chemically and/or physically in the solid or gas phase. They interfere during a particular stage of the process, e.g. during heating, pyrolysis, ignition or flame spread.

Several theories have been proposed for the mechanism of fire retardancy [7]. These are: (1) Barrier theory (the retardant insulates the forest species preventing oxygen reaching the fuel); (2) Thermal theory (heat is absorbed by the retardants preventing forest fuel from igniting); (3) Non-combustible gases theory (the retardant is decomposed to non-flammable gases, i.e. H_2O); (4) Free radical trap theory (formation of free radicals which inhibit the chain propagation mechanism of combustion); (5) Increased char/reduced volatiles theory (the retardant lowers the temperature at which pyrolysis occurs, directing the degradation pathway towards more char production and fewer volatiles).

Fire retardants are classified as either long-term or short-term retardants (or suppressants). Long-term fire retardants are applied ahead of a wildfire front to reduce the rate of fire spread or the intensity. The chemical elements most responsible for retardancy are phosphorus, antimony, chlorine, bromine, boron, and nitrogen. In most cases the active ingredients of retardants for wildland fires are combinations of ammonium salts of sulfuric and phosphoric acids, such as ammonium sulfate (AS), monammonium phosphate (MAP), diammonium phosphate (DAP) and ammonium polyphosphate (APP). The above chemicals alter the thermal decomposition (pyrolysis) mechanism of forest species, usually by acid catalyzed dehydration reactions. Thus, promoting the formation of H_2O, CO_2 and char, at the expense of flammable gases, i.e. aldehydes [8,9]. However, the mechanism by which this happens depends on the particular fire retardant and the thermal–physical environment (i.e., temperature, relative humidity, wind, etc.).

It has been reported that ammonium phosphates are effective against both flaming and glowing combustion, while ammonium sulfates are effective primary against the flaming phase. The high effectiveness of ammonium phosphates (i.e., DAP is 1.5 times of order more efficient than AS) is attributed to the synergistic effects of nitrogen and phosphorus. This success of DAP, however, comes with a relative high cost [10].

The short-term retardants are used to extinguish the flaming and glowing phases of combustion by direct application on the burning fuel. Their effectiveness relies almost solely on their ability to retain moisture and absorb heat by cooling. Thus, they remain effective until the water has been removed from the fuel by evaporation. Typical examples of short-term retardants are the foams and the water enhancers (elastomers and gels) which improve the ability of water to cling to vertical and smooth surfaces.

It is generally accepted that fire retardants, which inhibit the combustion process by chemical action, are more effective than those which act by physical means. In many cases, however, the boundary between chemical and physical effects is so indistinct that it is difficult to evaluate their respective contributions. There is also a trend towards synergistic combinations of retardants which are effective in smaller concentrations [11].

The retardant effectiveness can be predicted by burning forest fuels treated with chemical formulations. The parameters usually studied are: the rate of weight loss, the energy release rate and the amount of residue after burning [8]. In most cases the key elements for effective fire performance modifications are to delay ignition and to reduce heat, combustion rate, smoke and gas production, at least during the early part of fire exposure [11].

A number of fire performance tests has been developed for the evaluation of fire retardants [1,12,13]. Blakely has developed a method for determining the effectiveness of retardants according to their ability to extinguish combustion recovery [14,15]. A primary test used in the United States Department of Agriculture (USDA) employs a 25-ft tunnel for measuring flame spread index (FSI), which is a measure of the overall rate of flame spreading in the direction of air flow, according to a standard method [16,17]. Moreover, the cone calorimeter is the most common used bench-scale apparatus for evaluating the flammability of untreated and treated wood products [17–19].

Various analytical methods have been applied to investigate the chemical mechanism of fire retardants such as gas chromatography–Fourier transformation infrared spectroscopy (GC–FTIR) [20], pyrolysis gas chromatography (Py-GC) [21], direct mass spectrometry (DI-MS) [22] and thermal analysis [23–26]. However, the small samples used and the rapid removal of pyrolysis or combustion products, can lead the above analytical methods to erroneous interpretations in terms of forest fuel flammability performance in actual situations. Therefore, the information provided by the analytical methods on pyrolysis and combustion mechanisms of forest species must be supported by other fire tests [27].

The main purpose of this work is to evaluate the fire extinguishing effectiveness of various chemicals (metals, metallic oxides and inorganic salts) using a new simple bench-scale laboratory apparatus constructed for this purpose. The method is based on comparing the relative flammability properties of pine needles (ignition delay time, combustion duration, heat release, mass residue, etc.) with those obtained after treatment the pine needles with the chemicals tested. In addition, this research may lead to a better understanding of the mechanisms of fire retardancy which will facilitate the development of new wildfire retardant products.

2. Experimental

2.1. Sampling data collection

The pine needles were mature, collected after a long drought period in order to avoid moisture effects. The collection site was the mountainside Kalopoula of Ymittos near Athens, located W–NW with dominated rock limestone, geographic coordinates 37°58′13″ N and 23°48′20″ E, height 487 m and average slope 70%. The date of collection was 26 August 2004. According to previous reports [28], the composition of a forest species depends on various factors: part of plant (bark, wood, leaves), plant age, type of soil, climate, etc. As a conse-

Table 1
Chemical additives used for treatment of *P. halepensis* needles

Metals	Oxides	Halides	Carbonates	Sulphates	Phosphates	Others
Fe	$SiO_2 \cdot H_2O$	NaCl	NH_4HCO_3	$(NH_4)_2SO_4$	$NH_4H_2PO_4$	Na_2SiO_3
Cu	Fe_2O_3	KCl	$(NH_4)_2CO_3$	$ZnSO_4 \cdot 7H_2O$	$(NH_4)_2HPO_4$	$Na_2B_4O_7 \cdot 10H_2O$
	Al_2O_3	KBr	$CaCO_3$	$MnSO_4 \cdot 5H_2O$	Na_2HPO_4	Commercial
		KI	Na_2CO_3	$CuSO_4 \cdot 5H_2O$	$Zn_3(PO_4)_2 \cdot 2H_2O$	
		NH_4Cl	$NaHCO_3$			
		NH_4Br				
		$MgCl_2 \cdot 6H_2O$				

quence, a special care was taken to ensure that the bulk samples collected were representative to the forest species examined [27].

2.2. Sample preparation

The collected pine needle samples were placed into firmly closed polyethylene bags, taken immediately to the laboratory and dried into a vacuum oven for 24 h under 10 Torr pressure and at a temperature of 60 °C.

The flammability tests were performed after reducing plant leaves into a fine, uniform substance (particle foliar flammability). Thus, the study eliminates the influence of plant structure and the external characteristics of combustion (i.e., weather, climate and location) and counts the intrinsic components of the fuel (i.e., chemical composition). The dried samples were ground and the size fraction from 315 to 200 μm was selected, in order to have satisfactory repeatability [27].

The forest species were stored into a conditioning box, at 32 °C and relative humidity 12.5%. Thus, the equilibrium moisture content of forest samples retained 2.8%, according to the insertion tables given in literature [29].

The fire retardant samples were prepared by adding and mixing well a certain quantity of chemical retardant in fine powdered form (Table 1) with a certain quantity of ground pine needles. The concentration level chosen (1 g of active retardant per 9 g of forest species) was similar to that applied by Hellenic Fire Service in real forest fires. All chemicals used were Merck p.a. reagents of purity $\geq$99.0%. The commercial retardant was Fire-Trol GTS-R, containing both DAP and AS and was supplied by the Hellenic Fire Service.

2.3. Apparatus for testing fire retardants effectiveness

The apparatus consisted of a vertical cylindrical furnace chamber with internal diameter 38 mm and length 300 mm (Fig. 1) heated by coil electric resistance heaters. Temperature control accuracy was ±2 °C in the range ambient to 1200 °C, whereas a precise programming system was used to control the heating rate between 0.1 and 100 °C min^{-1}. A set of three Chromel/Alumel thermocouples, 0.05 mm diameter, was used to monitor sample, oven and ambient temperatures with an accuracy higher than 0.3 °C and a response time of 2–4 ms. An analog thermocouple input module, Advantech model Adam-4018, stored up all temperature measurements, taken every 0.01–5 min, and converted them into digital for data handling.

The sample holder was made from stainless wire mesh with 0.045 mm openings folded into open topped 20 mm cube. The 8 cm^3 cubic sample holder was filled with each treated sample and then suspended into the center of the oven with a thermocouple located at the center of the cube (Fig. 1). Details on the design of the sample holder and the position of the thermocouple are given elsewhere [27]. The sample mass was about 2.5 g, depending on the apparent density of the forest species used.

The oven and sample temperatures were measured every 5 s, while the oven temperature was increased to 500 °C, at a rate of 0.5 °C min^{-1} under static air atmosphere. The experimental conditions applied were similar to the ones described by the

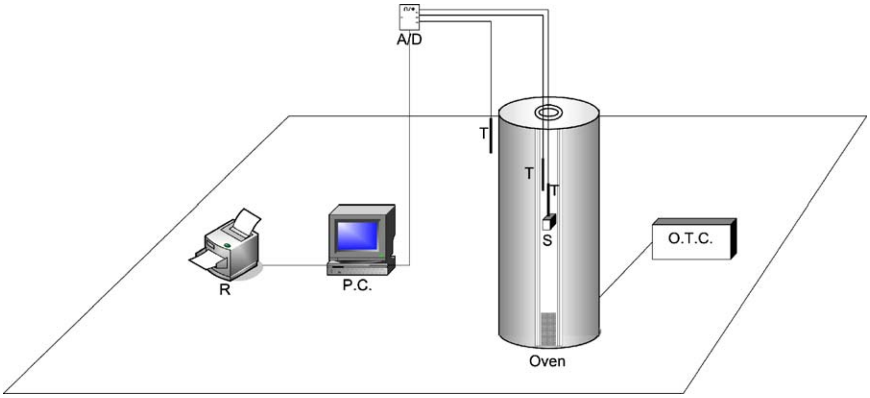

Fig. 1. Schematic diagram of the apparatus used for testing the effectiveness of chemical retardants. T: thermocouples; S: sample holder; OTC: oven temperature controller; A/D: analog-to-digital converter; PC: personal computer; R: recorder.

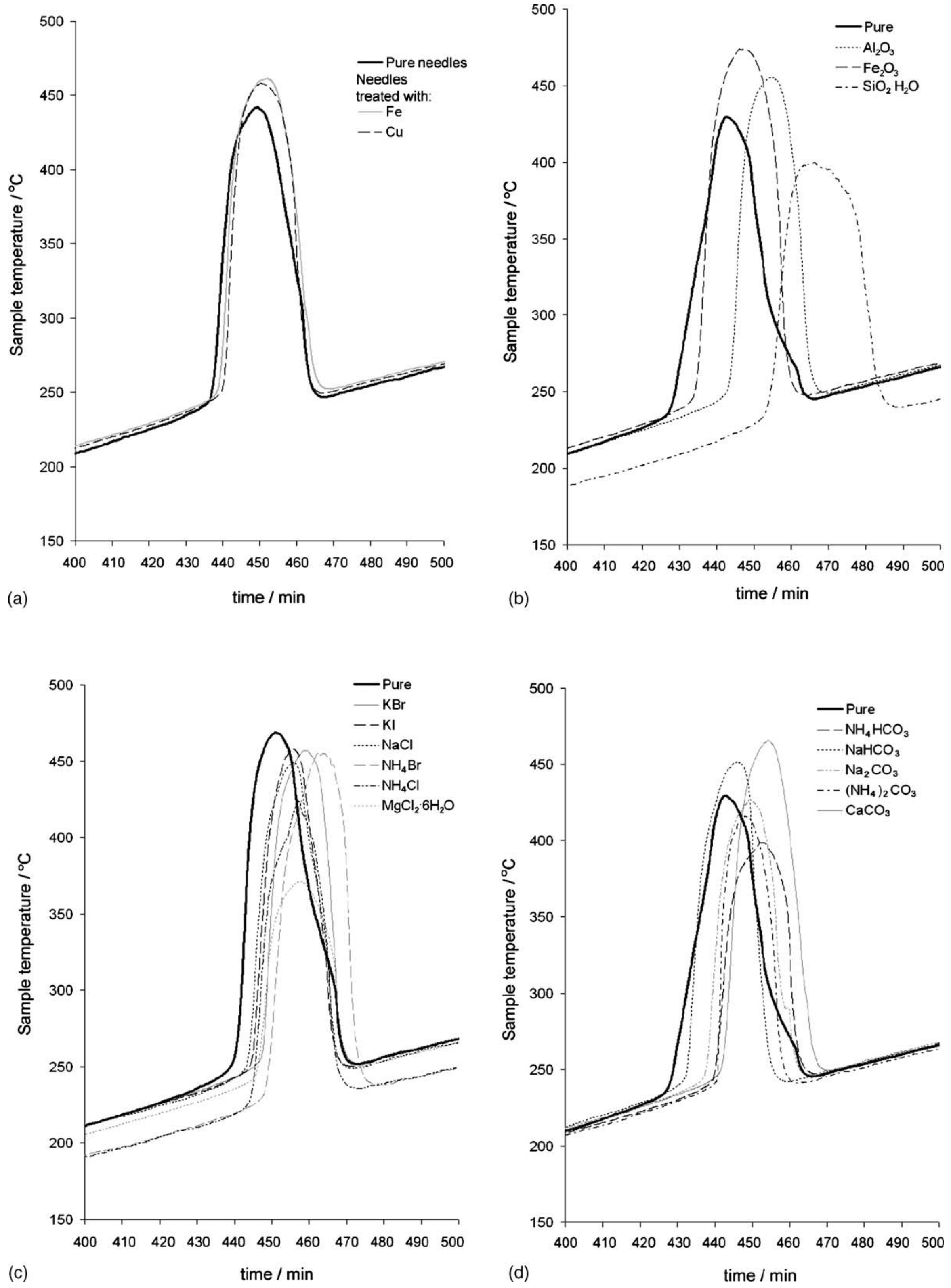

Fig. 2. The effect of various inorganic chemicals on the temperature vs. time curves of *Pinus halepensis* needles: (a) metals; (b) oxides; (c) halides; (d) carbonates; (e) sulphates; (f) phosphates; (g) other chemicals.

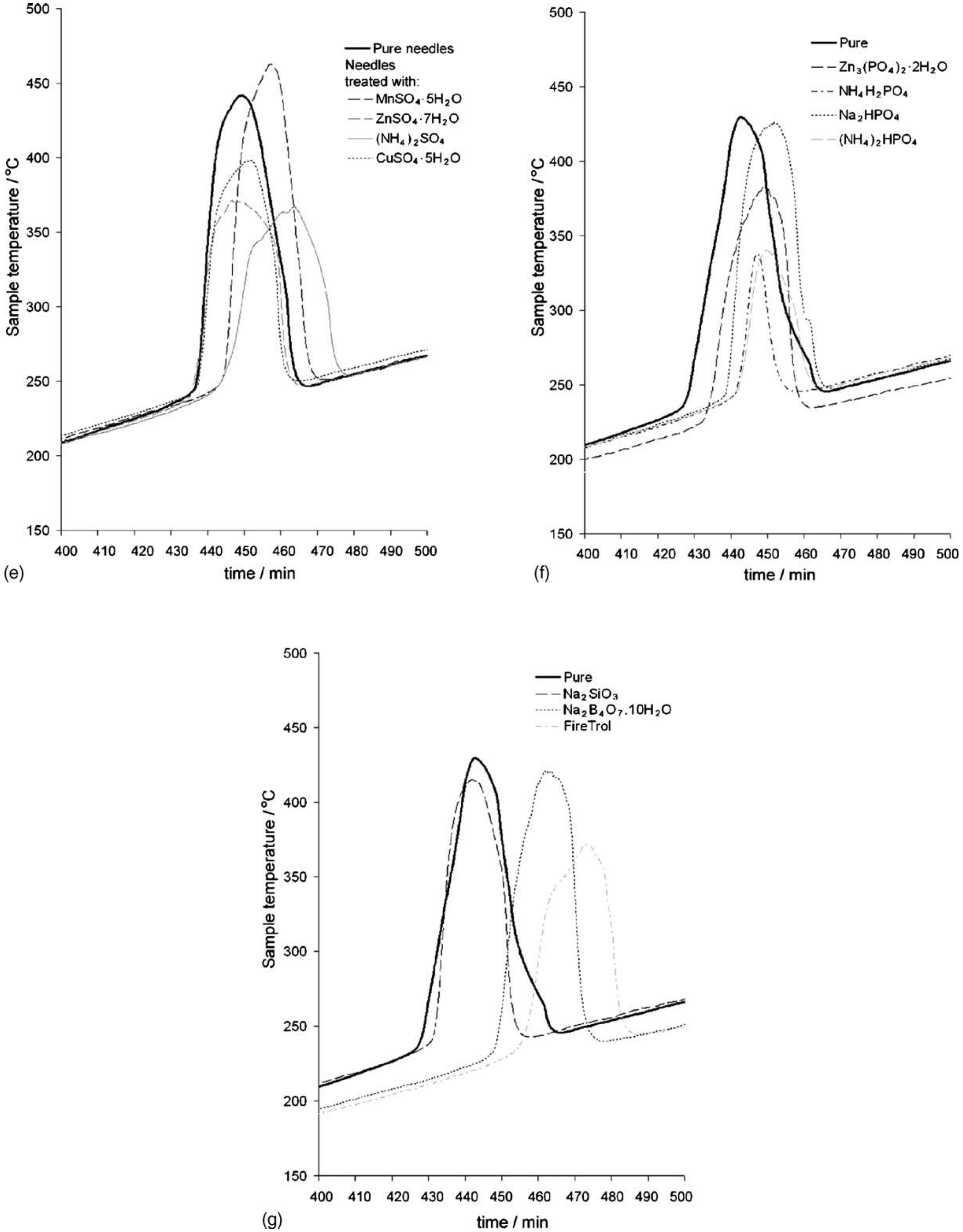

Fig. 2. (*Continued*).

79/831 European Commission Directive for measuring the relative self-ignition temperature of solid materials (i.e. polymers) with a low heating rate value, in order to have satisfactory detail on the decomposition reactions taking place during the heating [30,31]. Thus, the forest species temperature profiles were recorded. Finally, the %burning mass residue was determined by weighing the treated pine needles after burning to 500 °C.

3. Results and discussion

Under the experimental conditions employed in this study (very low heating rate and static air atmosphere) a smoldering type of combustion took place.

Fig. 2 shows the sample temperature–time profiles of pine needles treated with retardants. From these profiles the max-

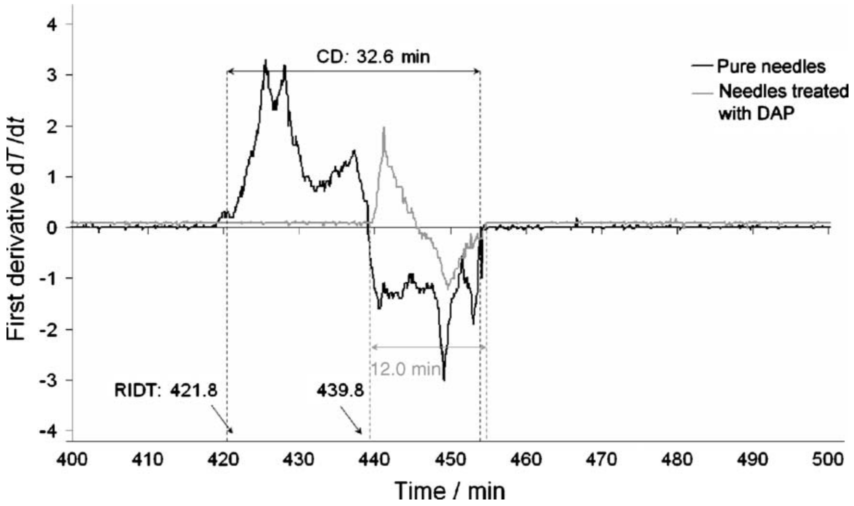

Fig. 3. Typical example of first derivative curves of temperature profiles of *P. halepensis* needles prior and after treatment with chemicals. CD: combustion duration; RIDT: relative ignition delay time.

imum combustion temperature and the peak temperature area were determined. According to previous experimental work employing a bomb calorimeter, the maximum combustion temperature can be related to the sustainability of the burning rate and the peak temperature area is proportional to the heat content of the forest species [27].

Also, the starting point of the combustion (related to the relative ignition delay time) and the combustion duration (related to the heat release rate) were determined, using the first derivative curve of the temperature profile as seen in Fig. 3 [27].

The relative flammability data determined before and after the treatment of the forest species with the chemicals, which were the relative ignition delay time, maximum (peak) combustion temperature, peak temperature area, combustion duration and %mass residue, are presented in Table 2.

An effective fire chemical retardant for wood is expected to increase the relative ignition delay time and the mass burning residue, and to decrease the heat release rate (related to the quotient of peak temperature area with combustion duration) and the sustainability of burning (related to peak temperature).

The effect of chemicals tested on the relative ignition delay time and the %mass burning residue of pine needles is presented in Fig. 4. The most efficient chemicals are located on the top right hand corner of the diagram. Thus, the most effective fire retardants for pine needles are the commercial one (which contains both DAP and AS), the ammonium phosphate salts, followed by the silica. The high efficiency of ammonium phosphates is attributed to the synergistic effect of phosphorus and nitrogen [7].

The influence of chemicals tested on the quotient of peak temperature area with combustion duration (relative heat release rate) and the maximum combustion temperature (relative sustainability of burning) is presented in Fig. 5. Based on this diagram, the most efficient chemical retardants are located on the bottom left hand corner. Similarly, as shown in Fig. 4, the most effective chemicals are: the commercial retardant, ammonium phosphate salts followed by the silica.

Ammonium phosphates and ammonium sulfates act via a dehydration mechanism of acids (phosphoric or sulfuric acid) and ammonia, formed during their thermal decomposition, directing the degradation pathway of cellulose toward more char production and fewer volatiles [7,32]. The disadvantage of these chemicals is that easily leach out [13].

The retardancy effect of $(NH_4)_2HPO_4$ can be explained by its thermal decomposition according to the scheme:

$$(NH_4)_2HPO_4 \rightarrow NH_3 + NH_4H_2PO_4 \qquad (155\,^{\circ}C)$$

$$NH_4H_2PO_4 \rightarrow NH_3 + H_3PO_4$$

$$2H_3PO_4 \rightarrow H_2O + H_4P_2O_7 \qquad (170\,^{\circ}C)$$

$$H_4P_2O_7 \rightarrow 2H_2O + P_2O_5$$

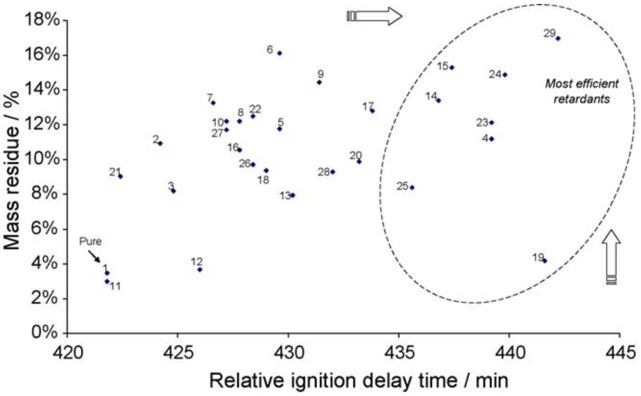

Fig. 4. Effect of chemical additives on pine needles relative ignition delay time and burning mass residue. 1: pure needles; 2: Fe; 3: Cu; 4: $SiO_2{\cdot}H_2O$; 5: Fe_2O_3; 6: Al_2O_3; 7: NaCl; 8: KCl; 9: KBr; 10: KI; 11: NH_4Cl; 12: NH_4Br; 13: $MgCl_2{\cdot}6H_2O$; 14: NH_4HCO_3; 15: $(NH_4)_2CO_3$; 16: $CaCO_3$; 17: Na_2CO_3; 18: $NaHCO_3$; 19: $(NH_4)_2SO_4$; 20: $ZnSO_4{\cdot}7H_2O$; 21: $MnSO_4{\cdot}5H_2O$; 22: $CuSO_4{\cdot}5H_2O$; 23: $NH_4H_2PO_4$; 24: $(NH_4)_2HPO_4$; 25: Na_2HPO_4; 26: $Zn_3(PO_4)_2{\cdot}2H_2O$; 27: Na_2SiO_3; 28: $Na_2B_4O_7{\cdot}10H_2O$; 29: commercial.

Table 2
Flammability properties of *P. halepensis* needles before and after treatment with chemicals

No.	Type	Chemical additive	MCT (°C)	RIDT (min)	PTA (arbitrary units $\times 10^4$)	CD (min)	Mass residue (%)
1	Pure	None	460	421.8	31.1	32.6	3.48
2	Metals	Fe	479	424.2	37.9	31.1	10.9
3		Cu	477	424.8	34.1	29.3	8.18
4	Oxides	$SiO_2 \cdot H_2O$	397	439.2	52.4	32.3	11.2
5		Fe_2O_3	504	429.6	40.1	23.2	11.8
6		Al_2O_3	476	429.6	32.0	26.9	16.1
7	Halides	NaCl	440	426.6	23.3	25.5	13.3
8		KCl	400	427.8	26.3	27.9	12.2
9		KBr	448	431.4	25.4	23.4	14.4
10		KI	454	427.2	23.5	24.8	12.2
11		NH_4Cl	416	421.8	10.2	32.0	3.00
12		NH_4Br	447	426.0	16.7	35.1	3.68
13		$MgCl_2 \cdot 6H_2O$	401	430.2	27.5	22.3	7.94
14	Carbonates	NH_4HCO_3	429	436.8	23.3	19.2	13.4
15		$(NH_4)_2CO_3$	446	437.4	18.0	13.0	15.3
16		$CaCO_3$	486	427.8	34.1	30.0	10.5
17		Na_2CO_3	457	433.8	28.6	20.2	12.8
18		$NaHCO_3$	482	429.0	30.8	18.3	9.36
19	Sulphates	$(NH_4)_2SO_4$	398	441.6	23.6	29.4	4.18
20		$ZnSO_4 \cdot 7H_2O$	401	432.0	24.1	25.6	9.28
21		$MnSO_4 \cdot 5H_2O$	454	428.4	25.9	25.5	12.5
22		$CuSO_4 \cdot 5H_2O$	416	422.4	28.4	27.5	9.03
23	Phosphates	$NH_4H_2PO_4$	368	439.2	11.2	4.70	12.1
24		$(NH_4)_2HPO4$	370	439.8	15.0	12.0	14.9
25		Na_2HPO_4	456	435.6	27.9	21.0	8.38
26		$Zn_3(PO_4)_2 \cdot 4H_2O$	413	428.4	10.6	21.6	9.70
27	Other chemicals	Na_2SiO_3	445	427.2	27.1	17.7	11.7
28		$Na_2B_4O_7 \cdot 10H_2O$	415	433.2	71.7	26.8	9.88
29		Commercial	366	442.2	20.8	28.9	17.0

MCT: maximum combustion temperature; RIDT: relative ignition delay time; PTA: peak temperature area; CD: combustion duration.

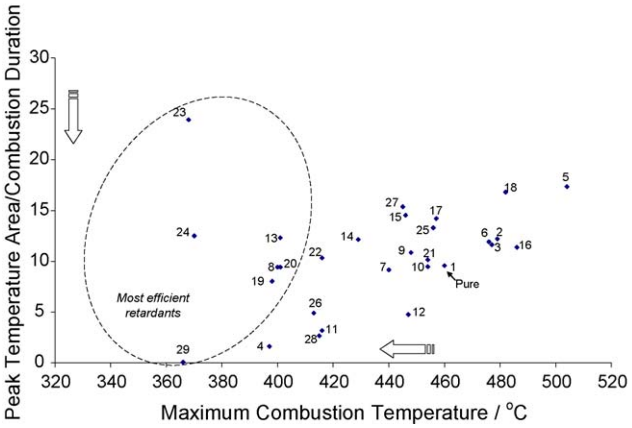

Fig. 5. Effect of chemical additives on pine needles relative burning heat release rate (peak temperature area/combustion duration) and relative sustainability of burning (maximum combustion temperature). 1: pure needles; 2: Fe; 3: Cu; 4: $SiO_2 \cdot H_2O$; 5: Fe_2O_3; 6: Al_2O_3; 7: NaCl; 8: KCl; 9: KBr; 10: KI; 11: NH_4Cl; 12: NH_4Br; 13: $MgCl_2 \cdot 6H_2O$; 14: NH_4HCO_3; 15: $(NH_4)_2CO_3$; 16: $CaCO_3$; 17: Na_2CO_3; 18: $NaHCO_3$; 19: $(NH_4)_2SO_4$; 20: $ZnSO_4 \cdot 7H_2O$; 21: $MnSO_4 \cdot 5H_2O$; 22: $CuSO_4 \cdot 5H_2O$; 23: $NH_4H_2PO_4$; 24: $(NH_4)_2HPO_4$; 25: Na_2HPO_4; 26: $Zn_3(PO_4)_2 \cdot 2H_2O$; 27: Na_2SiO_3; 28: $Na_2B_4O_7 \cdot 10H_2O$; 29: commercial.

The presence of phosphoric acid and phosphorous pentoxide, would cause an earlier dehydration of cellulose through reaction with hydroxyl groups of glucosan units. Ammonia could also facilitate the decomposition by reacting with intermediate carbonyl compounds to form glycosylamines or Sciff bases. The retardancy effect of $(NH_4)_2SO_4$ (AS) can be explained similarly to $(NH_4)_2HPO_4$ (DAP) [32]. However, AS affects primarily flaming combustion, which is not examined in this study.

Bicarbonates (i.e., NH_4HCO_3, $NaHCO_3$) and hydrates (i.e., $MgCl_2 \cdot 6H_2O$, $ZnSO_4 \cdot 7H_2O$, $MnSO_4 \cdot 5H_2O$, $CuSO_4 \cdot 5H_2O$, $Zn_3(PO_4)_2 \cdot 2H_2O$), act via the formation of non-combustible gases (i.e., CO_2 and H_2O) which dilute the volatile flammable products produced during the thermal degradation of forest species, primary affecting flaming combustion [7].

More specifically, the retarding behaviour of $NaHCO_3$ can be explained with reference to its thermal decomposition to CO_2 (g) and H_2O (g), according to the following equation:

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

$$(270\,^{\circ}C)$$

Both gases evolved (CO_2 and H_2O) during decomposition are incombustible. In addition, the decomposition of sodium bicarbonate is an endothermic reaction ($\Delta H = +0.81\ kJ\ g^{-1}$) and causes a decrease in the temperature of combustion. Moreover, the carbonate ions are hydrolyzed by water formed during pyrolysis, according to the following equation:

$$CO_3{}^{2-} + H_2O \rightarrow HCO_3{}^{-} + OH^{-}$$

The hydroxides, in accordance with the Lewis electron theory, then cause an earlier dehydration of the cellulose molecule through the formation of carbanions [33].

Halides (i.e., NaCl, KCl, KBr, KI, NH_4Cl, NH_4Br, $MgCl_2 \cdot 6H_2O$) affect mainly the gas-phase (flame) combustion by releasing free radical inhibitors (i.e., $Br^{\bullet}$) that interrupt the chain propagation mechanism of flammability [7]. Among all the halides tested, the most effective were the bromides and this is in agreement with previous works [7,13,34].

Borax ($Na_2B_4O_7 \cdot 10H_2O$) has been reported to reduce mainly flame spread. Moreover, it has exhibited satisfactory action on the smoldering combustion examined in this work. It is generally accepted that the primary retardancy mechanism of boron compounds is the formation of a coating on the wood surface at high temperature. Besides, it has been reported that boric acid (formed during decomposition) catalyses the dehydration of wood at a relatively low temperature promoting the charring [20].

The oxides (i.e., $SiO_2 \cdot H_2O$, Fe_2O_3, Al_2O_3) act according to Barrier Theory [7] by forming a glassier on the sample surface, preventing oxygen reaching the forest fuel. Among the oxides tested the most effective was $SiO_2 \cdot H_2O$.

Metals are expected to absorb heat preventing forest fuel from igniting. However, the metals tested (Fe, Cu) found to a have a minor effect on the flammability properties of pine needles.

4. Conclusions

Using a relatively inexpensive but reliable and accurate method, we have ranked 28 chemical substances according to their fire retarding behaviour on smoldering combustion of pine needles. The device used to rank those chemical substances has the potential of determining many flammability parameters at once, and is advantageous over other common thermal analysis techniques [27].

Among the chemicals examined the best performance exhibited: a commercial retardant (containing both DAP and AS), the ammonium phosphates $(NH_4)_2HPO_4$ (DAP) and $NH_4H_2PO_4$ (MAP), $SiO_2 \cdot H_2O$, $(NH_4)_2SO_4$ (AS) and borax. Similar results are reported in the literature with the exception of $SiO_2 \cdot H_2O$ which has surprisingly high efficiency. The main drawback of $SiO_2 \cdot H_2O$ is that it is insoluble in water and therefore can only be used in solid form.

The chemicals studied had different influence on the flammability properties examined. Thus, $(NH_4)_2SO_4$ had best performance on the initial combustion temperature (relative ignition delay time), and $(NH_4)_2HPO_4$ the best one on the peak temperature area (heat release). This leads to the conclusion that the highest overall retardant efficiency can be obtained from chemical mixtures. This was confirmed experimentally; among all chemicals examined, a commercial retardant (containing mixture of AS and DAP) exhibited the highest overall smoldering combustion retardancy.

As far as halogen compounds are concerned, it was found that bromine compounds are better fire retardants than chlorides, as was expected from the literature. However, the suggested method does not count the toxicity of chemicals tested and it is likely that halogen compounds will not be able to be used in real forest fires, as highly toxic.

In further work the retardants effect on flaming combustion of forest species should be studied, using oxygen atmosphere and higher heating rate conditions. In addition, the retardancy effect on each intrinsic component of wood (i.e. lignin, cellulose, extractives, etc.) should be studied for a better understanding of the mechanisms of fire retardancy. This will facilitate the development of new fire retardant products.

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