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Testing the fire retardancy of Greek minerals hydromagnesite and huntite on WUI forest species *Phillyrea latifolia* L.

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Abstract

The fire retardancy of pure hydromagnesite and other natural mixtures of hydromagnesite and huntite minerals has been tested using forest species samples of *Phillyrea latifolia* L., collected from a wildland/urban interface (WUI) zone near Athens. Three different methods were employed for this study. The first was thermal analysis (TG, DTG, SDTA), using samples of few mg, relatively slow heating rate ($10\,^{\circ}\mathrm{C\,min^{-1}}$) and atmosphere conditions of: (a) O_2, in order to favor complete combustion, (b) N_2, to isolate pyrolysis and (c) air, in order to approach real combustion conditions. The second was a laboratory-scale method, based on a specially constructed preparative-scale DTA, using samples of few grams, static air atmosphere and low heating rate ($0.5\,^{\circ}\mathrm{C\,min^{-1}}$) to favor smoldering combustion. The third was a new flame spread test, using 10–12 g samples formed into a train mold. Some common forest fire retardant media (i.e. DAP, MAP, AS), as well as a widely used commercial forest fire retardant (i.e. Phos-Chek D 75-F) were also studied as means of comparison.

Keywords: Huntite and hydromagnesite minerals; Fire retardancy; Thermal analysis; Combustion; Pyrolysis; Flame spread; Wildland/urban interface (WUI)

1. Introduction

In forests, there are three major fuel types: (a) crown fuel (foliage and branches in the overstory), (b) fine fuel in ground vegetation and litter (living vegetation and twigs, leaves and needles) and (c) duff in the ground layer (layers of decomposing litter and decomposed organic soil) [1–3].

Exposing a forest fuel to a sufficiently high heat flux, results to its thermal degradation which can be considered as two consecutive steps. The first is pyrolysis which is an endothermic process that breaks down the main constituents of forest material (cellulose, hemicelluloses and lignin) into low molecular mass gases, known as volatiles, tars, carbonaceous char and mineral ash. Among the pyrolysed components the most significant is cellulose which is the principal component in forest species, comprising 41–53% (w/w) of the total weight. Thermal degradation of cellulose takes place between 250 and 400 °C and follows two competing pathways: one is the dehydration which leads to char and gases (mainly CO, CO_2, H_2O) and the other is the depolymerisation which leads to tar and volatiles through the formation of levoglucosan [4]. Hemicelluloses, which comprise 15–25% (w/w) of forest species, have similar chemical structure to cellulose and therefore, their thermal degradation behaviour is close to cellulose (250–400 °C). Lignin (16–33%, w/w) is more complex and thermally stable than the other cellulosic constituents and is pyrolysed in the temperature range of 280–500 °C, contributing more to char formation.

The second step is combustion which is an exothermic process. Wildland fires consume biomass through flaming or smoldering combustion. Flaming combustion is a gas phase oxidation, accompanied by emission of flames and occurs over short time periods in localized areas. It typically occurs in the crown and fine fuel (surface) layers. Smoldering (or glowing) combustion is associated with solid phase oxidation of the char and can last long after flaming combustion has occurred, consuming ground layer fuels. Crown and surface fires usually occur in conjunction with smoldering ground fires.

Forest fire suppression systems include: (1) long-term retardants which inhibit combustion even after the loss of their watery

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matrix, (2) short-term retardants which reduce the surface tension of water or increase its viscosity and their effectiveness vanishes with the evaporation of water, (3) fire-fighting foams which form small bubbles when mixed with water and (4) wetting agents which reduce the surface tension of water and increase its spreading ability. These systems may be applied aerially using airtankers and helicopters or from the ground using engine-powered pumps [5].

There are six basic theories explaining the mechanism of fire retardants on pyrolysis and combustion of wood: barrier theory, thermal theory, dilution by non-combustible gases theory, free radical trap theory, increased char/reduced volatiles theory and reduced heat content of volatiles theory.

Among long-term forest fire retardants, diammonium phosphate (DAP), monoammonium phosphate (MAP) and ammonium sulphate (AS) have dominated use, because of their intrinsic effectiveness and their similarity to agricultural fertilizers. This has assured their abundance, relative cheapness and environmental compatibility. Thus, they have a primary place in the market, being the basic active components in the formulation of commercially available forest fire retardants.

The use of minerals as fire retardants has been reported in the literature [6–8]. Huntite [$Mg_3Ca(CO_3)_4$] and hydromagnesite [$Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$] are classified as salt type carbonate minerals. Their fire retardancy effectiveness has already been tested on polymer mixtures [9,10]. Moreover, their extraction from Greek mines in large quantities with relatively low cost, supports their potential for commercial fire retardant use [11].

Various methods have been developed for evaluating the performance of fire retardants such as thermal analysis, tunnel flame spread tests, critical oxygen index tests, smoke production tests, and analysis of solid residue or gaseous products of thermal decomposition [12–18]. Among them, thermal analysis has a primary place [4,12–14,19,20]. However, the small samples used in thermal analysis and the rapid removal of pyrolysis or combustion products can lead to an erroneous interpretation in terms of forest fuel flammability performance in field conditions. Therefore, the information provided by thermal analysis on forest species fire retardancy should be supported by laboratory-scale flammability tests [21–23].

This study aims to evaluate the fire retardancy of Greek minerals hydromagnesite and huntite/hydromagnesite mixtures on *Phillyrea latifolia* L. (Mock privet), a species frequently devastated by forest fires, especially in wildland/urban interface (WUI) zones near Athens. Furthermore, this study could contribute to a better understanding of the fire retardancy mechanism of carbonate minerals, thus facilitating the development of new fire retardant products. For this purpose, DAP, MAP and AS which are in commercial use as active fire retardants ingredients, as well as a widely used commercial forest fire retardant (i.e., Phos-Chek) were also studied as means of comparison. The experiments were performed employing thermal analysis and lab-scale combustion and flame spread tests.

2. Experimental

2.1. Methods

2.1.1. Thermal analysis

Each sample, weighing around 15–17 mg and having particle size 0.1–0.2 mm, was introduced in an open type alumina sample holder. The experiments were carried out under non-isothermal conditions (from 25 to 600 °C) with a linear heating rate of 10 °C min^{-1}, using a Mettler TGA/SDTA 851 module, supported by a PC and software for control and data handling. This relatively low heating rate was selected in order to achieve high resolution on DTG and SDTA curves and to ensure a minor deviation between sample and oven temperature [24].

Three different atmosphere conditions (with a flow rate of 100 mL min^{-1}) were used: (a) oxygen, to favor complete combustion conditions, (b) nitrogen, to isolate the pyrolysis step and (c) air, to approach actual combustion conditions [24].

2.1.2. Lab-scale flammability tests

The lab-scale flammability tests were performed using a specifically designed apparatus for monitoring the forest species temperature, under precisely controlled temperature and static air atmosphere conditions. A detailed description of the apparatus and the operating conditions used are given in previous reports [21–23].

The 8 cm^3 cubic sample holder was filled with 2.5–3.0 g sample with particle size 0.1–0.2 mm. The oven temperature was increased from 20 to 500 °C with a low heating rate of 0.5 °C min^{-1}, to favor smoldering combustion. Oven and sample temperatures were recorded every 5 s, whereas the initial combustion temperature and combustion duration were determined, based on the first derivative curves of sample temperature profiles [22].

2.1.3. Flame spread tests

The description of the apparatus and the experimental conditions used are given detailed in previous work [25], based on standard test methods [26,27].

Approximately, 10–12 g samples with particle size 0.1–0.2 mm were poured to fill up the triangular cross section of the mold loosely. The sample holder with the loaded sample was placed on the heating plate to keep the sample at 70 °C. Then, a hot flame from a gas burner (diameter about 5 mm) was applied to the start of the sample path until ignition. When combustion occurred, the stopwatch was set to measure the flaming combustion time from line B to C (100 mm) and from line C to D (100 mm distance). Thus, the mean flame spread rate was determined in mm s^{-1}. In addition, the flame combustion duration was recorded by measuring the flaming combustion time from line B until the flame was extinguished. The test was performed six times, using a clean cool sample holder each time and the RSD values were determined. The whole process was video recorded and the flame height and flame intensity were determined. Flame height measurements were taken every 20 mm during each experiment committed and the flame intensity was calculated by the equation: $I = 273\ (h)^{2.17}$, where: I is the flame intensity (kW m^{-1}) and h is the flame height (m) [28].

2.2. Materials

P. latifolia L. (Mock privet) was chosen because it is a very common shrub forest species in Mediterranean WUI regions. The leave samples were collected on 23 October 2006, after a long drought period in order to avoid moisture effects, from “Thrakomakedones” which is a WUI area located at the foothill of mountain Parnitha, northern of Athens, Greece. The sampling site had geographical coordinates: 38° 08′ 46″ N, 23° 45′ 26″ E, altitude: 590 m, average inclination: 60%, exposition: S (190°) and dominating petrologic formation: limestone, dolomites limestone and dolomite. The collected foliage samples were brought immediately to the laboratory, dried into a vacuum oven for 24 h under pressure of 10 Torr and temperature of 60 °C and then ground. A fraction between 100 and 200 μm was separated and used for the tests.

The examined minerals hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$] and the natural mixture of hydromagnesite and huntite [$Mg_3Ca(CO_3)_4$] were mined from the Kozani basin, located in northern Greece [29]. DAP [$(NH_4)_2HPO_4$], MAP [$NH_4H_2PO_4$] and AS [$(NH_4)_2SO_4$] were all Merck laboratory reagents, whereas the commercial retardant (CR) was a Phos-Chek product (Astaris LLC), containing AS (>65%), MAP (>15%) and DAP (>5%) as active substances, as well as various additives, such as thickeners, color pigments, stabilizers and other performance additives (trade secrets). These retardants were ground and a fraction of less than 20 μm was selected and used for the tests.

The retardant treated samples were prepared by mixing well the forest species with the retardant powders. The samples were then placed into a conditioning box to achieve a minimum level of moisture content (2%) [30]. The amount of retardant applied to the forest species (10%, w/w), was based on data used by Hellenic Fire Services in real forest fires.

It is not expected that forest species in actual wildfire conditions exhibit the same flammability properties as the samples prepared in the laboratory. However, the tests were performed after reducing plant leaves into a fine uniform substance (particle foliar combustibility) and making an ideal mixture of *P. latifolia* L. and the retardant. Under these conditions, the results taken were more consistent, counting the intrinsic components (i.e. chemical composition) of forest species, suitable for comparison use [24].

3. Results and discussion

3.1. Thermal analysis

3.1.1. Thermal analysis in N_2 atmosphere

In Fig. 1 are presented the DTG curves of *P. latifolia* samples treated with hydromagnesite (Hyd) and huntite/hydromagnesite (HunHyd), in nitrogen atmosphere. The thermal analysis data taken from the TG/DTG/SDTA graphs for all treated samples: initial and final pyrolysis temperatures, peak temperatures, maximum weight loss rate (MWLR) and pyrolysis mass residue at 600 °C, are shown in Table 1. Each value in Table 1 is the mean of three replicate measurements, accompanied by the corresponding RSD values in parenthesis.

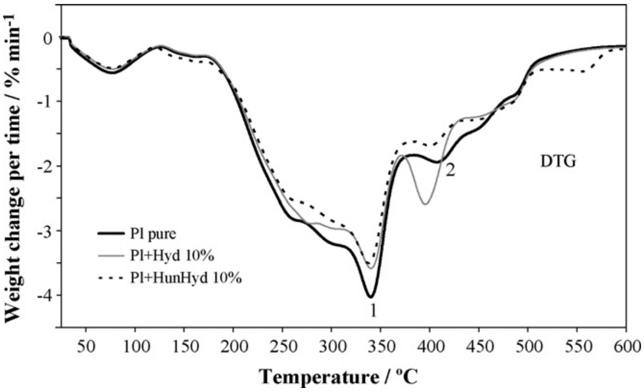

Fig. 1. DTG curves of *Phillyrea latifolia* (*Pl*) pyrolysis before and after treatment with Hyd and HunHyd minerals, in N_2 atmosphere (100 mL min^{-1}) and heating rate 10 °C min^{-1}.

Five different temperature ranges (peaks) may be distinguished on the DTG curves of untreated *P. latifolia* samples (Fig. 1). The first, at <100 °C corresponds to the evaporation of moisture; the second in the range 120–180 °C is attributed to the evaporation of volatile constituents; the peak in the range 200–280 °C corresponds mainly to hemicellulose decomposition, whereas the ones between 280–370 °C and 370–550 °C to cellulose and lignin decomposition, respectively [4,31–34].

Based on thermal analysis data, the following criteria were used to evaluate the effectiveness of fire retardants examined: (a) shift of pyrolysis temperature to lower values (the evolved volatiles could dissipate before their ignition temperature); (b) decrease of MWLR values; (c) alteration of pyrolysis shape in DTG curves and (d) increase in mass residue [12].

As shown in Fig. 1 and Table 1, the minerals shift the secondary weight loss peak (peak 2) referring to lignin decomposition to lower temperatures. This temperature shift was 11 °C for pure hydromagnesite and 6 °C for the huntite/hydromagnesite mixture (Fig. 1, Table 1). On the contrary, MAP, DAP, AS and CR affect mainly peak 1 (cellulose decomposition).

Both minerals and all other retardants examined lower the MWLR of peak 1 (cellulose decomposition), whereas the effect of retardants on MWLR of peak 2 (lignin decomposition) is inconsistent. Furthermore, the presence of minerals complicates the thermal degradation DTG profile of pure *P. latifolia* (Fig. 1). Finally, the pyrolysis mass residue, which is directly related to flammability properties [4,31], increases by the presence of minerals (and other retardants examined). Increases of 7.6% and 14.4% were recorded for pure hydromagnesite and huntite/hydromagnesite respectively, whereas the best performance according to this criterion was recorded by MAP (24.4% increase).

Table 1
Thermal analysis data of *Phillyrea latifolia* (*Pl*) pyrolysis, before and after treatment with fire retardants, in N_2 atmosphere (100 mL min^{-1}) and heating rate 10 °C min^{-1}

Sample	Initial pyrolysis temperature (°C)	Final pyrolysis temperature (°C)	Primary peak 1 (°C)	MWLR at peak 1 (%, min^{-1})	Secondary peak 2 (°C)	MWLR at peak 2 (%, min^{-1})	Mass residue at 600 °C (%, w/w)
Pl pure	246 (<0.01)	404 (<0.01)	338 (<0.01)	4.0 (0.02)	406 (<0.01)	1.9 (0.05)	29.1 (0.02)
Pl + Hyd 10%	241 (<0.01)	408 (<0.01)	339 (<0.01)	3.6 (0.03)	395 (<0.01)	2.6 (0.04)	31.3 (0.01)
Pl + Hun/Hyd 10%	242 (<0.01)	392 (<0.01)	337 (<0.01)	3.5 (0.03)	400 (<0.01)	1.7 (0.06)	33.3 (0.01)
Pl + DAP 10%	208 (<0.01)	412 (<0.01)	256 (<0.01)	2.8 (0.04)	420 (<0.01)	1.8 (0.05)	34.7 (<0.01)
Pl + MAP 10%	208 (<0.01)	397 (<0.01)	259 (<0.01)	3.0 (0.03)	414 (<0.01)	1.7 (0.06)	36.2 (<0.01)
Pl + AS 10%	225 (<0.01)	395 (<0.01)	296 (<0.01)	3.8 (0.03)	408 (<0.01)	1.7 (0.06)	29.9 (<0.01)
Pl + CR 10%	215 (<0.01)	406 (<0.01)	282 (<0.01)	3.3 (0.03)	418 (<0.01)	1.9 (0.05)	31.1 (<0.01)

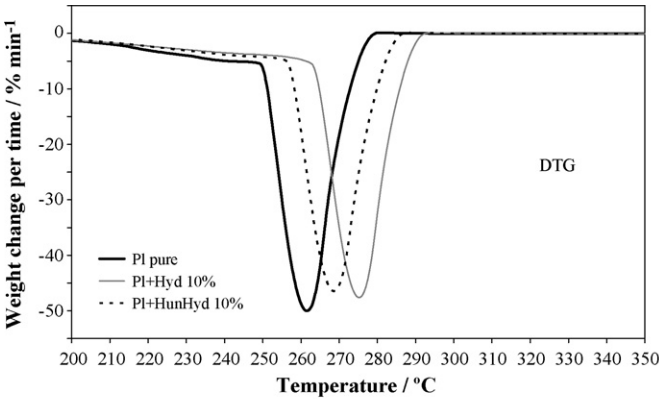

Fig. 2. DTG curves of *Phillyrea latifolia* (*Pl*) combustion before and after treatment with Hyd and HunHyd minerals, in O_2 atmosphere (100 mL min^{-1}) and heating rate 10 °C min^{-1}.

3.1.2. Thermal analysis in O_2 atmosphere

In Fig. 2 are presented the DTG curves of *P. latifolia* samples treated with hydromagnesite (Hyd) and huntite/hydromagnesite (HunHyd), in oxygen atmosphere. The thermal analysis data taken from the TG/DTG/SDTA graphs for all treated samples: relative self-ignition delay time, initial combustion temperature, final combustion temperature, combustion duration, maximum weight loss rate, temperature at maximum weight loss rate, combustion mass residue at 600 °C, maximum temperature change ($\Delta T_{\max}$) and SDTA peak temperature are shown in Tables 2a and 2b. Each value in Tables 2a and 2b is the mean of three replicate measurements, accompanied by the corresponding RSD values in parenthesis.

The criteria used for evaluating the efficiency of fire retardants examined were: (a) shift of combustion temperature to higher values, (b) decrease of MWLR values and (c) increase of combustion mass residue [12].

Tables 2a and 2b show that all examined fire retardants shift the initial combustion temperature to higher values, with AS being the most effective (increase of 13 °C). Hydromagnesite demonstrates a good retardancy performance according to this criterion (increase of 9 °C), whereas the mixture huntite/hydromagnesite is less effective (increase of 4 °C). The MWLR value is also decreased by all retardants examined, with MAP exhibiting the best performance. The minerals Hyd and HunHyd exhibit satisfactory performance (decrease of 2.2 and 3.3% min^{-1}, respectively). Finally, combustion mass residue at 600 °C increases by the presence of all retardants examined, with DAP and MAP being the most effective (two and three times increase, respectively). HunHyd exhibits a good performance with an increase of 185.7%, whereas Hyd is less efficient with an increase of 110.7%. However, regarding to this criterion, AS seems to have minor efficiency (mass residue increase of 10.7%). This is confirmed by previous studies [21].

Regarding the SDTA curves, complete combustion which is achieved by the oxygen atmosphere provokes a strongly exothermic reaction, accompanied by high heat release. As seen in Table 2b, both minerals shift this exothermic reaction to higher temperature levels (8.5 °C for Hyd and 3.5 °C for HunHyd).

Table 2a
Thermal analysis data of *Phillyrea latifolia* (*Pl*) combustion, before and after treatment with fire retardants, in O_2 atmosphere (100 mL min^{-1}) and heating rate 10 °C min^{-1}

Sample	Relative ignition delay time (min)	Initial combustion temperature (°C)	Final combustion temperature (°C)	Combustion duration (min)	MWLR (%, min^{-1})	Temperature of MWLR (°C)	Mass residue at 600 °C (%, w/w)
Pl pure	26.9 (<0.01)	269 (<0.01)	324 (0.02)	5.5 (0.05)	49.8 (<0.01)	302 (<0.01)	2.8 (0.04)
Pl + Hyd 10%	27.8 (0.01)	278 (0.01)	334 (0.02)	5.7 (0.07)	47.6 (<0.01)	310 (<0.01)	5.9 (0.05)
Pl + Hun/Hyd 10%	27.2 (<0.01)	273 (<0.01)	332 (0.01)	6.0 (0.03)	46.5 (<0.01)	306 (<0.01)	8.0 (0.02)
Pl + DAP 10%	27.5 (<0.01)	275 (<0.01)	329 (<0.01)	5.4 (0.01)	35.9 (<0.01)	307 (<0.01)	8.9 (0.08)
Pl + MAP 10%	27.6 (<0.01)	276 (<0.01)	336 (0.01)	6.0 (0.06)	31.6 (<0.01)	311 (<0.01)	10.6 (0.09)
Pl + AS 10%	28.2 (<0.01)	282 (<0.01)	349 (0.02)	6.7 (0.06)	42.5 (<0.01)	318 (<0.01)	3.1 (0.06)
Pl + CR 10%	27.7 (<0.01)	278 (<0.01)	339 (0.01)	6.1 (0.06)	44.4 (<0.01)	313 (<0.01)	3.6 (0.03)

Table 2b
Thermal analysis data of *Phillyrea latifolia* (*Pl*) combustion, before and after treatment with fire retardants, in O_2 atmosphere (100 mL min^{-1}) and heating rate 10 °C min^{-1}

Sample	ΔT_{max}/SDTA peak (°C)	SDTA peak temperature (°C)
Pl pure	81.4 (0.03)	271.0 (<0.01)
Pl + Hyd 10%	78.8 (0.01)	279.5 (0.01)
Pl + Hun/Hyd 10%	83.3(<0.01)	274.5 (<0.01)
Pl + DAP 10%	54.4 (0.03)	279.5 (<0.01)
Pl + MAP 10%	50.5 (0.03)	283.5 (<0.01)
Pl + AS 10%	78.1 (<0.01)	288.2 (<0.01)
Pl + CR 10%	76.4 (0.04)	282.5 (<0.01)

3.1.3. Thermal analysis in air atmosphere

In Fig. 3 are presented the DTG curves of *P. latifolia* samples treated with hydromagnesite (Hyd) and huntite/hydromagnesite (HunHyd), in air atmosphere. The thermal analysis data taken from the TG/DTG/SDTA graphs for all treated samples: initial and final combustion temperature, peak temperatures, maximum weight loss rate, mass residue at 600 °C, maximum temperature change (ΔT_{max}) and SDTA peak temperature are shown in Tables 3a and 3b. Each value in Tables 3a and 3b is the mean of three replicate measurements, accompanied by the corresponding RSD values in parenthesis.

The criteria used for evaluation of the fire retardancy effectiveness were: (a) alteration of combustion profile in terms of DTG curves; (b) decrease of MWLR values; (c) decrease of ΔT_{max} and (d) increase of mass residue [12].

As shown in Fig. 3 and Tables 3a and 3b, the presence of minerals complicates the DTG thermal degradation profile of pure *P. latifolia* (Fig. 3). Both examined minerals decrease the MWLR value of peak 1 and increase that of peak 2. Based on this criterion, DAP and MAP exhibit the best performance. Also, mass residue increases by the presence of the minerals: increases of 1.8% and 9.5% were recorded for Hyd and HunHyd, respectively, whereas the best performance was recorded by MAP (63.9% increase).

On the SDTA curves, two peaks are observed. The first is mainly attributed to cellulose combustion and the second to

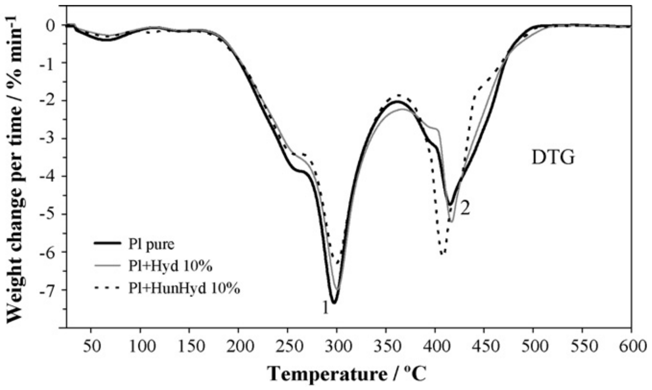

Fig. 3. DTG curves of *Phillyrea latifolia* (*Pl*) combustion before and after treatment with Hyd and HunHyd minerals, in air atmosphere (100 mL min^{-1}) and heating rate 10 °C min^{-1}.

Table 3a
Thermal analysis data of *Phillyrea latifolia* (*Pl*) combustion, before and after treatment with fire retardants, in air atmosphere (100 mL min^{-1}) and heating rate 10 °C min^{-1}

Sample	Initial combustion temperature (°C)	Final combustion temperature (°C)	Primary peak 1 (°C)	MWLR at peak 1 (%, min^{-1})	Secondary peak 2 (°C)	MWLR at peak 2 (%, min^{-1})	Mass residue at 600 °C (%, w/w)
Pl pure	256 (0.01)	380 (0.02)	305 (0.03)	7.3 (0.01)	427 (0.04)	4.8 (0.02)	16.9 (0.01)
Pl + Hyd 10%	255 (<0.01)	377 (0.01)	304 (<0.01)	7.0 (0.01)	424 (0.01)	5.2 (0.02)	17.2 (0.01)
Pl + Hun/Hyd 10%	328 (0.01)	435 (0.01)	303 (0.01)	6.5 (0.03)	413 (0.04)	6.1 (0.01)	18.5 (0.02)
Pl + DAP 10%	233 (0.01)	403 (0.03)	303 (0.02)	4.5 (0.04)	473 (0.04)	2.6 (0.07)	23.2 (<0.01)
Pl + MAP 10%	225 (0.01)	391 (0.03)	292 (<0.01)	4.2 (0.02)	480 (0.03)	2.2 (0.04)	27.7 (<0.01)
Pl + AS 10%	247 (0.01)	377 (0.01)	293 (0.01)	6.3 (0.03)	427 (0.01)	3.7 (0.03)	16.9 (0.01)
Pl + CR 10%	233 (<0.01)	390 (0.02)	287 (<0.01)	5.1 (0.02)	445 (0.01)	3.0 (0.03)	20.6 (0.01)

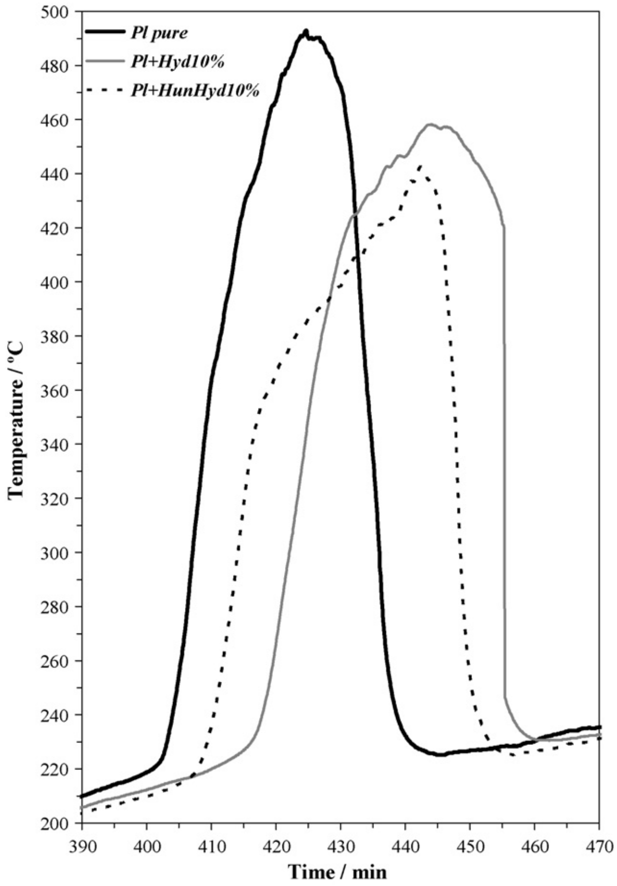

Fig. 4. Sample temperature curves of *Phillyrea latifolia* (*Pl*), before and after treatment with Hyd and HunHyd minerals, taken from the lab-scale flammability apparatus.

lignin combustion where more heat is released. As seen in Table 3b, both minerals decrease both cellulose $\Delta T_{\max}$ (3 °C for Hyd and 3.2 °C for HunHyd) and lignin $\Delta T_{\max}$ (3.2 °C for both Hyd and HunHyd).

3.2. Lab-scale flammability tests (smoldering combustion)

In Fig. 4 are shown the sample temperature profile curves of *P. latifolia* before and after treatment with Hyd and HunHyd minerals, taken from the lab-scale flammability test apparatus described in Section 2.1.2. From these graphs, the following data were derived: relative ignition delay time, maximum combustion temperature, combustion duration, temperature peak area and combustion mass residue at 500 °C, as presented in Table 4. The values in Table 4 are given as the mean ones of three replicate measurements, accompanied by the corresponding RSD values in parenthesis.

Criteria for evaluating the fire retardancy effectiveness on smoldering combustion of forest species were: the increase of relative ignition delay time and combustion mass residue and the decrease of maximum combustion temperature, smoldering combustion duration and temperature peak area [21].

As shown in Fig. 4 and Table 4, the minerals increase significantly the relative ignition delay time of *P. latifolia* forest species (i.e., by 16 min for Hyd and 8 min for HunHyd), whereas

Table 3b
Thermal analysis data of *Phillyrea latifolia* (*Pl*), before and after treatment with fire retardants, in air atmosphere (100 mL min^{-1}) and heating rate 10 °C min^{-1}

Sample	ΔT_{max}/SDTA peak 1 (°C)	SDTA temperature peak 1 (°C)	ΔT_{max}/SDTA peak 2 (°C)	SDTA temperature peak 2 (°C)
Pl pure	12.1 (0.03)	319.2 (<0.01)	15.7 (0.02)	428.7 (<0.01)
Pl + Hyd 10%	9.1 (<0.01)	319.0 (<0.01)	12.3 (<0.01)	426.5 (<0.01)
Pl + Hun/Hyd 10%	8.9 (0.02)	319.2 (<0.01)	12.4 (0.02)	414.3 (0.01)
Pl + DAP 10%	6.6 (0.07)	333.5 (<0.01)	5.3 (0.09)	475.8 (0.01)
Pl + MAP 10%	6.1 (0.08)	333.7 (<0.01)	4.5 (0.09)	482.3 (<0.01)
Pl + AS 10%	8.3 (0.09)	332.7 (<0.01)	8.1 (0.09)	428.0 (<0.01)
Pl + CR 10%	7.9 (0.05)	334.0 (<0.01)	6.4 (0.04)	447.3 (<0.01)

AS exhibits the best retardancy performance (29 min) according to this criterion. Also, the minerals increase smoldering combustion mass residue. Increases of 80.8% and 109.6% were recorded for Hyd and HunHyd, respectively, whereas the highest mass residue values were exhibited by DAP (173.1%) and MAP (203.8%). Furthermore, the maximum combustion temperature was decreased by all examined retardants, with the minerals exhibiting satisfactory performance (decreases of 38 °C and 49 °C for Hyd and HunHyd, respectively).

3.3. Flame spread tests

In Table 5 are presented the data taken from the flame spread test (Section 2.1.3) on *P. latifolia* (i.e. burning rate, flame duration, flame height and maximum flame height). The values shown in Table 5 are the means of three replicate measurements, with the corresponding RSD values given in parenthesis.

As shown in, both minerals significantly decrease the burning rate (66% and 43% for Hyd and HunHyd, respectively), whereas the flame duration increases by the presence of minerals (92% and 45% for Hyd and HunHyd, respectively). Also, both minerals reduce the flame height (46% and 26% for Hyd and HunHyd, respectively) and the maximum flame height (71% and 64% for Hyd and HunHyd, respectively). Finally, the flame intensity is reduced by both minerals (73% and 48% by Hyd and HunHyd, respectively). Similar results were obtained with the conventional retardants (DAP, MAP, AS, CR) at concentration 5% (w/w), whereas at concentration 10% (w/w) no flame was obtained.

3.4. Retardancy mechanisms

The shift of all thermal analysis curves to higher or lower values (referred to combustion or pyrolysis, respectively) can be explained with reference to the decomposition mechanism of fire retardants examined.

Ammonium phosphates and sulphates act via a dehydration mechanism of acids (phosphoric or sulphuric acid) and ammonia, formed during their thermal decomposition, directing the degradation pathway of cellulose towards more char production and fewer volatiles [12].

The retardancy effect of DAP and MAP can be explained by their thermal decomposition, which takes place according to the following scheme [35]:

$$(NH_4)_2HPO_4 \rightarrow NH_4H_2PO_4 + NH_3(g) \qquad (150\,^{\circ}C)$$

$$2NH_4H_2PO_4 \rightarrow (NH_4)_2H_2P_2O_7 + H_2O(g) \qquad (170\,^{\circ}C)$$

$$(NH_4)_2H_2P_2O_7 \rightarrow 2NH_4PO_3 + H_2O(g) \qquad (280\,^{\circ}C)$$

$$2NH_4PO_3 \rightarrow P_2O_5 + 2NH_3(g) + H_2O(g) \qquad (660\,^{\circ}C)$$

Both diammonium and monoammonium phosphates are easily converted to H_3PO_4 because the ammonia cations (NH_4^+) are driven off at low temperatures. The presence of phosphoric acid and phosphorus pentoxide would cause an earlier dehydration of the cellulose of the forest material through reaction with hydroxyl groups of glucosan units. Ammonia also could facilitate the decomposition by reacting with intermediate carbonyl compounds to form glycosylamines or Schiff bases [12].

The thermal degradation of AS can be subdivided into two steps. During the first step, the salt loses ammonia and water at 250 °C forming $(NH_4)_2S_2O_7$. The second step takes place at 300 °C leading to formation of $(NH_4)_3H(SO_4)_2$ and NH_4HSO_4, according to the following equations [37]:

$$2(NH_4)_2SO_4 \rightarrow (NH_4)_2S_2O_7 + 2NH_3 + H_2O \qquad (250\,^{\circ}C)$$

Table 4
Lab-scale smoldering combustion data of *Phillyrea latifolia* (*Pl*) samples, before and after treatment with fire retardants

Sample	Relative ignition delay time (min)	Maximum combustion temperature (°C)	Combustion duration (min)	Temperature Peak area (arbitrary units × 10^4)	Combustion mass residue at 500 °C (%, w/w)
Pl pure	399 (<0.01)	495 (<0.01)	41 (0.02)	62.2 (0.03)	5.2 (0.01)
Pl + Hyd 10%	415 (<0.01)	457 (<0.01)	42 (0.02)	52.5 (0.06)	9.2 (0.01)
Pl + Hun/Hyd 10%	407 (<0.01)	446 (<0.01)	42 (0.02)	52.8 (<0.01)	10.8 (<0.01)
Pl + DAP 10%	409 (<0.01)	374 (<0.01)	34 (0.06)	31.7 (0.09)	14.2 (<0.01)
Pl + MAP 10%	411 (<0.01)	391 (<0.01)	34 (0.03)	34.4 (0.08)	15.8 (<0.01)
Pl + AS 10%	428 (<0.01)	445 (<0.01)	46 (0.04)	52.5 (0.06)	5.3 (0.01)
Pl + CR 10%	416 (<0.01)	388 (<0.01)	44 (0.02)	49.6 (0.04)	6.8 (0.01)

Table 5
Flame spread data of *Phillyrea latifolia* (*Pl*) samples, before and after treatment with fire retardants

Sample	Burning rate (mm s^{-1})	Flame duration (s)	Flame height (mm)	Max flame height (mm)	Flame intensity (kW m^{-1})
Pl pure	0.79 (0.03)	373 (0.01)	25.7 (0.1)	75.0 (0.04)	313.0 (0.05)
Pl + Hyd 10%	0.27 (0.01)	716 (0.04)	14.0 (0.1)	22.0 (0.06)	84.0 (0.04)
Pl + Hun/Hyd 10%	0.45 (0.02)	541 (0.03)	19.0 (0.1)	27.0 (0.06)	163.0 (0.03)
Pl + DAP 5%	0.37 (0.03)	509 (0.05)	15.0 (0.1)	23.8 (0.08)	97.0 (0.09)
Pl + DAP 10%	n.f.	n.f.	n.f.	n.f.	n.f.
Pl + MAP 5%	0.36 (0.03)	520 (0.05)	16.3 (0.1)	25.0 (0.07)	117.0 (0.04)
Pl + MAP 10%	n.f.	n.f.	n.f.	n.f.	n.f.
Pl + AS 5%	0.19 (0.02)	710 (0.05)	21.0 (0.1)	35.2 (0.06)	202.0 (0.06)
Pl + AS 10%	n.f.	n.f.	n.f.	n.f.	n.f.
Pl + CR 5%	0.30 (0.04)	892 (0.04)	20.5 (0.1)	40.0 (0.05)	192.0 (0.05)
Pl + CR 10%	n.f.	n.f.	n.f.	n.f.	n.f.

n.f., no flame.

$$2(NH_4)_2SO_4 \rightarrow 2NH_4HSO_4 + 2NH_3 \qquad (300\,^{\circ}C)$$

$$3(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + (NH_4)_3H(SO_4)_2 + 2NH_3 \qquad (300\,^{\circ}C)$$

The pyrosulphate is chemically unstable and decomposes at 350 °C to SO_3 and NH_4HSO_4, according to the following equation [36]:

$$(NH_4)_2S_2O_7 \rightarrow NH_4HSO_4 + SO_3 + NH_3 \qquad (350\,^{\circ}C)$$

In contrast, the mineral hydromagnesite and the mixture of minerals huntite and hydromagnesite have different fire retardancy behaviour, comparatively to DAP, MAP and AS. Their action can be explained by their endothermic thermal decomposition to gaseous CO_2 and H_2O, which however takes place at relatively high temperatures (i.e. above 350 °C), according to the theory of dilution by non-combustible gases and thermal theory.

The thermal decomposition of hydromagnesite is according to the following equations [37,38]:

$$Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O \rightarrow 4MgCO_3{\cdot}Mg(OH)_2 + 4H_2O \qquad (< 250\,^{\circ}C)$$

$$MgCO_3{\cdot}Mg(OH)_2 \rightarrow MgCO_3 + MgO + H_2O(\text{Fig.3, peak1}) \qquad (250\text{–}350\,^{\circ}C)$$

$$MgCO_3 \rightarrow MgO + CO_2 \qquad (\text{Fig.3, peak2}) \qquad (350\text{–}550\,^{\circ}C)$$

The following equations can be attributed to the thermal decomposition of huntite [39]:

$$Mg_3Ca(CO_3)_4 \rightarrow CaCO_3{\cdot}nMgCO_3 + (3-n)MgO + (3-n)CO_2 \qquad (570\text{–}620\,^{\circ}C)$$

(Mg-calcite)(n gradually changes with increasing temperature from 0.2 to 0.05),

$$CaCO_3{\cdot}nMgCO_3 \rightarrow nMgO + CaO + (1+n)CO_2 \qquad (750\text{–}920\,^{\circ}C)$$

($n \leq 0.05$).

The above minerals endothermically decompose at temperatures between 200 and 400 °C, liberating water steam and carbon dioxide, which are both non-combustible. In addition, the decomposition of magnesium carbonate and magnesium hydroxide are endothermics causing a decrease in the temperature of the flame. Besides the cooling effect and quenching of the flames by inert gases, fire retardancy is also enhanced by a kind of ceramic layer being formed on the compound surface that protects the ignitable materials from further attacks by flames and heat [7].

4. Conclusions

The performance of minerals huntite and hydromagnesite as forest fire retardants has been evaluated by combining thermal analysis with laboratory-scale tests. The most interesting conclusions are:

1. As far as combustion is concerned, the minerals increased considerably ignition delay time and mass residue values of forest species *P. latifolia*, regardless the used experimental conditions.
2. On pyrolysis of forest species, both minerals exhibit satisfactory retardancy performance, by shifting DTG peaks to lower temperature values and increasing the mass residue.
3. Huntite/hydromagnesite demonstrated better performance than pure hydromagnesite, based on the increase of mass residue. Contrary results were recorded, regarding the shift of DTG curves to higher or lower (combustion/pyrolysis) temperatures. This leads to the conclusion that the highest overall retardancy performance can be obtained by using mixtures of the above minerals.

4. Regarding pyrolysis, retardants that are already in commercial use (DAP, MAP and AS) basically affect the decomposition of cellulose, whereas the minerals seem to affect mainly lignin decomposition. This enhances the potential of using mixtures, in order to achieve the highest overall retardancy performance. However, the commercial retardants are much more efficient on fire spread tests, when the same concentration level is applied.

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