



## Evaluating the use of minerals as forest fire retardants

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### ABSTRACT

The fire retardancy of carbonate minerals hydromagnesite, huntite and natural mixtures of hydromagnesite and huntite, on forest species was tested by analytical (differential thermogravimetry under air atmosphere) and laboratory-scale (flame spread test) methods. The selected forest species (*Pinus halepensis* Mill. and *Cistus incanus* L.) were collected from a wildland/urban interface zone near Athens and were treated with 5%, 10%, 15% and 20% w/w of the minerals. On the basis of differential thermogravimetric analysis, minerals decrease forest species combustibility (by increasing maximum weight loss rate and combustion duration) and consumability (by increasing combustion mass residue) and increase their sustainability (by increasing combustion duration). Additionally, the flame spread tests indicate that the minerals decrease forest species ignitability (increase time for ignition) and combustibility (decrease flame spread rate, maximum flame height and mean flame intensity), and affect their sustainability (by increasing the flame duration) and consumability (by increasing the mass residue). Among minerals examined, the most efficient retardant was the mixture of huntite and hydromagnesite.

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### 1. Introduction

Wildland fires represent a serious problem, burning thousands of hectares all over the world each year. Fire retardant studies on forest species are very important for forest fire management.

Flammability of forest species is a combination of ignitability, sustainability, combustibility and consumability. Ignitability determines how easily the fuel ignites; sustainability is a measure of the ability to maintain the combustion reaction with or without a heat source; combustibility reflects the rapidity with which a fuel is consumed; consumability accounts for the completeness of combustion (mass loss as proportion of total mass) [1–4].

Thermal degradation of forest fuels comprises two consecutive steps [5]. 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 ash and mineral ash [6–10].

The second step is combustion, which is a rapid exothermic physical chemical process [5]. There are two different types of combustion: flaming (or gas-phase) and glowing combustion. The combustion of volatiles (gas-phase combustion) and the heat produced from it accelerates the rate of pyrolysis, increasing the release of combustible gases. Glowing combustion is the solid-

phase combustion of char and normally follows flaming combustion, until only ash residue remains [5,11,12].

Two types of ignition are distinguished, piloted and spontaneous. In piloted ignition, flaming is usually initiated with an electrical spark or a flame, whereas in spontaneous ignition, it is developed spontaneously by heating the fuel [2].

Long-term fire retardants are used to modify the burning process. Depending on their nature, fire retardants can act chemically and/or physically in the solid or gas phase [11]. They are applied ahead of a wildfire front to reduce the rate of fire spread and intensity. They can inhibit combustion even after the loss of their watery matrix [11,13]. Among them, diammonium phosphate (DAP), monoammonium phosphate (MAP), ammonium polyphosphate (APP) and ammonium sulfate (AS) have been the most used [11]. However, their relatively high cost tends to restrict their wide use globally. In addition, the acidic compounds produced by their thermal decompositions may cause environmental problems. For instance, it was reported that the use of DAP facilitates extraction of some toxic metals (i.e., Zn, Mn, Cu) from ground, due to the acidic conditions set by its decomposition to phosphoric acid [14]. Therefore, obtaining new chemical retardants (such as minerals), of low cost and environmental impact, to be applied in forest fires extinction operations, is very important.

The use of minerals as fire retardants for polymers has been already reported in the literature [15–17]. The mixture of huntite and hydromagnesite is a very effective flame retardant additive for polymers and it has been in the market since the late 1980s.

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## Nomenclature

APP	ammonium polyphosphate
AS	ammonium sulfate
Ci	<i>Cistus incanus</i>
CMR	combustion mass residue
DAP	diammonium phosphate
DTG	differential thermogravimetry
<i>I</i>	flame intensity
<i>h</i>	mean flame height
HunHyd	huntite/hydromagnesite mixture
Hun	huntite
Hyd	hydromagnesite

MAP	monoammonium phosphate
MWLR	maximum weight loss rate
OCD	overall combustion duration
<i>Ph</i>	<i>Pinus halepensis</i>
RSD	relative standard deviation
WUI	wildland/urban interface

## Subscripts

1	refers to peak 1, first major stage
2	refers to peak 2, second major stage

Commercial huntite and hydromagnesite deposits may be found in the Kozani Basin, located in northern Greece [18]. 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 effectiveness as forest fire retardants has been examined preliminarily and the need for further investigation has been reported [19].

Various analytical techniques have been used for evaluating the performance of fire retardants, such as gas chromatography, Fourier transform infrared spectroscopy, mass spectrometry and thermal analysis [20–30]. However, the small samples used and the rapid removal of pyrolysis or combustion products can lead to erroneous interpretations in terms of forest fuel flammability in real situations. Therefore, the information provided by the analytical methods should be supported by other laboratory-scale fire tests [11].

Among the laboratory-scale tests for measuring flammability, flame spread tests have a primary place. Flame spread is defined as the progress of flame over a surface. It requires that successive section of surface be brought to the ignition temperature as a result of heat flux from the advancing flame [31]. Flame spread can also be considered as an advancing ignition front in which the leading edge of the flame acts both as the source of heat and as the source of pilot ignition [32]. Blakely has developed a laboratory-scale flame spread method for determining the effectiveness of forest fire retardants, using fuel beds of forest species, sprayed with the retardants [33]. This test is, however, tedious and has low reproducibility.

The cone calorimeter, a common bench-scale apparatus that uses oxygen consumption to obtain heat release rate, has also been used for fire retardancy measurements on wood products [34–37]. This equipment, apart from its high cost, is applied with reproducible results on rather solid and thick materials (such as building materials, plastics, wood boards, wood products, etc.) than on foliar samples.

In the present work, the use of carbonate minerals as forest fire retardants was evaluated using an analytical technique (DTG) and a new laboratory-scale flame spread method, based on a specifically constructed apparatus. Combining the above techniques, the influence of carbonate minerals on all flammability parameters (i.e., ignitability, combustibility, sustainability and consumability) of forest species was examined.

## 2. Experimental

### 2.1. Materials and sample preparation

The forest species used – *Pinus halepensis* Mill. (Aleppo pine) and *Cistus incanus* L. (Pink rockrose) – were selected because they are very

common in Mediterranean wildland/urban interface regions. According to a previous report, *P. halepensis* is a highly flammable forest fuel, whereas *C. incanus* is of low flammability [2].

The samples were mature foliage and were collected on 25 February 2008, after a long drought period, to avoid moisture effects, such as microbes (i.e., fungi, molds and bacteria) growth [38]. Foliage samples were collected from “Thrakomacedones”, a WUI area located at the confines of mountain Parnitha, northern Athens (Greece). The geographical coordinates of the sampling site are 38° 08′ 12″ N, 23° 45′ 21″ E; its altitude is 423 m; its average inclination is 30%; its exposition is E (90°); its dominating petrologic formation consists of old scree and talus cones. The collected foliage samples were placed into firmly closed polyethylene bags and were brought immediately to the laboratory. The samples were first dried in a vacuum oven for 24 h under a pressure of 10 Torr and a temperature of 60 °C and were then ground. A fraction between 0.1 and 0.2 mm was separated and used for the tests.

The minerals used in this study (hydromagnesite, huntite and a natural huntite/hydromagnesite mixture at the ratio 60%/40%) were mined from the Kozani basin. They were ground and a fraction of less than 20 μm was selected and used for the tests.

The retardant treated samples were prepared by thoroughly mixing the forest species powder with the retardant powder and the sample uniformity was checked with a reflected-light microscope. The amount of retardant applied on forest species varied by 5–20% w/w. Prior to the tests, the samples were placed into a conditioning box (32 °C and relative humidity 12%) for 24 h, to attain a minimum level of moisture content (2.8%) [39].

### 2.2. Methods

#### 2.2.1. Thermal analysis

Each sample of 15–17 mg, was introduced into an open type alumina ( $Al_2O_3$ ) 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<sup>-1</sup>, using a Mettler Toledo TGA/SDTA 851 module.

The heating rate employed was relatively low, to increase the resolution of DTG peaks and to minimize the deviation between sample and oven temperature. The atmosphere chosen was air, with a flow rate of 100 mL min<sup>-1</sup>, to achieve complete combustion.

Fire retardancy evaluation was based on the following TG/DTG analysis data, recorded by the STAR-e software system of Mettler Toledo apparatus:

1. Maximum weight loss rate (MWLR). These parameters refer to the peak heights of DTG graphs and it was measured in

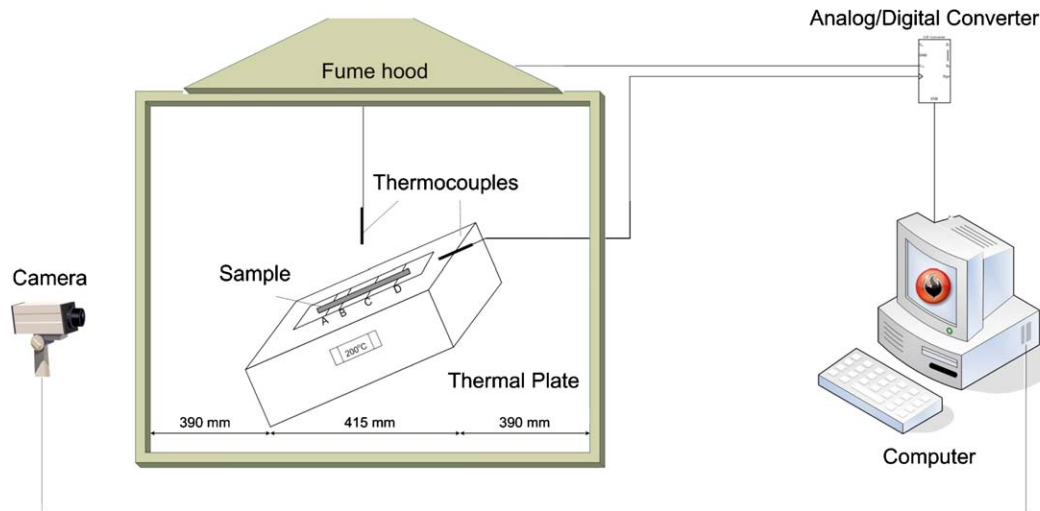


Fig. 1. Diagrammatic representation of apparatus used for the flame spread tests.

- $\% \text{ min}^{-1}$ . MWLR is related to fuel combustibility; retardants should decrease MWLR values, according to their efficiency [19].
- Overall combustion duration (OCD). This was measured in minutes by subtracting the onset from the endset values of DTG peaks. This parameter may be related to the combustibility, as well as to the sustainability of forest fuels. Efficient retardants are expected to increase OCD values [40].
  - Combustion mass residue of forest species (CMR). It was determined at a temperature of  $600^\circ\text{C}$ , in  $\% \text{ w/w}$  units. It is related to the consumability of fuel. The retardant additives should increase CMR values, according to their efficiency [19,23,27,41].

### 2.2.2. Flame spread tests

The apparatus used for the flame spread tests is shown in Fig. 1. Design and construction details of this apparatus are given in previous publications [2,19].

The aluminum heating plate of  $410 \text{ mm} \times 260 \text{ mm}$  was placed at the center of the fume hood. The thermocouple was placed above the heating plate at  $20 \text{ cm}$  and the other one is directly connected to the heating plate. The web camera was placed in front of the fume hood.

For this series of experiments the aluminum heating plate was placed at  $30^\circ$  inclination (Fig. 1) to determine the flame spread rate upwards, because: (a) the flame spread is favored on inclined surfaces [32] and (b) the Mediterranean terrain contains many steep inclinations. Also, the main inclination in the Thrakomacedones region is  $30^\circ$ .

Ten grams of powder samples were placed on the alumina sample holder plate via a train mold. The sample holder with the loaded sample was placed on the heating plate to keep the sample at  $75\text{--}80^\circ\text{C}$ . The heating plate ensures standard initial temperature conditions in samples. Four lines were marked on the sample holder plate (A–D). Line A indicates the start of the sample path (bottom edge of the sample), whereas lines B and C indicate the start and end points, respectively, for measuring the time that the front of the flame passes through these lines. Finally, line D indicates the end of the sample path (top edge of the sample), where the flame gets extinguished.

A hot flame (at least  $1000^\circ\text{C}$ ) from a propane burner (diameter about  $5 \text{ mm}$ ) was applied to the start of sample path (line A) until ignition, and the time for ignition was recorded. When ignition occurred, the stopwatch was set to measure flaming combustion

time from line B to C ( $100 \text{ mm}$ ). These lines (A,B,C) are marked on the sample holder for the previous measurements. Thus, the mean flame spread rate was determined in  $\text{mm s}^{-1}$ . The air velocity during experiments was approximately  $0.7 \text{ m s}^{-1}$  (measured by an anemometer).

The test was replicated six times, using a clean cool sample holder each time, and the RSD values were determined. The whole test was video recorded and the instantaneous flame height, maximum flame height and flame intensity were determined. Flame height measurements were taken every  $5 \text{ s}$  and the mean flame intensity was calculated by [5]

$$I = 273(h)^{2.17} \quad (1)$$

which applies in turbulent flames, where  $I$  is the flame intensity ( $\text{kW m}^{-1}$ ) and  $h$  the mean flame height (m), measured by a video recording camera [2,19].

In addition, the flame duration was recorded by measuring the time of flame from line B until the flame is extinguished. Mass residue values ( $\% \text{ w/w}$ ) were also determined.

Based on the flame spread experiments, the following parameters were determined to evaluate the fire retardancy of the minerals examined: (1) time for ignition (s); (2) flame spread rate ( $\text{mm s}^{-1}$ ); (3) maximum flame height (mm); (4) mean flame intensity ( $\text{kW m}^{-1}$ ); (5) flame duration (s) and (6) combustion mass residue ( $\% \text{ w/w}$ ).

The retardants should increase time for ignition (related to ignitability), decrease parameters 2–4 (related to combustibility), decrease parameter 5 (related to sustainability) and increase combustion mass residue (related to consumability) [19,23,27,41].

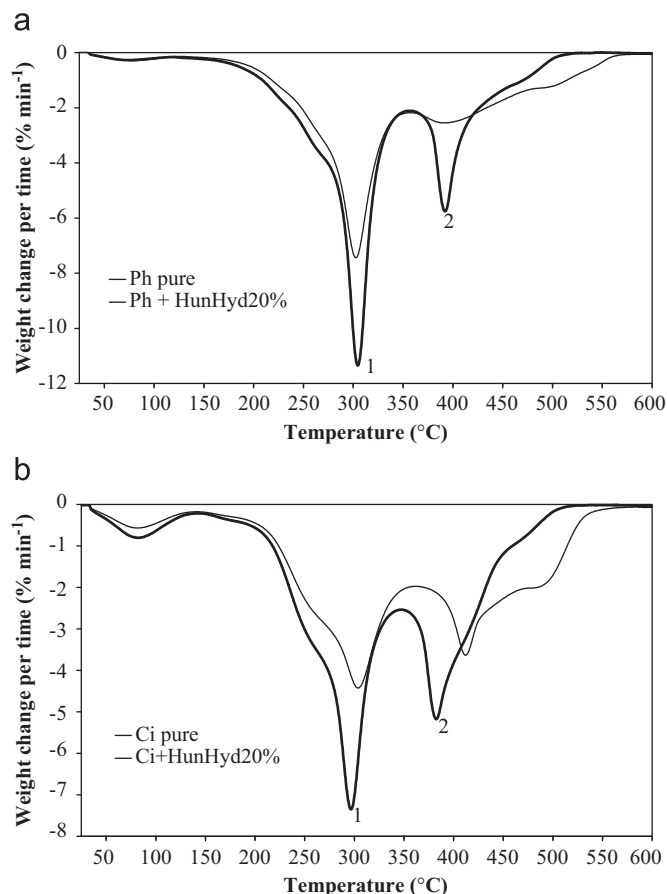
## 3. Results and discussion

### 3.1. Thermal analysis in air atmosphere

Representative DTG curves of forest species, untreated and treated with 20% huntite/hydromagnesite mixture in air atmosphere conditions are shown in Fig. 2. Both stages (peaks 1 and 2) are different reaction decomposition schemes for solid degradation that may involve oxidative pyrolysis. The TG/DTG analysis data of *P. halepensis* and *C. incanus*, before and after treatment with hydromagnesite (Hyd), huntite (Hun) and huntite/hydromagnesite mixture (HunHyd) are shown in Tables 1 and 2.

Each value in Tables 1 and 2 is the mean of three replicate measurements, with RSD lower than 3%.

The minerals examined decrease the MWLR<sub>1</sub> value (Tables 1 and 2), indicating reduced combustibility of the fuels. Overall, the best performance is exhibited by 20% huntite/hydromagnesite. Thus, the application of 20% HunHyd decreases the MWLR<sub>1</sub> value of *P. halepensis* by 34.5% and the one for *C. incanus* by 40.5%. Similar results were obtained for the 2nd peak stage (decrease of MWLR<sub>2</sub>, Tables 1 and 2). The application of 20% HunHyd caused a decrease of 56.9% in the MWLR<sub>2</sub> value of *P. halepensis*, whereas application of huntite to *C. incanus* caused MWLR<sub>2</sub> to decrease by 38.5%.

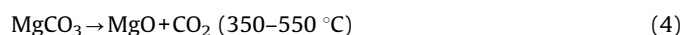
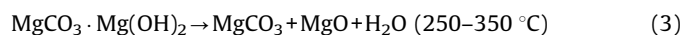
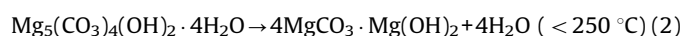


**Fig. 2.** Representative DTG curves of: (a) *P. halepensis* (Ph) and (b) *C. incanus* (Ci), before and after treatment with 20% mineral mixture huntite/hydromagnesite (HunHyd), in air atmosphere conditions.

Furthermore, the 2nd stage (peak 2) combustion is shifted to higher temperatures, which indicated an increase in the overall combustion duration of forest fuels (increase of OCD, Tables 1 and 2). Thus, the minerals increase the sustainability and further reduce the combustibility of fuels. Based on the OCD data, the huntite/hydromagnesite mixture exhibits the best performance among the minerals tested (i.e., application of 20% HunHyd causes an increase of 5.6 min in *P. halepensis* and 3.4 min in *C. incanus*, Tables 1 and 2).

The presence of minerals also reduces the consumability of forest fuels by increasing the mass residue (increase of CMR, Tables 1 and 2). Based on CMR measurements, the best performance is exhibited by the huntite/hydromagnesite mixture on *P. halepensis* and huntite on *C. incanus* (i.e., application of 20% HunHyd on *P. halepensis* causes a CMR increase of 198.2% and application of 20% Hun on *C. incanus* causes a CMR increase of 88.2%).

The influence of carbonate minerals hydromagnesite, huntite and their mixture on the flammability parameters of forest fuels can be interpreted by their endothermic thermal decompositions. Hydromagnesite decomposes according to [42,43]

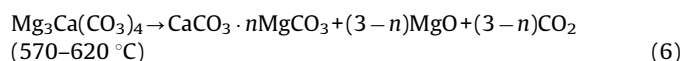


MgO is hydrolysed by water formed during pyrolysis, according to

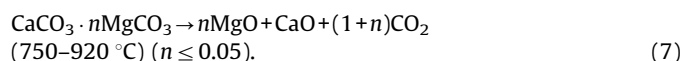


The hydroxyl ions, in accordance with the Lewis acid theory, cause dehydration of cellulose (the main constituent of forest species), through the formation of carbanions, altering the rate of its decomposition.

Huntite decomposes according to Eq. (6) and (7)[44]:



(*n* gradually changes with increasing temperature from 0.2 to 0.05),



**Table 1**

TG/DTG analysis data of *P. halepensis* (Ph), before and after treatment with Hyd, Hun and HunHyd minerals (5–20% w/w), under air atmosphere (combustion conditions).

Sample	MWLR <sub>1</sub> (% min <sup>-1</sup> )	MWLR <sub>2</sub> (% min <sup>-1</sup> )	OCD (min)	CMR at 600 °C (% w/w)
Ph untreated	11.3	5.8	29.2	5.6
Ph+5% Hyd	7.0	6.4	31.5	8.6
Ph+10% Hyd	7.1	5.5	32.0	9.8
Ph+15% Hyd	7.6	4.8	32.8	12.2
Ph+20% Hyd	7.9	4.2	33.2	14.1
Ph+5% Hun	10.1	4.0	31.9	9.1
Ph+10% Hun	9.0	3.2	32.9	11.9
Ph+15% Hun	8.4	2.9	33.7	13.6
Ph+20% Hun	7.7	2.7	34.6	16.1
Ph+5% HunHyd	9.3	4.2	31.9	9.1
Ph+10% HunHyd	8.9	3.3	33.3	11.2
Ph+15% HunHyd	7.8	2.8	34.2	13.8
Ph+20% HunHyd	7.4	2.5	34.8	16.7

The above reactions liberate water and carbon dioxide, which are both non-combustible. In addition, the decomposition reactions of  $\text{MgCO}_3$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{CaCO}_3$  are endothermic and cause a further decrease in flame temperature. Apart from the cooling effect and quenching of the flames by inert gases, fire retardancy of carbonate minerals is also enhanced by a kind of ceramic layer being formed on the surface of forest fuels that protects the ignitable materials from further attack by flames and heat [19].

### 3.2. Flame spread tests

Typical photos taken from video recordings of the flame spread tests are shown in Figs. 3 and 4. Also, data taken from the flame spread tests are presented in Tables 3 and 4. The data derived from the flame spread test of *P. halepensis* and *C. incanus* were time for ignition, flame spread rate, maximum flame height, mean flame intensity, flame duration and mass residue. The values

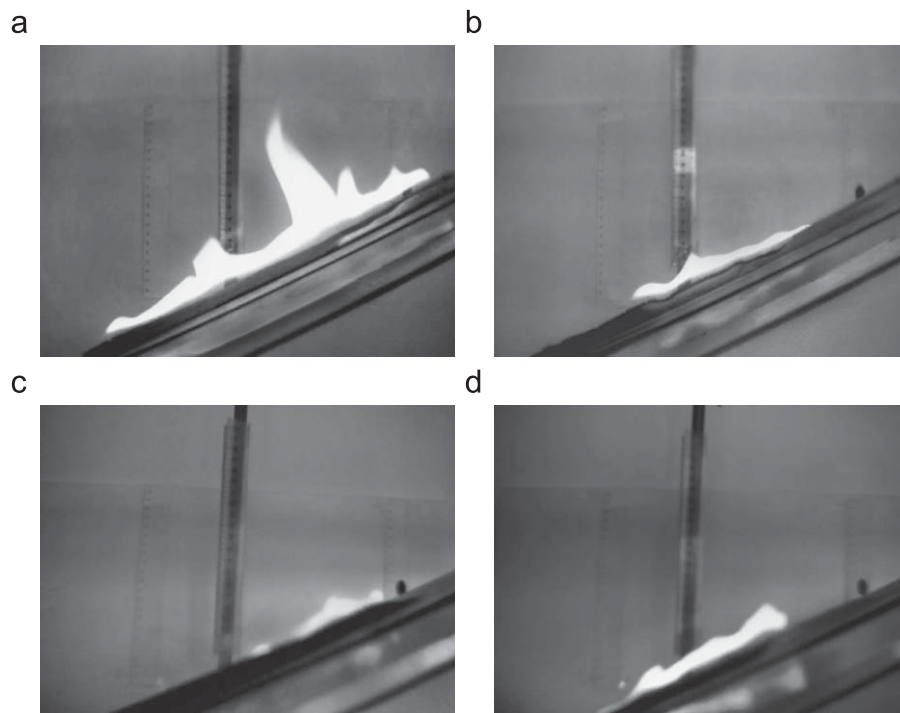
given in Tables 3 and 4 are the means of six replicate measurements, with RSD values lower than 5%.

Among the samples examined, those that did not ignite were *P. halepensis* treated with 20% hydromagnesite and *C. incanus* treated with 15% and 20% of all minerals (Tables 3 and 4). Also, *P. halepensis* treated with 15% hydromagnesite, 20% huntite and 20% huntite/hydromagnesite did not undergo flaming combustion for the whole length of 100 mm, but only for 42.0, 56.5 and 52.0 mm (mean values of six replicate tests), respectively. Similarly, the *C. incanus* samples treated with 5% hydromagnesite, 5% huntite and 5% huntite/hydromagnesite burnt only for 22.0, 35.0 and 30.0 mm (mean values of six replicate tests), respectively. For the above mentioned samples, the flame spread rate measurements were based on the above length values.

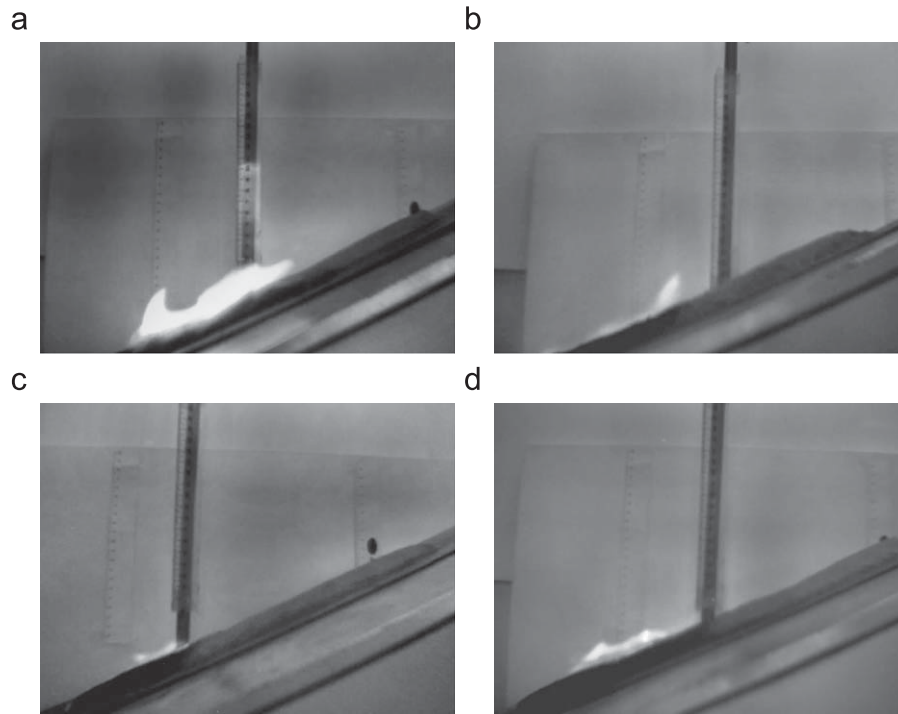
Minerals reduce the ignitability of forest fuels by increasing the time for ignition (Tables 3 and 4). Based on these time for ignition measurements, hydromagnesite exhibits the best performance on *C. incanus* and huntite/hydromagnesite on *P. halepensis* (i.e., application of 10% Hyd on *C. incanus* increases the time for

**Table 2**  
TG/DTG analysis data of *C. incanus* (Ci), before and after treatment with Hyd, Hun and HunHyd minerals (5–20% w/w), under air atmosphere (combustion conditions).

Sample	MWLR <sub>1</sub> (% min <sup>-1</sup> )	MWLR <sub>2</sub> (% min <sup>-1</sup> )	OCD (min)	CMR at 600 °C (% w/w)
Ci untreated	7.4	5.2	31.1	11.9
Ci+5% Hyd	6.2	4.8	31.9	13.4
Ci+10% Hyd	5.9	4.7	32.7	14.4
Ci+15% Hyd	5.4	4.5	32.9	15.9
Ci+20% Hyd	5.1	4.5	33.0	17.7
Ci+5% Hun	6.4	5.0	31.6	14.6
Ci+10% Hun	5.8	4.7	32.2	17.2
Ci+15% Hun	5.1	4.3	32.8	20.1
Ci+20% Hun	4.6	3.2	34.0	22.4
Ci+5% HunHyd	5.9	5.1	31.1	13.6
Ci+10% HunHyd	5.5	4.6	32.2	17.3
Ci+15% HunHyd	4.9	4.1	33.4	19.1
Ci+20% HunHyd	4.4	3.6	34.5	20.9



**Fig. 3.** Photos taken from video recording during the flame spread tests of the following samples: (a) *P. halepensis* untreated; (b) *P. halepensis* + 5% Hyd; (c) *P. halepensis* + 5% Hun; (d) *P. halepensis* + 5% HunHyd.



**Fig. 4.** Photos taken from video recording during the flame spread tests of the following samples: (a) *C. incanus* untreated; (b) *C. incanus* + 5% Hyd; (c) *C. incanus* + 5% Hun and (d) *C. incanus*+5% HunHyd.

**Table 3**

Flame spread data of *P. halepensis* (*Ph*), before and after treatment with Hyd, Hun and HunHyd minerals (5–20% w/w).

Sample	Time for ignition (s)	Flame spread rate (mm s <sup>-1</sup> )	Max. flame height (mm)	Mean flame intensity (kW m <sup>-1</sup> )	Flame duration (s)	Combustion mass residue (% w/w)
<i>Ph</i> untreated	3.50	2.14	75.0	310	117	19.0
<i>Ph</i> +5% Hyd	6.90	1.72	53.0	166	148	27.4
<i>Ph</i> +10% Hyd	8.70	1.50	38.0	51.0	134	40.6
<i>Ph</i> +15% Hyd	10.1	1.38	13.0	4.40	59.7	48.7
<i>Ph</i> +20% Hyd	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.
<i>Ph</i> +5% Hun	8.20	1.74	56.0	181	128	38.5
<i>Ph</i> +10% Hun	10.7	1.57	44.0	106	58.7	45.6
<i>Ph</i> +15% Hun	11.3	1.43	35.0	57.8	41.0	58.6
<i>Ph</i> +20% Hun	12.2	1.13	18.0	35.3	36.3	60.5
<i>Ph</i> +5% HunHyd	8.00	1.73	55.0	173	135	33.7
<i>Ph</i> +10% HunHyd	9.50	1.54	40.0	62.2	125	41.7
<i>Ph</i> +15% HunHyd	11.1	1.44	27.0	53.6	99.2	52.0
<i>Ph</i> +20% HunHyd	12.8	1.30	20.0	27.6	30.7	55.2

n.f.: no flame.

**Table 4**

Flame spread data of *C. incanus* (*Ci*), before and after treatment with Hyd, Hun and HunHyd minerals (5–20% w/w).

Sample	Time for ignition (s)	Flame spread rate (mm s <sup>-1</sup> )	Max. flame height (mm)	Mean flame intensity (kW m <sup>-1</sup> )	Flame duration (s)	Combustion mass residue (% w/w)
<i>Ci</i> untreated	10.2	1.36	20.0	40.4	49.0	21.9
<i>Ci</i> +5% Hyd	14.8	0.90	14.0	11.5	12.7	33.8
<i>Ci</i> +10% Hyd	15.7	n.f.	n.f.	n.f.	n.f.	n.f.
<i>Ci</i> +15% Hyd	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.
<i>Ci</i> +20% Hyd	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.
<i>Ci</i> +5% Hun	14.0	0.97	18.0	18.6	8.0	41.2
<i>Ci</i> +10% Hun	15.0	n.f.	n.f.	n.f.	n.f.	n.f.
<i>Ci</i> +15% Hun	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.
<i>Ci</i> +20% Hun	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.
<i>Ci</i> +5% HunHyd	13.9	0.95	17.0	16.4	6.50	38.8
<i>Ci</i> +10% HunHyd	15.0	n.f.	n.f.	n.f.	n.f.	n.f.
<i>Ci</i> +15% HunHyd	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.
<i>Ci</i> +20% HunHyd	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.

n.f.: no flame

ignition 54%, whereas 20% HunHyd on *P. halepensis* causes an increase of 266%).

Minerals reduce the combustibility of forest fuels by decreasing the flame spread rate, the maximum flame height and the mean flame intensity (Figs. 3 and 4; Tables 3 and 4). Based on these data, we found that hydromagnesite exhibits better performance than the other minerals examined. Thus, application of 15% Hyd on *P. halepensis* causes a flame spread rate decrease of 36%, a maximum flame height decrease of 83% and a mean flame intensity decrease of 99%, whereas application of 5% Hyd on *C. incanus* causes a flame spread rate decrease of 34%, a maximum flame height decrease of 30% and a mean flame intensity decrease of 72%.

Minerals also affect the sustainability of forest fuels by modifying the flame combustion duration (Tables 3 and 4). Thus, by applying 5–10% Hyd (or HunHyd) or 5% Hun on *P. halepensis*, the sustainability increases, due to the flaming combustion retardation (Figs. 3 and 4). On the contrary, application of 15–20% Hyd (or HunHyd) or 10–20% Hun reduces the sustainability of *P. halepensis*, since the flame is retained. Similarly, the flame duration of *C. incanus* decreases by the presence of minerals, with the mixture of huntite/hydromagnesite exhibiting the best performance (i.e., 5% HunHyd on *C. incanus* decreased flame duration at 87%).

Finally, the presence of minerals affects the consumability of forest fuels by increasing the combustion mass residue (Tables 3 and 4). Huntite exhibits the best performance among all minerals examined. Thus, application of 20% Hun on *P. halepensis* causes a combustion mass residue increase of 218%, whereas the application of 5% Hun on *C. incanus*, 88%. However, the major part of mass residue obtained in the mineral treated forest species (especially huntite) is due to the undecomposed mineral added.

The above effects of minerals on forest species flammability properties can be interpreted by the thermal decomposition reactions stated earlier. However, huntite's retarding capacity is mainly attributed to the formation of a ceramic layer on the forest species particles, protecting them from flame and heat, because the average temperature recorded during the flame spread tests (600 °C, measured by a thermocouple) was found to be below the thermal decomposition temperatures of huntite.

#### 4. Conclusions

Two simple methods were employed for measuring the fire retardancy in terms of forest species flammability. The first was based on DTG analysis, under air atmosphere and the second was a flame spread test. These methods were applied for testing fire retardancy of carbonate minerals "(i.e., hydromagnesite, huntite and natural mixtures of huntite and hydromagnesite)" on combustion of *P. halepensis* and *C. incanus*. Applying these methods, all flammability parameters (ignitability, combustibility, sustainability and consumability) can be determined.

It is not expected that forest species in actual wildfire conditions exhibit the same flammability properties as the particle flammability measured in this work. However, the particle flammability measurements are far more consistent than the foliar ones and can be used for comparison purposes [19,45]. The data provided on a numerical scale can be used for comparison purposes in order to develop retardants for real forest fires.

The following conclusions were drawn:

1. On the basis of DTG analysis, the minerals decrease the combustibility of forest fuels, by decreasing the MWLR<sub>1</sub> and MWLR<sub>2</sub> (1st and 2nd peak stage) of combustion and by increasing the overall combustion duration of forest fuels. Also, the minerals increase the sustainability of forest fuels by increasing their overall combustion duration and decrease the consumability by increasing their combustion mass residue.
2. Similar results were obtained with the flame spread tests. Thus, the minerals decrease: (a) the ignitability of forest fuels, by increasing the time for ignition; (b) the combustibility of forest fuels, by decreasing the flame spread rate, the maximum flame height and the mean flame intensity; (c) the consumability of forest fuels by increasing the combustion mass residue and (d) the sustainability (in contrast to DTG analysis findings) by increasing the flame duration.
3. Based on the flame spread rate, maximum flame height and mean flame intensity measurements, hydromagnesite exhibits the best fire retarding performance, among all minerals examined. Huntite exhibits the best performance, based on the combustion mass residue data and huntite/hydromagnesite has the best one regarding MWLR and combustion duration data. Hence, mixtures of huntite and hydromagnesite can lead to the highest overall fire retardant performance.
4. The retardant efficiency increases with the amount of mineral applied on forest species (i.e., the best overall performance was achieved by 20% application).
5. Comparing the performance of these minerals with other fire retardants in common use (DAP, MAP and AS), based on similar experimental studies, we found that the minerals overall are less effective than commonly used long-term forest fire retardants [19]. However, the acidic compounds produced by the thermal decomposition of those common use retardants may cause serious environmental problems [14]. Moreover, the extraction of minerals studied from Greek mines in large quantities, with relatively low cost, supports their potential for commercial use [19].

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