

FOREST FIRE RETARDANCY EVALUATION OF CARBONATE MINERALS USING DTG AND LOI

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Two methods were employed for measuring fire retardancy of minerals hydromagnesite, huntite and natural hydromagnesite/huntite mixtures, on forest species. The first was based on DTG under N₂ atmosphere, to isolate pyrolysis of forest species and the second on LOI for combustion measurements. The selected forest species: *Pinus halepensis* Mill. and *Cistus incanus* L., were collected from a WUI zone and were treated with 5, 10, 15 and 20 mass/mass% of minerals. Regarding DTG analysis, the minerals decrease pyrolysis rate and increase mass residue of forest species. Regarding LOI tests, minerals increase pilot ignitability of forest fuels. Hydromagnesite exhibits the best overall performance.

Keywords: DTG, fire retardancy, hydromagnesite and huntite minerals, LOI, WUI forest species

Introduction

Wild forest fires comprise a serious problem, burning thousands of hectares all over the world each year. In Greece, during the last 30 years, a serious fire problem in wildland/urban interfaces has been observed, mostly intensified around metropolitan and tourist locations. Wildland/urban (WUI) is the area where houses meet or intermingle with undeveloped wildland vegetation and is composed of both interface and intermix communities. Their development, due to either the expansion of large cities or the development of summer housing, coincides with the increase in both forest fire numbers and burnt areas [1]. Therefore, the research on flammability of forest species and furthermore, fire retardant studies on forest species, are very important to forest fire management.

Combinations of various techniques are used for fighting forest fires. Among them, very important are those involving fire-fighting chemicals [2]. These include: (1) long-term retardants, which inhibit combustion even after the loss of their watery 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; (4) wetting agents, which reduce the surface tension of water and increase its spreading ability [3].

Among the long-term forest fire retardants, diammonium phosphate (DAP), monoammonium phosphate (MAP), ammonium polyphosphate (APP) and

ammonium sulphate (AS) have dominated use [4]. However, their relatively high cost tends to restrict their wide use globally. Therefore, new chemicals should be introduced in the sector of forest fire retardancy, to reduce end product cost.

The use of minerals as fire retardants for polymers has already been reported in [5–9]. Huntite [Mg₃Ca(CO₃)₄] and hydromagnesite [Mg₅(CO₃)₄(OH)₂·4H₂O] are classified as salt type carbonate minerals. Their effectiveness as forest fire retardants has preliminary been tested on *Phillyrea latifolia* L. (Mock privet) and the need for further investigation has been reported [10]. Moreover, their extraction from Greek mines in large quantities with relatively low cost, supports their potential for commercial fire retardant use [11].

Various analytical techniques have been used for evaluating the performance of fire retardants and investigating their mechanism, such as: gas chromatography, Fourier transformation infrared spectroscopy, mass spectrometry and thermal analysis [2, 12–23]. 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 forest species fire retardancy should be supported by other lab-scale fire tests [4].

Blakely has developed a lab-scale method for determining the effectiveness of fire retardants according to their ability to extinguish combustion recovery. He used fuel beds of forest species, which he

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sprayed with the retardant formulations and then placed in a wind tunnel for the tests [24, 25]. The U.S. department of agriculture (USDA) has suggested a flame spread test in a 25-ft tunnel, for measuring fire retardancy [26, 27]. Also, the cone calorimeter, a common bench-scale apparatus, has been used for fire retardancy measurements on wood products [27–29]. However, the above methods do not measure all the parameters of flammability [30]. In addition, they have high equipment and operation cost.

Another direct and reliable method for measuring combustibility is the limiting oxygen index (LOI) method, which measures the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that will just support flaming combustion [31]. High flammable materials are likely to have a low oxygen index. The LOI test is inexpensive, easy to run and reproducible [32, 33]. It has been formalized as an ASTM method, for measuring the pilot ignitability of polymers, using planar shape samples [34], and for evaluating the flame retardant properties of various polymer additives [35–37]. However, this method has not been yet applied on particle ignitability measurements.

This work aims: (1) to employ low cost methods for fire retardancy studies on forest species, by measuring various flammability parameters (i.e., ignitability, sustainability and combustibility) [1], (2) to apply the above methods for evaluating the forest fire retardancy of Greek carbonate minerals (i.e., hydromagnesite, huntite and natural mixtures of huntite and hydromagnesite) and (3) to investigate the mechanism of fire retardancy of minerals examined on forest species. The experiments were performed employing DTG analysis and LOI tests. In previous works, the pyrolysis of cellulose and forest species, as well as the fire retardancy of salts and oxide-hydroxides was studied using thermal analysis [17, 38]. However, under the conditions used, no obvious results on fire retardancy were obtained.

Experimental

Materials and sample preparation

The forest species selected: *Pinus halepensis* Mill. (Aleppo pine) and *Cistus incanus* L. (Pink rockrose) were chosen because they are very common in Mediterranean WUI regions. According to previous report, *P. halepensis* is considered as a high flammable forest fuel, whereas *C. incanus* as a low flammable one [1].

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 [39]. The foliage samples were collected from ‘Thrakomacedones’, which is a

WUI area located at the confines of the national park of mountain Parnitha, northern of Athens in Greece. The sampling site was determined by GPS, it had geographical coordinates: 38° 07′ 50″ N, 23° 46′ 22″ E; altitude 323 m; average inclination 10%; exposition E (97°); and dominating petrologic formation of marls, sandstones and conglomerates. The collected foliage samples were placed into firmly closed polyethylene bags and were brought immediately to the laboratory. The samples were first dried into a vacuum oven for 24 h under pressure of 10 Torr and temperature of 60°C and then were ground. A fraction between 100 and 200 µm was separated and used for the tests.

The examined minerals: hydromagnesite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$], huntite [$\text{Mg}_3\text{Ca}(\text{CO}_3)_4$] and natural mixtures of huntite and hydromagnesite, were mined from the Kozani basin, located in northern Greece [40]. 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 mixing well 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 from 5–20 mass/mass%. Prior the tests, the samples were placed into a conditioning box (set at temperature of 32°C and relative humidity of 12%) for 24 h, to attain a minimum level of moisture content (2.8%) [41].

For the LOI experiments, cylindrical pellet samples of 19 mm diameter and 15 mm height were used. Each pellet was prepared from 0.5 g of forest species powder under pressure of 8 ton, using a manually operated hydraulic press (Specac 15 ton module). Then, the pellets were placed into the conditioning box, prior the tests.

It is not expected that forest species in actual wildfire conditions exhibit the same flammability properties as the samples made in the laboratory. The tests were performed after reducing plant leaves into fine uniform particles (particle foliar flammability) and making ideal mixtures of forest species and retardants. Under these conditions, the results taken are consistent, counting the intrinsic components (i.e., chemical composition) of forest species and are suitable for comparison use [42].

Methods for measuring fire retardancy

DTG analysis in N₂ atmosphere (pyrolysis study)

Each sample of 15–17 mg, was introduced into an open type alumina (Al₂O₃) 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 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 nitrogen, with a flow rate of 100 mL min⁻¹, to isolate the pyrolysis step [10, 42].

The criteria adopted for measuring fire retardancy were based on the following TG/DTG analysis data, recorded by the STAR-e software system of Mettler Toledo apparatus:

- Maximum mass loss rate (MWLR) for each thermal decomposition 'reaction', in % min⁻¹, measured by the respective DTG peak height. Retardant additives decrease MWLR values and this decrease is a measure of fire retardancy [10].
- Pyrolysis net mass residue of forest species (PNMR), in mass/mass%, which is determined by subtracting the pyrolysis mass residue of retardant at 600°C, from the mass residue of retardant treated forest species at 600°C [2, 43]. Retardant additives increase PNMR values and this increase is a measure of fire retardancy [2, 10, 17, 43].

Relative limiting oxygen index (RLOI) test (combustion study)

LOI measurements were carried out using a Dynisco Limiting Oxygen Index Chamber. A method has been developed to determine the efficiency of fire retardants, based on previous work [34, 44]. According to the method suggested, LOI measurements were conducted at ambient temperature, with a 20 mL s⁻¹ gas flow of oxidative media passing through a quartz glass column of 95 mm diameter. The forest species pellets, before and after treatment with the retardants, were placed vertically in the center of the glass column, using a sample holder. The oxygen ratio variation in the gas flow was 0.2%, whereas the lowest visible part of natural gas flame was applied to the top edge of pellets for 10 s. Relative limited oxygen index (RLOI) was defined as the lowest oxygen concentration (v/v%) in the carrier gas flow at which full flaming combustion of the pellets was observed. RLOI is a measure of pilot ignitability; thus, high ignitable fuels have low RLOI values [44]. The retardants increase the RLOI values of forest species and this increase is a measure of their fire retardancy.

Results and discussion

DTG analysis in N₂ atmosphere (pyrolysis study)

In Figs 1 and 2 are presented the DTG curves of *P. halepensis* and *C. incanus*, before and after treatment with hydromagnesite (Hyd), huntite (Hun) and

mixture huntite/hydromagnesite (HunHyd), in nitrogen atmosphere.

The peaks 1–4 (Figs 1 and 2) refer to the pyrolysis of forest species [10, 16, 38, 45–47], as follows: (1) the peak number 1, at temperatures below 100°C, is attributed to the evaporation of moisture; (2) the peak number 2, in the temperature range 200–280°C, is mainly attributed to the hemicellulose decomposition; (3) the peak number 3, in the range 280–370°C, is mainly attributed to the cellulose decomposition; (4) the peak number 4, in the range 370–550°C, is attributed to the lignin decomposition.

The peaks with the code names HY and HU (Figs 1 and 2) refer to the hydromagnesite and huntite decomposition, respectively [10].

The presence of minerals decreases the MWLR of cellulose decomposition (Figs 1 and 2, peaks 2 and 3). Thus, the minerals reduce the decomposition rate of cellulose. In contrast, the influence of hydromagnesite on the decomposition rate of lignin is not clearly established (Fig. 1, peak 4).

A linear relation was found between the maximum thermal decomposition rate of cellulose (MWLR₃) and the mineral content applied on forest species (Fig. 3). Hence, the maximum retardant effectiveness is achieved when 20% mineral is applied. Based on these MWLR₃ measurements, we conclude that all minerals tested have similar fire retardant properties (Fig. 3). Also, the minerals exhibit better performance, when they are applied on high flammable fuels (i.e., *P. halepensis*) than on low flammable ones (i.e., *C. incanus*). Thus, application of 20% hydromagnesite causes a MWLR₃ decrease of 19.6% in *P. halepensis* and 14.7% in *C. incanus*. Comparing minerals performance with other common use fire retardants (DAP, MAP and AS), in terms of MWLR cellulose decrease, we found that minerals are more effective than AS, but less effective than DAP and MAP [10].

Another criterion for measuring fire retardant efficiency is the increase of pyrolysis net mass residue (PNMR) of forest species. A linear relation was found between PNMR and the mineral content applied on forest species (Fig. 4). On the basis of these graphs (Fig. 4), huntite (Hun) and mixture huntite/hydromagnesite (HunHyd) exhibit very poor fire retardancy. On the contrary, hydromagnesite (Hyd) exhibits very good performance, particularly when high concentrations (i.e., 20 mass/mass%) are applied on forest species (Fig. 4). Also, hydromagnesite exhibits better performance, when applied on high flammable fuels (i.e., *P. halepensis*) than on low flammable ones (i.e., *C. incanus*). Thus, application of 20% hydromagnesite causes a PNMR increase of 19.3% in *P. halepensis* and 6.9% in *C. incanus*. Comparing

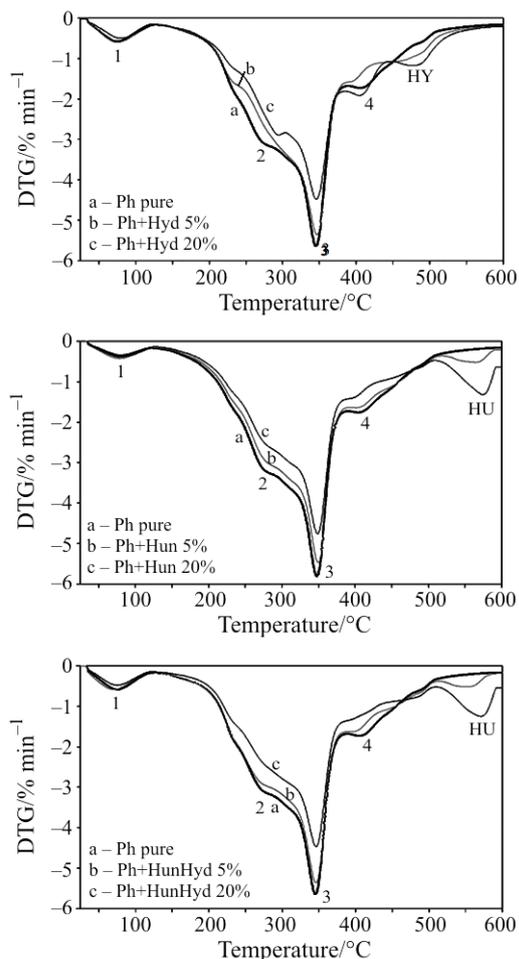


Fig. 1 DTG curves of *P. halepensis* (*Ph*), before and after treatment with hydromagnesite (*Hyd*), huntite (*Hun*) and mixture huntite/hydromagnesite (*HunHyd*) minerals (5 and 20 mass/mass%), in N_2 atmosphere

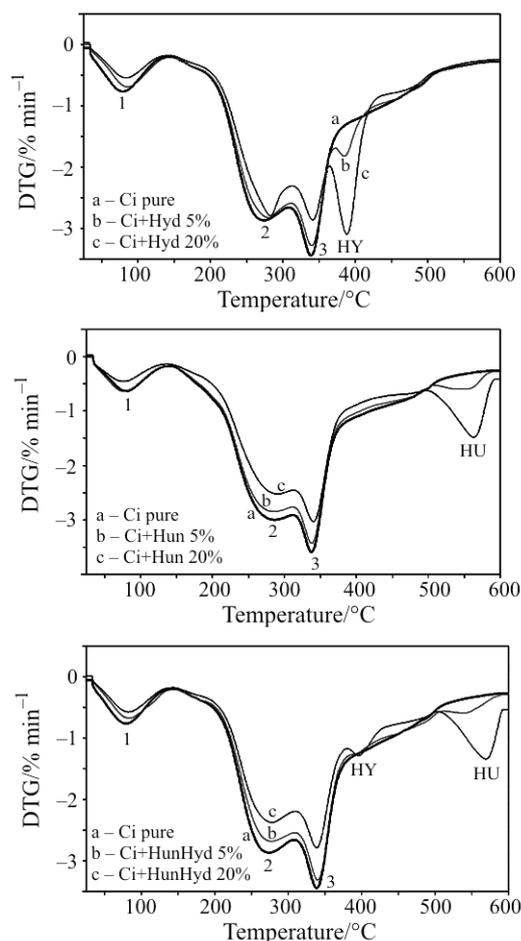
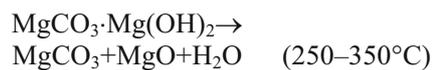
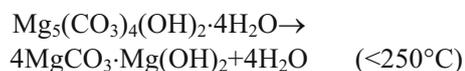


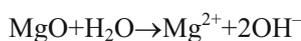
Fig. 2 DTG curves of *C. incanus* (*Ci*), before and after treatment with hydromagnesite (*Hyd*), huntite (*Hun*) and mixture huntite/hydromagnesite (*HunHyd*) minerals (5 and 20 mass/mass%), in N_2 atmosphere

hydromagnesite performance with other common use fire retardants (DAP and AS), in terms of PNMR increase, we found that hydromagnesite is not as effective as DAP and AS [2, 43].

The fire retardancy of hydromagnesite can be interpreted by the following reactions [10, 48]:



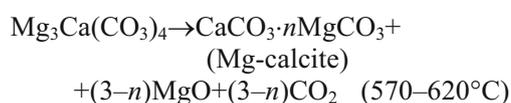
MgO is hydrolysed by water formed during pyrolysis, according to the following chemical equation [17]:



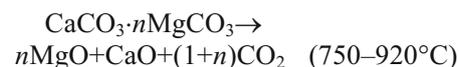
The hydroxyl ions, in accordance with the Lewis electron theory, cause dehydration of cellulose,

through the formation of carbanions, altering the rate of its decomposition [17].

Huntite has a minor effect on the pyrolysis of forest species, because its decomposition takes place at high temperatures, according to the following equations [10]:



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



($n \leq 0.05$).

Huntite retardancy can be interpreted by the formation of a kind of ceramic layer on the forest species particles, reducing their pyrolysis rate [10].

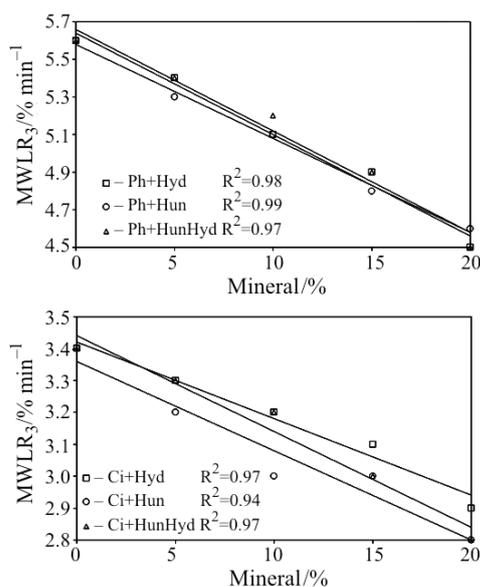


Fig. 3 Decomposition rate of cellulose vs. mineral content (%) applied on forest species: MWLR₃ is the maximum mass loss rate of cellulose (Figs 1 and 2, peak 3)

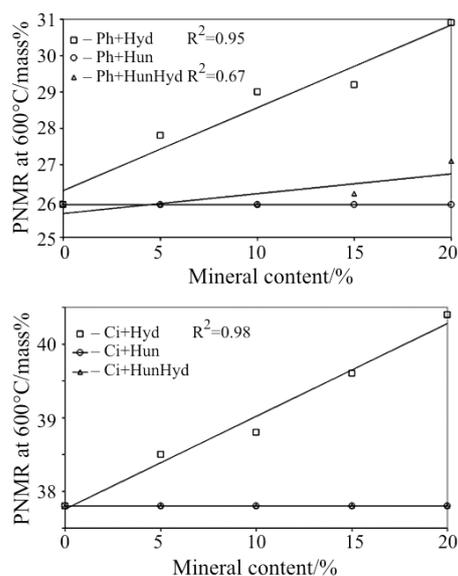


Fig. 4 Pyrolysis net mass residue (PNMR) vs. mineral content (%) applied on forest species

Relative LOI tests (combustion study)

A linear proportional relationship was found between RLOI values and mineral content applied on forest species, as is shown in Fig. 5. All RLOI data presented in Fig. 5 are the average values of 10 measurements, with RSD values lower than 1%.

As is shown in Fig. 5, hydromagnesite exhibits better performance than huntite, since: (1) hydromagnesite increases the RLOI values of *P. halepensis* 5.5–16.5%, whereas huntite 0.9–8.3% and the mixture

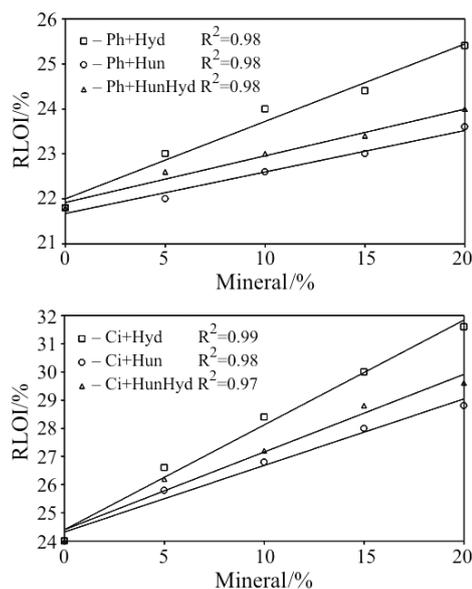


Fig. 5 Relative limiting oxygen index (RLOI) vs. mineral content (mass/mass%) applied on forest species

huntite/hydromagnesite 3.7–10.1%; (2) hydromagnesite increases the RLOI values of *C. incanus* 10.8–31.7%, whereas huntite 7.5–20.0% and the mixture huntite/hydromagnesite 9.2–23.3%. Also, the minerals tested exhibit better performance when applied on low flammable fuels (i.e., *C. incanus*), than on high flammable ones (i.e., *P. halepensis*).

According to previous report, the RLOI value is a measure of pilot ignitability of forest fuels [44]. Thus, as RLOI values increase, the pilot ignitability increases. Therefore, the presence of minerals decreases the pilot ignitability of forest fuels and this effect is pronounced, when high amounts of minerals are applied on forest species.

The influence of carbonate minerals examined on the ignitability properties of forest species can be interpreted by the endothermic decompositions of hydromagnesite and huntite, between 570 and 920°C. These reactions liberate water steam and carbon dioxide, which are both non-combustible. In addition, the decomposition of magnesium carbonate, magnesium hydroxide and calcium carbonate are endothermic and cause a further decrease in the flame temperature. Besides the cooling effect and quenching of the flames by inert gases, fire retardancy of carbonate minerals (i.e., hydromagnesite, huntite and mixture huntite/hydromagnesite) is also enhanced by a kind of ceramic layer being formed on the surface of forest fuels that protects the ignitable materials from further attacks by flames and heat [10].

Conclusions

Two simple methods were employed for measuring the fire retardancy on forest species. The first was based on DTG analysis, under nitrogen atmosphere, to study the pyrolysis of forest species in the presence of retardants. The second was based on LOI tests for measuring the flaming combustion properties of forest species treated with retardants. The above suggested methods were applied for testing the fire retardancy of carbonate minerals (i.e., hydromagnesite, huntite and natural mixtures of huntite and hydromagnesite) on *P. halepensis* and *C. incanus*. The following are our conclusions:

- On the basis of DTG analysis (pyrolysis of forest species), the minerals decrease the pyrolysis rate of cellulose and increase the net mass residue of forest species. However, no obvious effect of minerals on lignin decomposition is observed. Hence, other retardant constituents should be added to the minerals, to improve their efficiency [49].
- On the basis of LOI tests (flaming combustion of forest species), the minerals decrease the pilot ignitability of forest fuels.
- On the basis of pyrolysis study (DTG analysis), the minerals exhibit better performance when applied on high flammable forest species (i.e., *P. halepensis*), than on low flammable ones (i.e., *C. incanus*). In contrast, on the basis of combustion study (LOI tests), the minerals exhibit better performance when applied on low flammable fuels than on high flammable ones.
- Among the minerals examined, better overall performance is exhibited by hydromagnesite.
- The retardant efficiency is proportionally related to the amount of mineral applied on forest species. Thus, the best overall performance was achieved by 20% mineral application.
- This work further enhances the potential of hydromagnesite and huntite minerals for commercial forest fire retardant use [10].
- It is not expected that forest species in actual wild-fire conditions exhibit the same flammability properties as the particle flammability measured. However, the particle flammability measurements are far more consistent than the foliar ones, but should be used only for comparison reasons. Also, in actual forest fires, the minerals examined should be applied in the form of aqueous suspensions; forest fire retardants are generally applied aerially using airtankers and helicopters or from the ground using engine-powered pumps [50].

Nomenclature

DTG	differential thermogravimetry
LOI	limiting oxygen index
WUI	wildland urban interface
DAP	diammonium phosphate
MAP	monoammonium phosphate
APP	ammonium polyphosphate
AS	ammonium sulfate
<i>Ph</i>	<i>Pinus halepensis</i>
<i>Ci</i>	<i>Cistus incanus</i>
Hyd	hydromagnesite
Hun	huntite
HunHyd	huntite/hydromagnesite mixture
MWLR	maximum mass loss rate
MWLR ₃	maximum mass loss rate of cellulose
PNMR	pyrolysis net mass residue
RLOI	relative limiting oxygen index

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