

## Autoignition and thermogravimetric analysis of forest species treated with fire retardants

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### Abstract

Spontaneous ignition tests of various forest species were performed with a specifically designed apparatus. The forest species selected: *Arbutus andrachne*, *Cistus incanus*, *Pinus brutia*, *Pinus halepensis*, *Cupressus sempervirens*, *Pistacia lentiscus*, *Abies cephalonica* are very common in the Mediterranean region which is frequently devastated by forest fires. The same tests were performed in the presence of 20% (w/w)  $(\text{NH}_4)_2\text{HPO}_4$  (DAP) and 20% (w/w)  $(\text{NH}_4)_2\text{SO}_4$  (AS). The presence of DAP and AS prolonged the ignition delay time and this effect was more pronounced at low temperatures (i.e.  $<530^\circ\text{C}$ ). The autoignition delay properties of forest fuels treated with retardants were related to thermal analysis data obtained by thermogravimetry in nitrogen atmosphere. It was determined that the fire retardants shift the DTG major weight loss peaks of fuel to lower temperatures and increase the pyrolysis mass residue.

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### 1. Introduction

Forest fuels exposed at high heat flux in the absence of a pilot flame ignite, when the vapours emerging from the fuel and the surrounding air are at a sufficiently high temperature. The time period between the initiation of heating and the formation of visible flames is termed *ignition delay time*. The ignition delay time is a standard index of fuel ignitability provided that the experimental conditions (temperature, fuel particle

size, oxygen concentration, apparatus specifications, test procedure) remain constant.

During the ignition delay time period, dehydration and evolution of organic volatiles take place, followed by the pyrolysis of the main constituents of the forest fuels (cellulose, hemicellulose and lignin). 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. The thermal degradation of cellulose usually takes place between 250 and 400 °C, through two competing pathways [1–4]: one is the dehydration which leads to char and gases (mainly, CO, CO<sub>2</sub>, and H<sub>2</sub>O) and the other is the depolymerisation which leads to tar and volatiles through the formation of levoglucosan.

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The flammability and calorific values of various forest species have been determined by Núñez-Regueira et al. [5,6] in order to create fire risk maps in the context of wildland fire prevention.

As fire retardant is termed any substance that by chemical or physical action reduces or inhibits combustion thereby decreasing the rate of spread and the fireline intensity of a forest fire. The long-term retardants consist of flame inhibiting chemicals dissolved in water. They remain effective even after water has been removed by evaporation. The key ingredient in these retardants is the active fire retardant substance, usually referred as “active salt”, which is typically either an ammonium sulfate or ammonium phosphate. The retardant inorganic salts alter the pyrolysis mechanism, promoting the formation of char and water, decreasing the amount of heat and slowing the fire progression [7].

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 [8–14]. Among them, differential scanning calorimetry (DSC) and thermogravimetry (TG) have been extensively used to carry out thermal analysis of forest fuels in the presence of fire retardants, under air or inert gas flow [7,8]. Gases evolved during thermal decomposition have been analysed by direct mass spectrometry (DI-MS), pyrolysis–gas chromatography–flame ionisation detector (Py–GC–FID) and pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) [10–14]. The small samples used and the rapid removal of pyrolysis or combustion products, however, can lead the above methods to erroneous interpretations in terms of forest fuel flammability performance in the field. Therefore, the information provided by the analytical methods on pyrolysis and combustion mechanisms of forest species must be supported by other flammability tests in the laboratory.

The objective of this study was to assess the effectiveness of fire retardants on forest fuel flammability and thermal degradation using spontaneous ignition tests and TG analysis, and to contribute to a better understanding of the mechanisms of fire retardancy, which might facilitate the development of new fire retardant products.

## 2. Experimental

### 2.1. Apparatus for autoignition measurements

The autoignition delay time tests were performed with a custom-made apparatus, described in details elsewhere [15]. The furnace had internal dimensions 12.7 cm × 10.2 cm × 15.2 cm and temperature control within 1 °C. The samples, in the form of cylindrical pellets of 1 g, were dropped into a porcelain plate of 8 cm diameter, located at the bottom of the oven chamber, through a circular opening from the top of the furnace. The oven opening was also used to observe via a mirror any changes in the samples (ignition, smoking, smoldering, no change) as well as for ventilating the system (removal of combustion gases). A controlled air flow of 1.51 min<sup>-1</sup> ± 10% was inserted at the bottom of the oven through a stainless-steel tube, measured by a rotameter. Measurements of ignition delay time were conducted at constant air flow and temperature conditions by timing the period from insertion of the sample into the oven until the appearance of the first flame on the fuel's surface.

### 2.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out using a Mettler TGA/SDTA 851 module, supported by a PC and software for control and data handling. The sample, approximately 10 mg in weight, was introduced into an open alumina sample pan and was heated from 25 to 700 °C with a linear heating rate of 3.66 × 10<sup>-2</sup> K min<sup>-1</sup>. All runs were conducted in nitrogen atmosphere at a flow rate of 50 ml min<sup>-1</sup>. We have selected nitrogen atmosphere for TG analysis, in order to isolate the pyrolysis step, which is considered as the most important step in the burning procedure of forest fuels [15]. Furthermore, the retardants examined (DAP and AS) affect mainly the pyrolysis of forest species by dehydrating the cellulose, as is discussed later. The above were confirmed experimentally by performing some experiments at air atmosphere.

### 2.3. Samples

Tests were conducted on seven forest fuels: *Arbutus andrachne* (Eastern strawberry tree), *Cistus*

*incanus* (rockrose), *Pinus brutia* (Calabrian pine), *Pinus halepensis* (Aleppo pine), *Cupressus sempervirens* (Italian cypress), *Pistacia lentiscus* (Mastic tree), and *Abies cephalonica* (Greek fir). The selected species are very common in the Mediterranean region and are often devastated by forest fires. Table 1 presents the density and heat of combustion of the species tested, as well as a description of the sampling location.

The retardant inorganic salts used were  $(\text{NH}_4)_2\text{SO}_4$  p.a. grade Merck reagent and  $(\text{NH}_4)_2\text{HPO}_4$  BDH laboratory reagent. These two salts have prominent use as retardants since the early 1960s, because of their intrinsic effectiveness and their common use as agricultural fertilisers.

#### 2.4. Sample preparation for the autoignition tests

After field sampling, the forest species were dried at  $60^\circ\text{C}$  in a vacuum of 100 mmHg until constant weight within 1 mg. The approximate drying period of the

Table 1  
Description of the forest samples tested and the sampling location<sup>a</sup>

Species	Particle density ( $\text{g ml}^{-1}$ )	Heat of combustion ( $\text{kJ kg}^{-1}$ )
<i>Arbutus andrachne</i>	0.53	20.185
<i>Cistus incanus</i>	0.42	21.683
<i>Pinus brutia</i>	0.54	21.380
<i>Pinus halepensis</i>	0.45	22.185
<i>Cupressus sempervirens</i>	0.37	19.548
<i>Pistacia lentiscus</i>	0.51	22.018
<i>Abies cephalonica</i>	0.51	20.695

<sup>a</sup> Sampling data: the sample collection site of *Pinus halepensis*, *Pistacia lentiscus*, *Cupressus sempervirens*, *Cistus incanus*, *Pinus brutia* was the mountainside Kalopoula of Imitos, near Athens, located at  $37^\circ 58' 13''\text{N}$  and  $23^\circ 48' 20''\text{E}$ , elevation 487 m and average slope 70%. The dates of collection were 15 March, 7 May and 7 November 2000. The sample collection site of *Arbutus andrachne*, *Abies cephalonica*, was mountain Parnitha, near Athens, located at  $38^\circ 10' 24''\text{N}$  and  $23^\circ 40' 29''\text{E}$ , elevation 900 m and average slope 15%. The date of collection was 12 January 2001. All samples were mature foliage, taken from stems 4–6 years old, collected after a long drought period in order to avoid moisture effects.

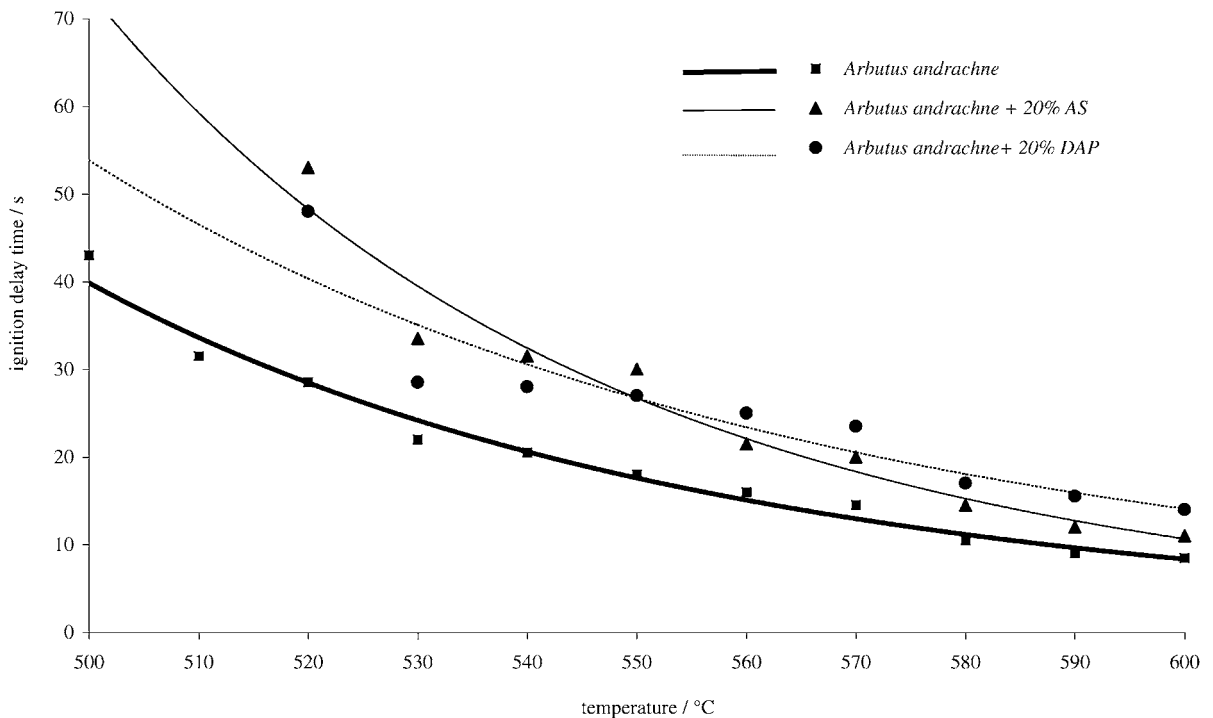


Fig. 1. Ignition delay time vs. temperature of *Arbutus andrachne* before and after treatment with 20% fire retardant additives (DAP and AS).

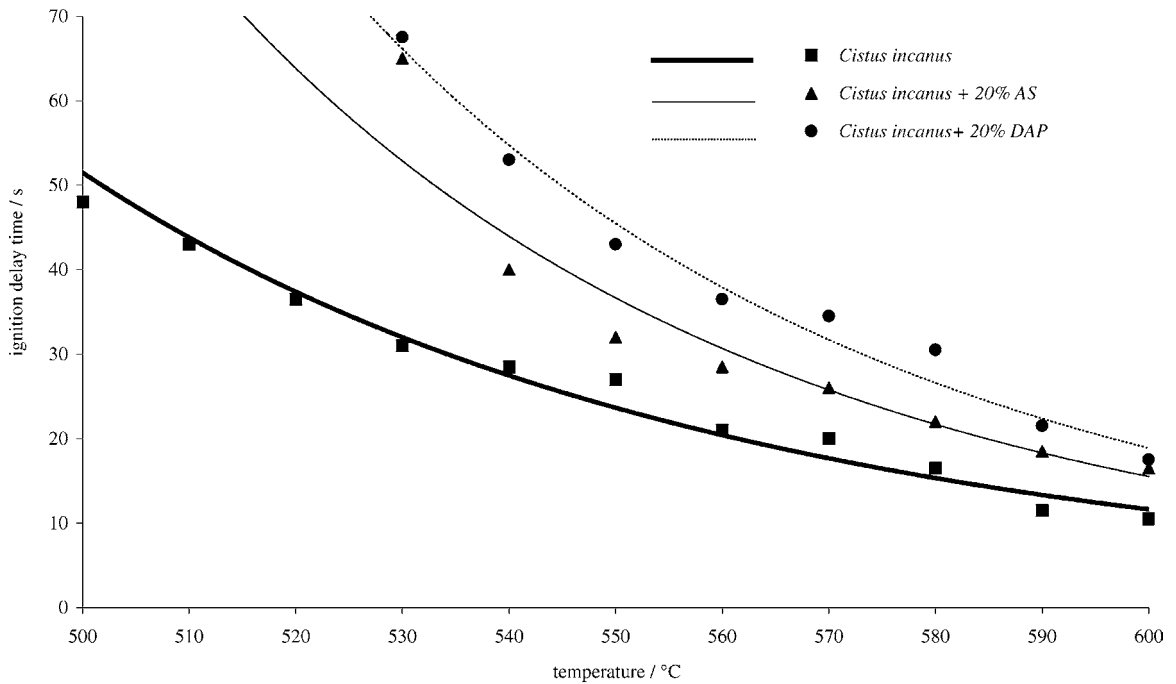


Fig. 2. Ignition delay time vs. temperature of *Cistus incanus* before and after treatment with 20% fire retardant additives (DAP and AS).

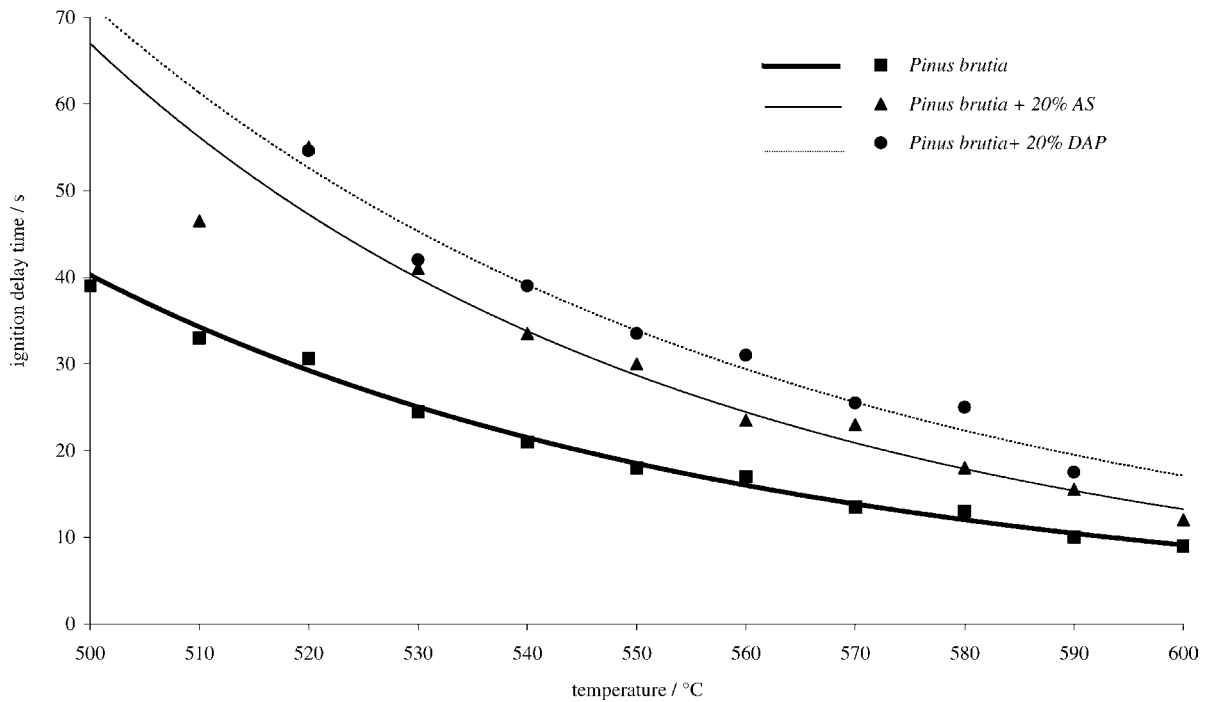


Fig. 3. Ignition delay time vs. temperature of *Pinus brutia* before and after treatment with 20% fire retardant additives (DAP and AS).

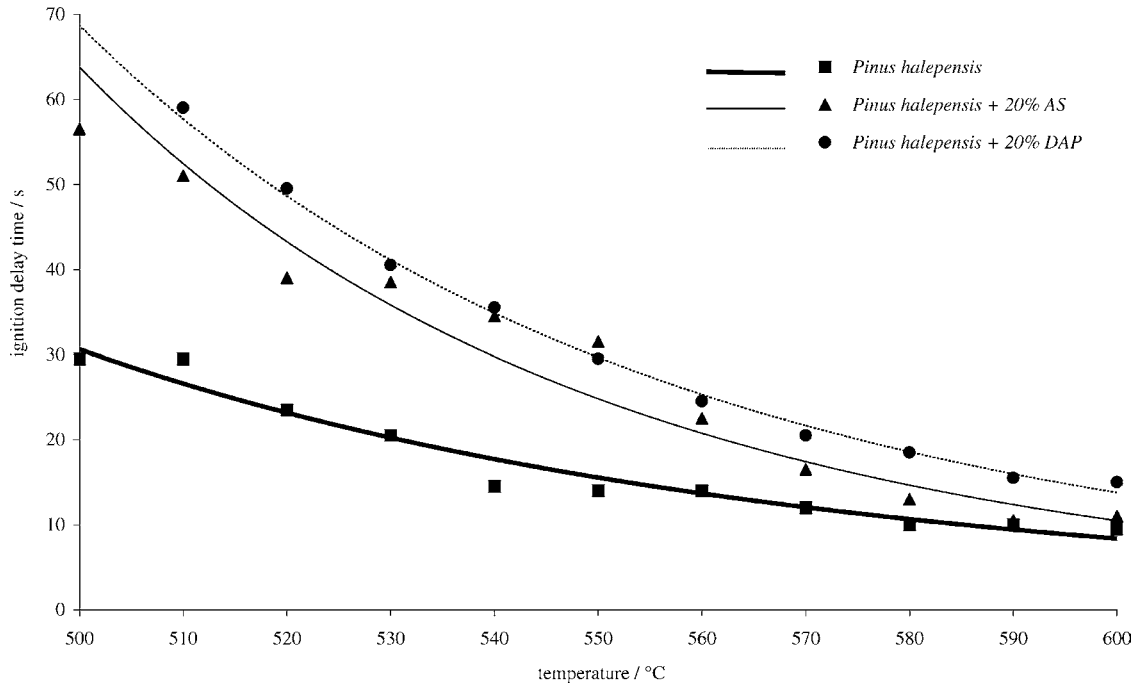


Fig. 4. Ignition delay time vs. temperature of *Pinus halepensis* before and after treatment with 20% fire retardant additives (DAP and AS).

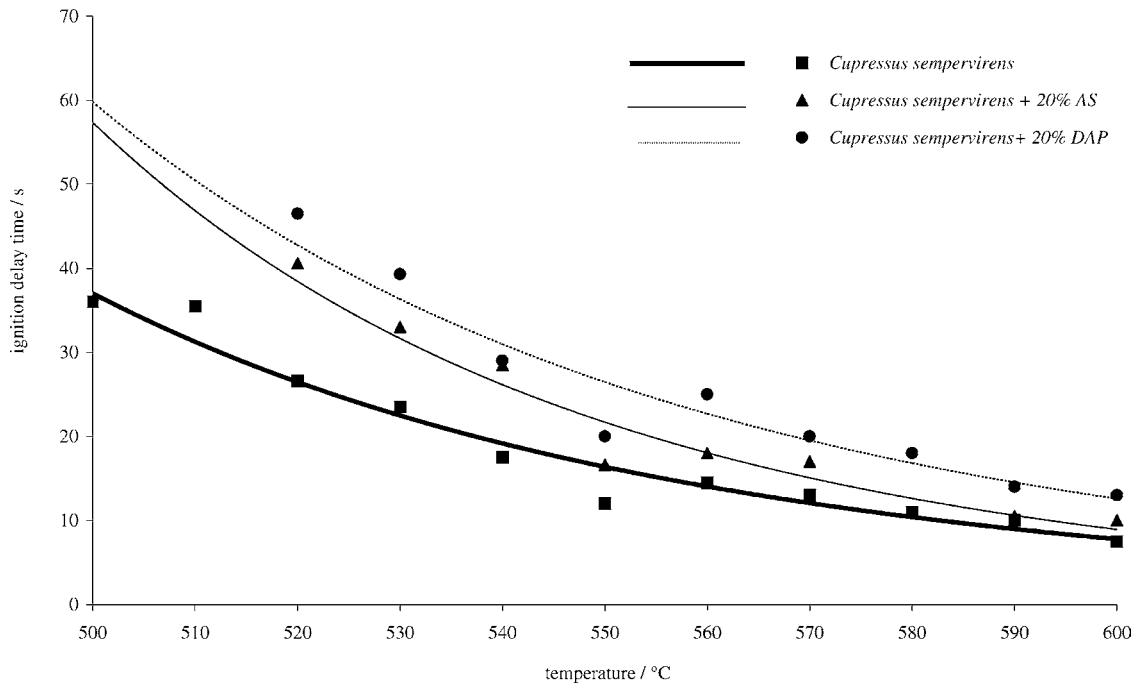


Fig. 5. Ignition delay time vs. temperature of *Cupressus sempervirens* before and after treatment with 20% fire retardant additives (DAP and AS).

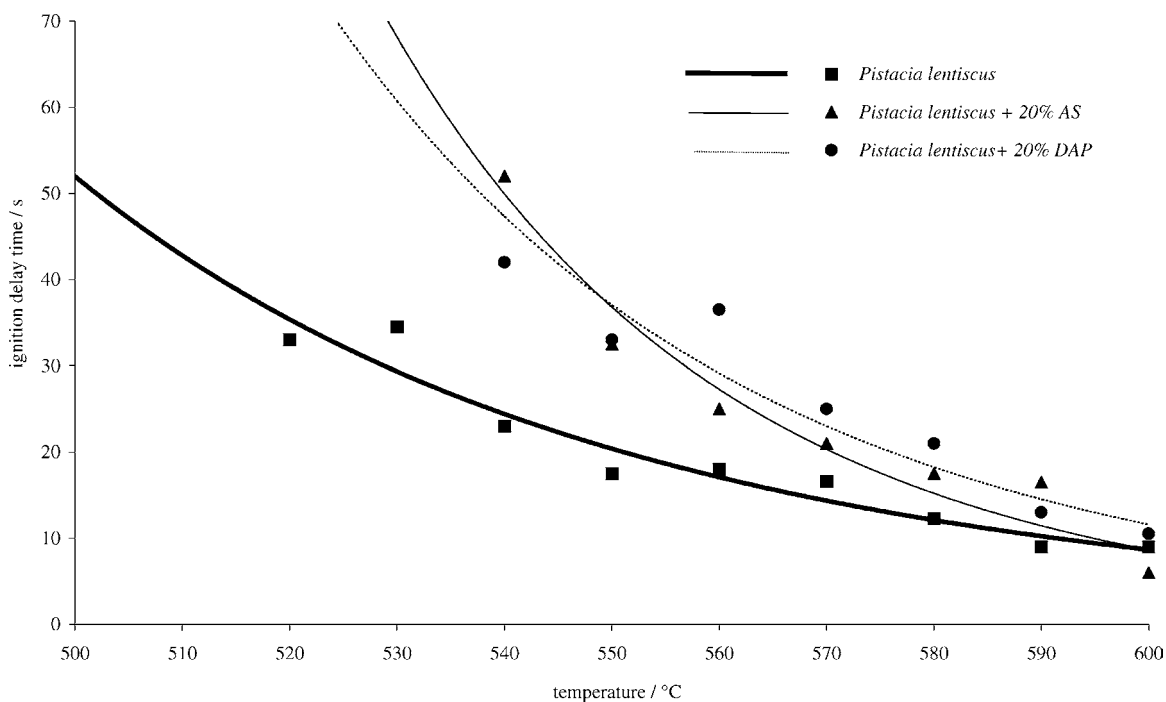


Fig. 6. Ignition delay time vs. temperature of *Pistacia lentiscus* before and after treatment with 20% fire retardant additives (DAP and AS).

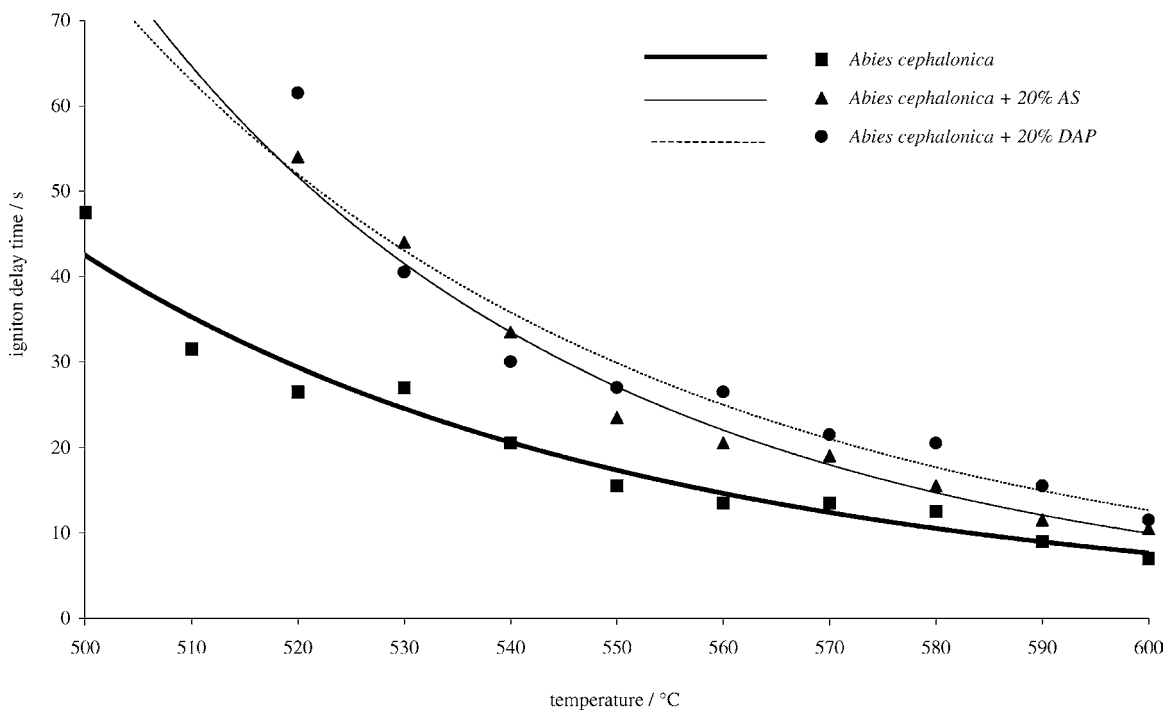


Fig. 7. Ignition delay time vs. temperature of *Abies cephalonica* before and after treatment with 20% fire retardant additives (DAP and AS).

samples was 48 h. Then the samples were ground and a fraction between 0.3 and 0.5 mm was selected. One gram of powder was pressed into cylindrical pellets of diameter of 1.3 cm and variable length at a pressure of 15.7 MPa (155 atm) in order to produce uniform pellets. The pellets were then dried at 60 °C under vacuum of 100 mmHg and stored in desiccators, until the time of the test. The density of the pellets was approximately 1.2 g cm<sup>-3</sup>.

The samples treated with fire retardants were prepared by adding an aqua stock solution of known concentration of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> to pre-weighed forest sample and vacuum evaporation of water. With this procedure all the quantity of salt remained with the forest sample to ensure the desired percent by weight (20% w/w). Then, the samples were dried at 60 °C under 100 mmHg vacuum for 48 h. The treated samples were pressed into pellets under the same conditions used for the untreated samples. The amount of retardant applied to the forest species

was based on data used by Hellenic Fire Services during real forest fires.

### 2.5. Sample preparation for the TG analysis tests

The samples for the thermal analysis were prepared with the drying and grinding procedure, described in the previous section, in order to ensure sample homogeneity.

## 3. Results and discussion

The effect of fire retardants on the ignition delay time at various temperatures for the forest species studied is shown in Figs. 1–7. Time and temperature measurements are the average of three replicate tests, while the relative standard deviation was <10% of the mean value.

Table 2

Thermogravimetric analysis data (peak temperature, weight loss at peak temperature and pyrolysis mass residue at 600 °C) of forest species before and after treatment with fire retardant additives in nitrogen atmosphere

No.	Sample	Primary peak		Secondary peak		Residue (%, 600 °C)
		Temperature (°C)	Weight loss (%)	Temperature (°C)	Weight loss (%)	
1	<i>Arbutus andrachne</i>	346	43			30
	<i>Arbutus andrachne</i> + 20% AS	272	26			34
	<i>Arbutus andrachne</i> + 20% DAP	282	28	205	12	45
2	<i>Cistus incanus</i>	347	40			36
	<i>Cistus incanus</i> + 20% AS	293	34			36
	<i>Cistus incanus</i> + 20% DAP	297	32	254	22	46
3	<i>Pinus brutia</i>	333	38			25
	<i>Pinus brutia</i> + 20% AS	247	21			29
	<i>Pinus brutia</i> + 20% DAP	280	30	160	6	37
4	<i>Pinus halepensis</i>	356	51	263	18	24
	<i>Pinus halepensis</i> + 20% AS	249	21			31
	<i>Pinus halepensis</i> + 20% DAP	284	32	212	12	41
5	<i>Cupressus sempervirens</i>	353	41			31
	<i>Cupressus sempervirens</i> + 20% AS	251	18			35
	<i>Cupressus sempervirens</i> + 20% DAP	279	28	216	15	40
6	<i>Pistacia lentiscus</i>	317	31	260	16	34
	<i>Pistacia lentiscus</i> + 20% AS	283	26	230	11	38
	<i>Pistacia lentiscus</i> + 20% DAP	279	24	206	10	46
7	<i>Abies cephalonica</i>	344	41			29
	<i>Abies cephalonica</i> + 20% AS	291	30			31
	<i>Abies cephalonica</i> + 20% DAP	287	26	219	9	43

As shown in Figs. 1–7, the presence of DAP and AS increases significantly the ignition delay time particularly at low temperatures, i.e.  $<530^{\circ}\text{C}$ .

Overall, DAP seems to be more effective than AS, since it has higher tendency to increase the ignition

delay times comparatively to AS (Figs. 1–7). However, in some cases (*Arbutus andrachne*, *Pistacia lentiscus*, *Abies cephalonica*) AS found to have a better retardation effect than DAP at low temperatures, i.e.  $<520^{\circ}\text{C}$ .

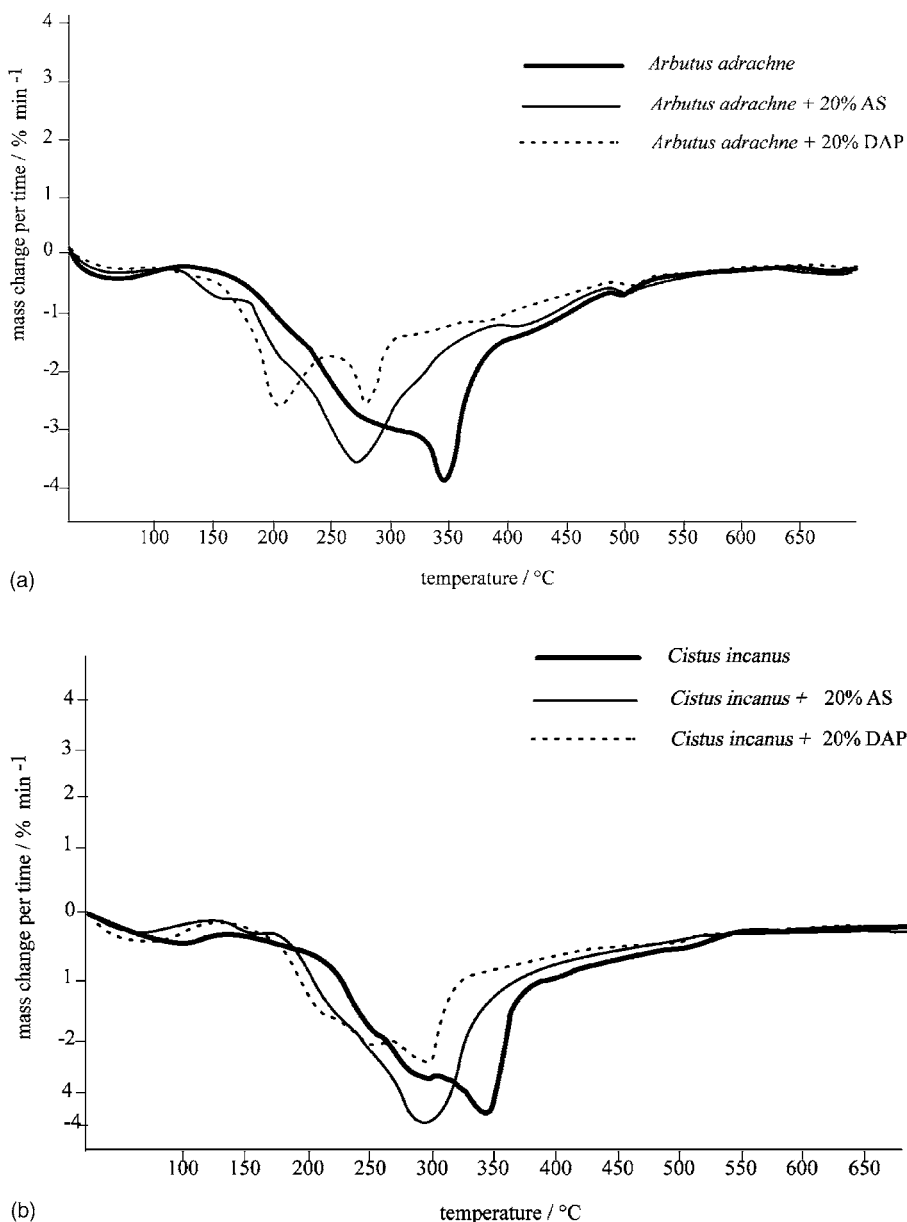
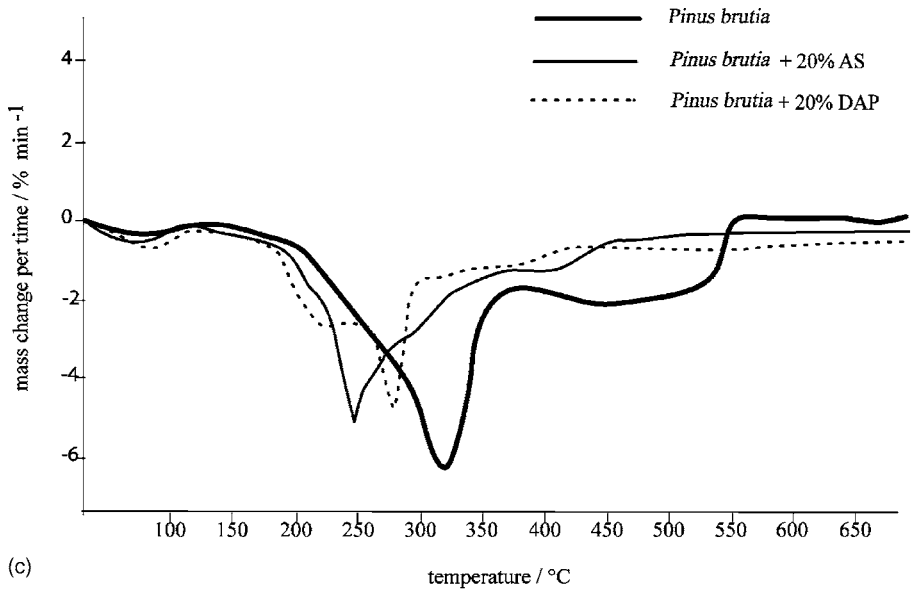
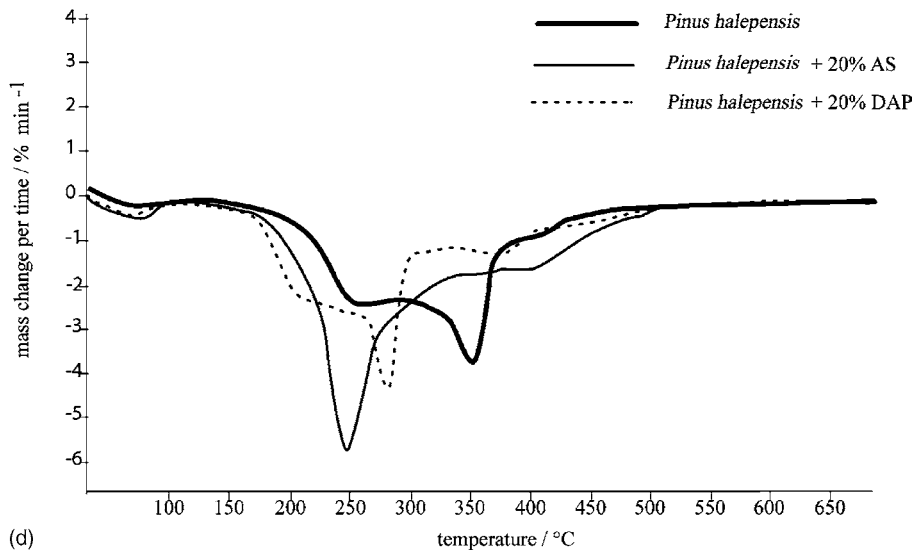


Fig. 8. DTGA curves of forest species before and after treatment with 20% DAP or AS. (a) *Arbutus andrachne*, (b) *Cistus incanus*, (c) *Pinus brutia*, (d) *Pinus halepensis*, (e) *Cupressus sempervirens*, (f) *Pistacia lentiscus*, and (g) *Abies cephalonica*.





(c)



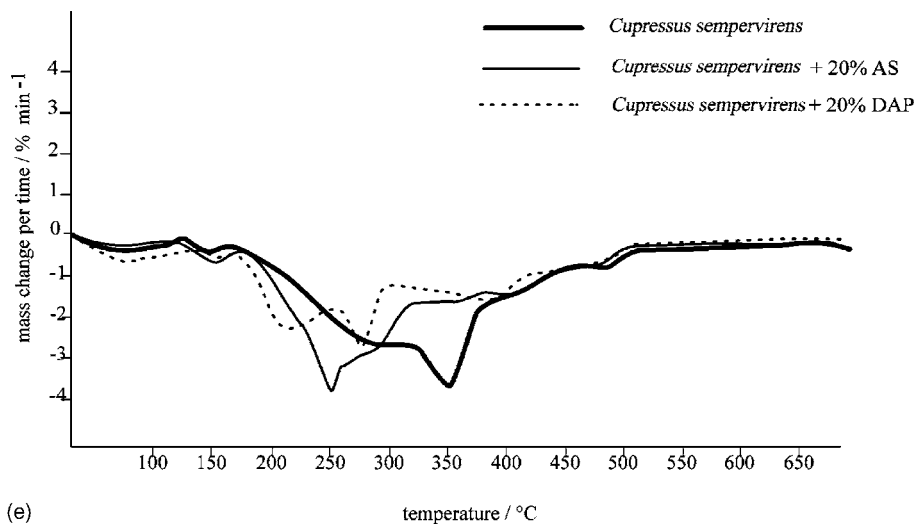
(d)

Fig. 8. (Continued).

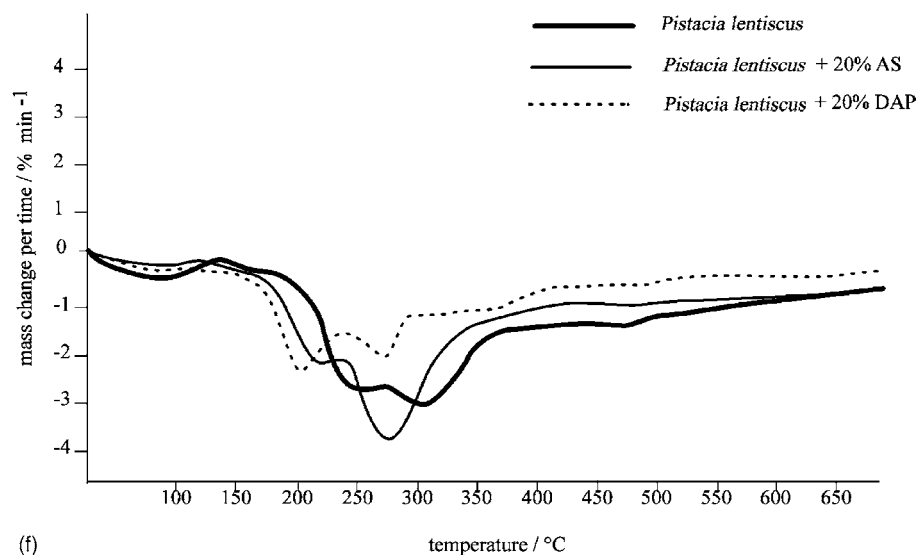
In addition, the examined retardant additives were found more effective with *Cistus incanus* and *Pistacia lentiscus*, which had been classified by previous experimental work as not flammable forest species [15].

The differential thermogravimetric (DTG) analysis data of forest species before and after the chemical treatment are summarised in Table 2 and Fig. 8.

Based on the DTG curves of untreated samples we may distinct five different temperature ranges (peaks) in which considerable weight losses take place. The first is <100 °C and corresponds to the evaporation of moisture. The second in the range of 120–160 °C, appeared only in *Cupressus sempervirens*, is attributed to the evaporation of volatile



(e)



(f)

Fig. 8. (Continued).

constituents. The peak in the range of 200–280 °C corresponds mainly to hemicellulose decomposition, while the next one, between 320 and 370 °C, is related to cellulose decomposition [15,16]. The last peaks in the range of 370–550 °C are related to the lignin decomposition [15,16]. It should be noted that the profile of the DTG curves varies depending on the forest sample examined and in many cases an

overlapping between the reactions taking place is observed.

As shown in Fig. 8 and Table 2, the retardant additives shift the primer weight loss peak referred to cellulose decomposition (appeared between 317 and 353 °C) to lower temperatures. Therefore, the combustible volatiles are probably liberated and dissipated earlier, before their ignition temperature is reached.

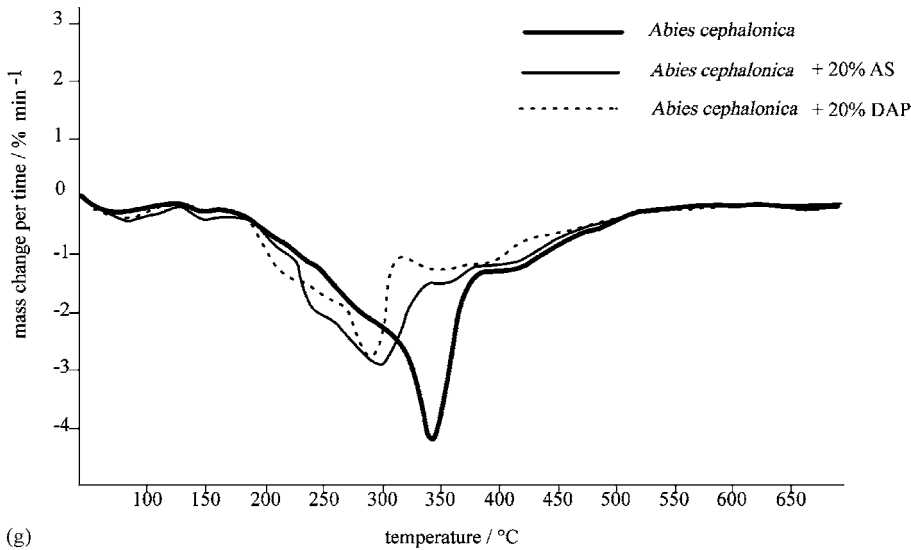
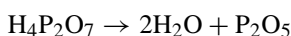
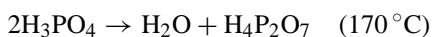
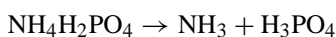
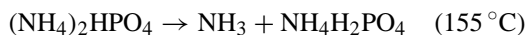


Fig. 8. (Continued).

This temperature shift varies between 34 and 107 °C with the major values recorded on the most flammable fuels (*Pinus halepensis*, *Cupressus sempervirens*). In addition, the presence of retardant additives complicates in some cases the thermal degradation pattern of forest species. Typical example is the effect of DAP on *Arbutus andrachne*, *Cupressus sempervirens* and *Pistacia lentiscus* which splits up the primer degradation peaks shown in DTG into two secondary earlier peaks (Fig. 8).

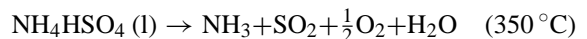
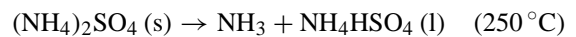
Finally, the solid pyrolysis residue, which is directly related to the flammability properties [15,17], increased by the presence of fire retardants. DAP exhibits a much higher effect than AS, in terms of mass residue changes. A maximum increase of 65% was recorded at 600 °C by applying 20% DAP on *Pinus halepensis* (Table 2).

The retardation effect of  $(\text{NH}_4)_2\text{HPO}_4$  can be explained by its thermal decomposition according to the scheme:



The presence of phosphoric acid and phosphorous pentoxide, would cause an earlier dehydration of cellulose 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 [10].

The retardation effect of  $(\text{NH}_4)_2\text{SO}_4$  can be explained similarly as  $(\text{NH}_4)_2\text{HPO}_4$ , according to the following equations:



#### 4. Conclusions

The effectiveness of forest fire retardants (DAP and AS) has been evaluated by combining a laboratory ignition test with thermogravimetric analysis. The most interesting conclusions are:

1. The fire retardant action depends on the ignition properties of forest fuel examined. The least flammable species examined: *Cistus incanus* and *Pistacia lentiscus* are the most affected by the retardants in terms of ignition delay prolongation.

2. The retardants tested (DAP and AS) increased considerably the ignition delay time and the pyrolysis mass residue. Also the retardant additive affects significantly the thermal degradation profile of forest fuels observed by TGA, i.e. shift of the primer DTG peaks to lower temperatures.
3. DAP has an overall better performance than AS. However, in some cases AS exhibits a better performance than DAP.

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