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The effect of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ on the spontaneous ignition properties of *Pinus halepensis* pine needles

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Abstract

The spontaneous ignitability of *Pinus halepensis* pine needles was evaluated. Fire points and times taken for irradiated fuels to be ignited were correlated, at given heat intensity, to the airflow around the specimen and the sample size. The tests showed that increase of the airflow rate above 1.51 min^{-1} increased considerably the fire point values and ignition delay times. On the contrary, the sample size in the range investigated (0.2–1.0 g) showed a negligible effect on the ignition properties. The influence of fire chemical retardants $(\text{NH}_4)_2\text{HPO}_4$ (DAP) and $(\text{NH}_4)_2\text{SO}_4$ (AS) on the ignitability characteristics was studied under various concentration levels. The data in this study showed that the presence of DAP and AS increases the fire point, as well as the time required for ignition, and this effect is pronounced at high concentration levels. However, at lower temperatures, i.e. below 500°C , flaming combustion appears sensitive to the AS quantity applied, whereas at high temperatures (i.e. above 600°C) the DAP concentration had a major influence on its flammability behavior. In addition the time of combustion was slightly extended, therefore, the energy release rate was reduced in the presence of fire retardants, particularly of AS. The purpose of this study was to quantify the fire extinguishing capabilities of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$, commonly used chemicals in forest fires, by comparing the ignition properties of samples, prior and after retardant loading. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: *Pinus halepensis* pine needles; Spontaneous ignition; Flaming combustion duration; Sample size; Airflow; Fire retardants

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1. Introduction

If a forest fuel, such as pine needles, is exposed to a sufficiently high heat flux (radiative, convective or a combination), its surface temperature rises. The temperature inside the solid also increases but at a lower rate than the surface. When the surface temperature reaches a certain value, pyrolysis begins to produce volatiles, tars, carbonaceous char and mineral ash. The fuel vapors emerging through the surface of solid fuel mix with air in the boundary layer and may ignite spontaneously, if the volatile-air mixture has a sufficiently high temperature, exceeding its flammability limit. Therefore, ignition requires a minimum supply rate of fuel vapors, known as the minimum pyrolysis rate. This is known as flaming combustion. The fire point¹ may be defined as the minimum temperature at which flaming combustion occurs.

Under different conditions, combustion can take place without a flame with the solid surface glowing. The combustion of a solid without a flame is termed *smoldering* or *glowing combustion* [2].

In general, high temperatures favor the evolution of volatile flammable gases, whereas low temperatures promote the production of tar and char leading to glowing combustion. Smoldering generally occurs in fuel arrays, which are more tightly packed than those that sustain flaming combustion. Forest duff, which has packing ratios >10%, exhibits smoldering, whereas litter, with packing ratios <10%, exhibits flaming combustion. Decomposing plant matter tends to smolder, because biological degradation removes cellulose cell wall material, leaving behind a higher lignin content [3].

Ignition is a transition between preheating (preignition) and combustion. By contrast, the spreading of fire can be considered as a series of ignitions. So, the phenomenon, which controls the advance of the flame front, is the release of volatile combustible gases from the vegetation, which is consumed in a homogenous diffusion flame. In piloted ignition, the flaming combustion is initiated in the vicinity of a small pilot (flame, spark or a glowing wire) located in the boundary layer. In spontaneous ignition, the initiation of flaming combustion occurs without a pilot. Obviously, spontaneous ignition requires a higher heat flux than piloted ignition, because a higher surface temperature is required, in the absence of a pilot source. Also, the spontaneous ignition values of the combustible solid, under radiative heat transfer, are higher than those obtained under convective heat transfer. With radiative heat transfer, the volatiles released from the surface of the combustible solid, must be hot enough to produce a flammable mixture above its auto-ignition temperature, when it mixes with unheated air. With convective heating, however, the volatiles enter a stream of air that is already at a higher temperature, hence they need not be so hot. Both heat transfer modes are important in forest fires. On calm days heat transfer to unburned fuel in advance of the fire will be dominated by thermal radiation. With wind speed above 10 ms^{-1} the convection heat transfer begins to dominate [4].

¹Firepoint is the minimum surface temperature at which the flow of volatiles can be ignited by a pilot ignition source.

Ideally, fire retardants completely extinguish all flaming and glowing combustion. Mostly, except in fires of limited size and intensity, the fire is only retarded or slowed for a short time. There are two basic forest retardant systems: short-term retardants and long-term retardants.

The short-term retardants are suppressants—basically water, or water with additives—which either reduce its surface tension (wetting agents) or increase its viscosity (thickening agents). These retardants are effective until they have been removed from the fuel by evaporation. Among them, foams have found many applications in recent years due to their superior properties to insulate, envelop and penetrate fuels. They act as a heat sink and exclude air, because they break down in a controlled manner, they further wet the fuels they encase [3].

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 salt, usually referred as “active salt”, which is typically either an ammonium sulfate or ammonium phosphate. All salts are not equally effective, when applied to fuels in the same concentration. By adjusting the amount of salt, applied to the fuel, we may achieve the maximum performance [5]. It has been reported that retardants with high nitrogen contents lead to fuel combustion with high yields of non-flammable gases. Also, a high phosphorous or sulfur content causes high dehydration of the matrix, forming a stable and heat isolating char [6]. 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 [7–17]. 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 [9–13]. Gases evolved during thermal decomposition have been analyzed by Direct Mass Spectrometry (DI-MS), Pyrolysis–Gas Chromatography–Flame Ionization Detector (Py–GC–FID) and Pyrolysis–Gas Chromatography–Mass Spectrometry (Py–GC–MS) [14–17]. 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 actual situations. Therefore, the information provided by the analytical methods on pyrolysis and combustion mechanisms of forest species must be supported by other fire tests.

The subject of this paper is limited to spontaneous ignition measurements of forest fuels, studying the effect of various factors such as the specimen mass, the airflow around the specimen and the presence of active fire retardant salts on the spontaneous ignitability of *Pinus halepensis* pine needles. The main purpose of this work is to devise a simple method for evaluating the fire extinguishing effectiveness of fire retardants, by comparing the ignition properties of forest species with those of forest species plus retardants. In addition, a better understanding of the mechanisms of fire retardancy might facilitate the development of new fire retardant products.

2. Experimental

2.1. Instruments

The apparatus used for the ignition measurements is shown in Fig. 1. The furnace chamber was heated by two open coil electric resistance heaters, which are insulated with ceramic fibers, and consumed electrical power at 1000 W. It had internal dimensions 12.7 cm × 10.2 cm × 15.2 cm (width, height, depth) and overall size 28.6 cm × 45.7 cm × 39.4 cm, respectively. Temperature control accuracy was $\pm 1^\circ\text{C}$ in the range 20–1200°C, whereas the temperature uniformity was $\pm 3^\circ\text{C}$ at 1000°C, according to the specifications given by the constructor (Thermolyne model 47900). At the bottom of the oven chamber, a porcelain vessel, with a diameter 8 cm and height 3 cm, was placed to accommodate the specimens, which were dropped into the vessel through a circular opening from the top of the furnace, as shown in Fig. 1. The oven had an opening diameter of 2.5 cm and was also used to observe through a mirror any changes in the specimens (“flaming, smoke, smouldering”) as well as for venting the system (removal of combustion gases).

Three thermocouples were used to measure the oven temperature with accuracy better than 0.3°C . The thermocouples (0.05 mm diameter) were made from Chromel/Alumel wires. Thermocouples T_1 and T_2 were located at points A, B, respectively, to monitor the surface temperature of the porcelain plate (Fig. 1). Thermocouple T_3 was located 3 cm above the plate, approximately at the geometric center of the oven, point C. A controlled flow of air, in the range of $1\text{--}5\text{ l min}^{-1} \pm 10\%$, was introduced at the bottom of the oven, measured by a rotameter. The airflow was adjusted,

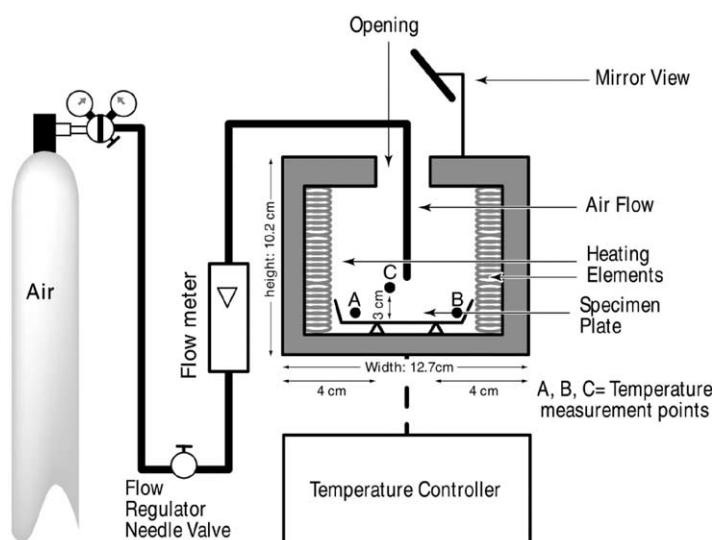


Fig. 1. Diagrammatic presentation of the apparatus used for measuring the spontaneous ignitability of forest species.

through an accurate flow regulator and the air entered the chamber through a circular stainless steel pipe jet. Also, the incoming air was at room temperature, without causing any substantial change on temperature setting.

2.2. Samples

Tests were conducted on *Pinus halepensis* pine needles. This forest specie is common in the Mediterranean region and is usually devastated by forest fires. The samples were collected from a mountainside in Kalopoula of Imitos, near Athens, located W–NW, with geographic coordinates 37°58'13"N and 23°48'20"E, height 487 m and average slope 70%. The ground was limestone.

The fire retardant “active 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 components have dominated forest fire retardant use, since the early 1960s, because of their intrinsic effectiveness and their similarity to agricultural fertilizers. This has assured their abundance, relative cheapness and environmental compatibility.

The samples were prepared according to the following procedure: the forest materials were dried at 60°C, under vacuum of 100 mmHg, until attainment of constant weight within 1 mg and then were ground. A fraction, between 0.3 and 0.5 mm, was separated and used for the test. Specific quantities of this powder (0.2, 0.5 or 1 g) were pressed into cylindrical pellets of diameter of 1.3 cm and variable height, at a pressure of 15.7 MPa (155 atm) in order to produce uniform samples. The density of the samples was $1.2 \pm 0.06 \text{ g cm}^{-3}$. The pellets were dried (60°C and 100 mmHg vacuum) and then stored in a desiccator, using as drying agent silica gel, until the ignition test.

The fire retarded samples were prepared by adding a certain quantity (0.05–0.25 g) of $(\text{NH}_4)_2\text{SO}_4$ or $(\text{NH}_4)_2\text{HPO}_4$ in fine powdered form to 1 g of ground forest specie. After mixing well, the samples were pressed into pellets, under the same conditions used for the preparation of pure forest species. The amount of retardant, applied to the forest species, was based on data used by Hellenic Fire Services in real forest fires.

2.3. Procedure

The temperature of the unloaded furnace was maintained for at least 15 min, to assure stability. The regulation of the current through the heating coils and the airflow were not changed during the test. Then the *Pinus halepensis* sample was dropped into the specimen plate through the oven opening (see Fig. 1). The ignition delay and the flaming combustion duration were measured. After each test, the porcelain vessel was taken out of the chamber for cleaning. Sufficient time was given, after placing back the vessel, to allow the settling of steady conditions inside the chamber.

3. Results and discussion

3.1. Reproducibility tests

The reproducibility of the method was assessed using different forest samples (collected on different dates within a month), while different persons performed the tests. The results of these tests are shown in Table 1. The ignition delay and flame duration data given in Table 1 are the average of three replicate tests. The relative standard deviation of these measurements was below 10 s.

3.2. The effect of air flow around the specimen

Ignition delay versus temperature, in relation to airflow conditions around the forest sample and sample size, is shown in Table 2. Times reported are the average of three replicate tests, while the flaming combustion duration is recorded in parentheses.

From the data shown in Table 2, we may express graphically the relationship between ignitability (ignition delay versus temperature) and air flow, as shown in Fig. 2. It is certain, from this graphical presentation, that an increase of air flow in the range of (1.5–4.5) l min^{-1} leads to considerably longer ignition delay times, due to the increased sample cooling, as well as to the decreased concentration of fuel vapors in the boundary layer. The above findings are consistent with those reported by other authors [18,19].

Fig. 3 shows that airflow rates have a significant influence on fire point values. This agreed with a report compiled by many laboratories during an ISO 5657 ignitability test meeting: drafts generated by opening or closing doors or by moving

Table 1
Reproducibility tests on the flammability properties of *Pinus halepensis* pine needles using samples of 1 g and airflow of 1.51 min^{-1}

Temperature (°C)	Ignition delay (combustion time) (s)				Standard deviation	RSD
	Test 1	Test 2	Test 3	Mean value		
500	NI	NI	NI	NI		
510	54 (88)	45 (102)	55 (89)	51 (93)	6 (8)	12 (9)
520	32 (111)	31 (105)	39 (99)	34 (105)	4 (6)	12 (6)
530	34 (104)	26 (114)	33 (111)	31 (110)	4 (5)	13 (4)
540	25 (118)	27 (117)	29 (126)	27 (120)	2 (5)	7 (4)
550	22 (112)	25 (101)	26 (115)	24 (109)	2 (7)	8 (6)
560	20 (113)	17 (118)	21 (120)	19 (117)	2 (4)	10 (3)
570	16 (111)	14 (116)	15 (125)	15 (117)	1 (7)	7 (6)
580	15 (124)	13 (111)	14 (119)	14 (118)	1 (6)	7 (5)
590	10 (100)	12 (103)	10 (118)	10 (107)	1 (8)	10 (7)
600	7 (121)	8 (120)	9 (114)	8 (118)	1 (4)	12 (3)

NI = no ignition.

Table 2

The effect of sample size and air flow on the flammability properties of *Pinus halepensis* pine needles

Air flow (l min^{-1})	Temperature ($^{\circ}\text{C}$)	Ignition delay (flaming combustion time) (s)		
		Sample size (g)		
		0.2	0.5	1.0
1.5	500	NI	59 (50)	NI
	510	20 (36)	49 (47)	51 (93)
	520	18 (39)	31 (59)	34 (105)
	530	16 (40)	29 (65)	31(110)
	540	15 (41)	26 (60)	27 (120)
	550	11 (43)	20 (64)	24 (109)
	560	10 (42)	19 (71)	19 (117)
	570	8 (41)	15 (68)	15 (117)
	580	6 (43)	14 (70)	14 (118)
	590	6 (44)	14 (69)	10 (107)
	600	5 (46)	13 (72)	8 (118)
3.0	500	NI	NI	NI
	510	NI	NI	NI
	520	NI	NI	NI
	530	NI	28 (61)	NI
	540	14 (40)	23 (63)	40 (124)
	550	11 (42)	22 (60)	25 (112)
	560	10 (41)	20 (56)	23 (120)
	570	9 (43)	17 (60)	16 (113)
	580	8 (45)	16 (65)	12 (123)
	590	7 (46)	15 (62)	11(107)
	600	6 (48)	14 (59)	10 (109)
4.5	500	NI	NI	NI
	510	NI	NI	NI
	520	NI	NI	NI
	530	NI	NI	NI
	540	NI	NI	NI
	550	NI	NI	NI
	560	NI	NI	NI
	570	NI	NI	29 (89)
	580	10 (46)	29 (50)	26 (115)
	590	8 (44)	23 (51)	24 (90)
	600	8 (47)	20 (53)	18 (98)

NI = no ignition.

persons had a noticeable influence on ignition delay time [20]. On the other hand, airflow was found to have a minor effect on the flaming combustion duration, within the flow rate range of (1.5–4.5) l min^{-1} examined, as shown in Table 2.

Finally, it should be noted that with no airflow *Pinus halepensis* samples tend to smolder, which is not clearly visible, under the specific experimental conditions studied.

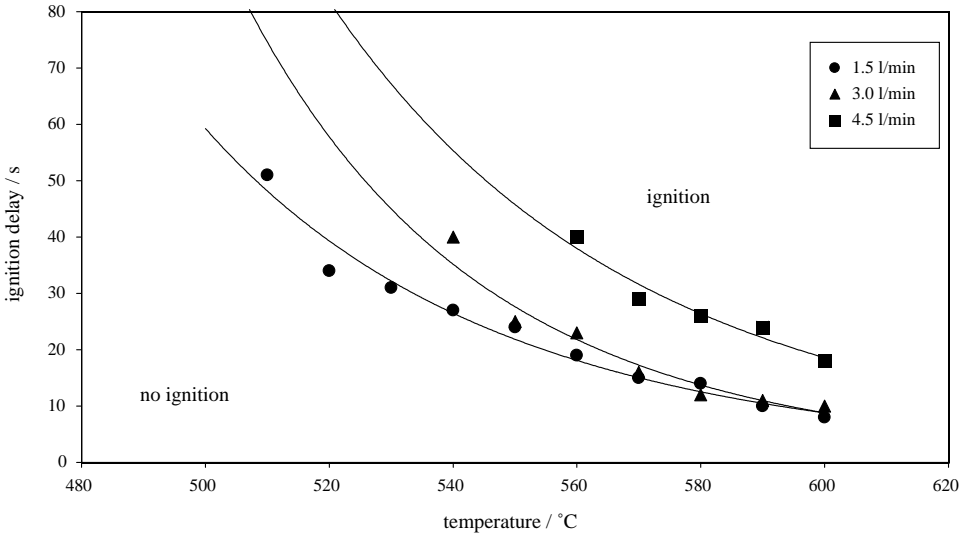


Fig. 2. The effect of air flow on the ignitability (temperature–ignition delay) of *Pinus halepensis* samples (constant sample mass 1.0 g).

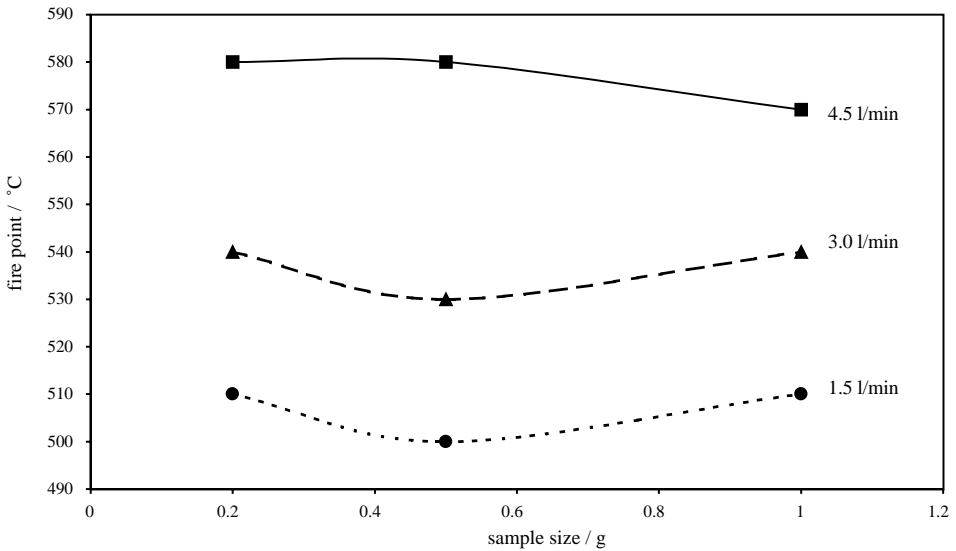


Fig. 3. The effect of sample size and air flow on the fire point values of *Pinus halepensis* samples.

3.3. The influence of sample size

Based on the data shown in Table 2, the ignition delay versus temperature for various mass sizes is depicted in Fig. 4. This graph shows that the ignition delay

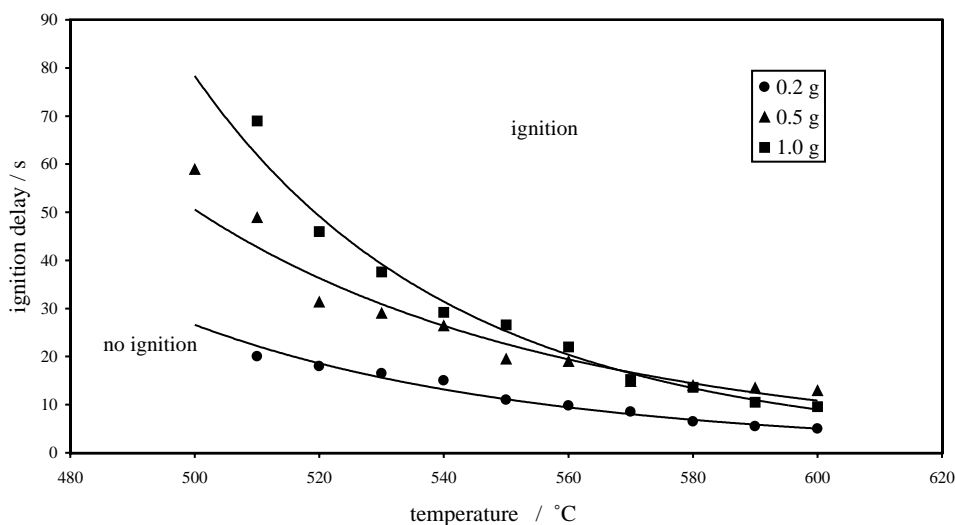


Fig. 4. The effect of sample size on the ignitability (temperature–ignition delay) of *Pinus halepensis* samples under air flow of 1.51 min^{-1} .

increases with specimen sample size, particularly at low temperatures. This can be explained if we consider the thermal mass of the sample, i.e., the amount of heat required to raise the sample to a uniform temperature. This is much greater for the large sample than for the small sample. Heat is being conducted from the surface of the sample into the body of the material so that the larger the sample, the more heat will be lost from the surface in this way and this will delay the achievement of a surface temperature at which spontaneous ignition occurs [1]. In contrast, other researchers obtained longer ignition times for smaller samples. They attributed this to the fact that for small samples the fuel vapors, emerging through the surface of solid fuel, are of relatively low concentration, insufficient to promote ignition [18]. By plotting fire point values versus sample size (Fig. 3) we found that specimen sample size does not significantly affect the ignition of forest fuel in the (0.2–1.0) g range examined. This disengagement from sample size suggests, that the ignition process depends mainly on the heating of a thin layer, near the sample surface. All samples apparently are thicker than this layer, hence the independence from sample size.

The flaming combustion duration time, by contrast, increases significantly (as was expected) with sample size (see Table 2). Based on the data, shown in Table 2, the duration of flaming combustion (using minimum, maximum and average values) versus sample size, for airflow rate 1.51 min^{-1} , is depicted in Fig. 5. However, the limit for zero mass does not correspond to zero flame duration time, as expected. This is interpreted by considering that the smaller samples had smaller sizes and much higher surface to volume ratio, than the bigger ones, thus causing easier evolution of volatiles. Further investigation, with smaller samples was not possible with the method used for preparing the pellets.

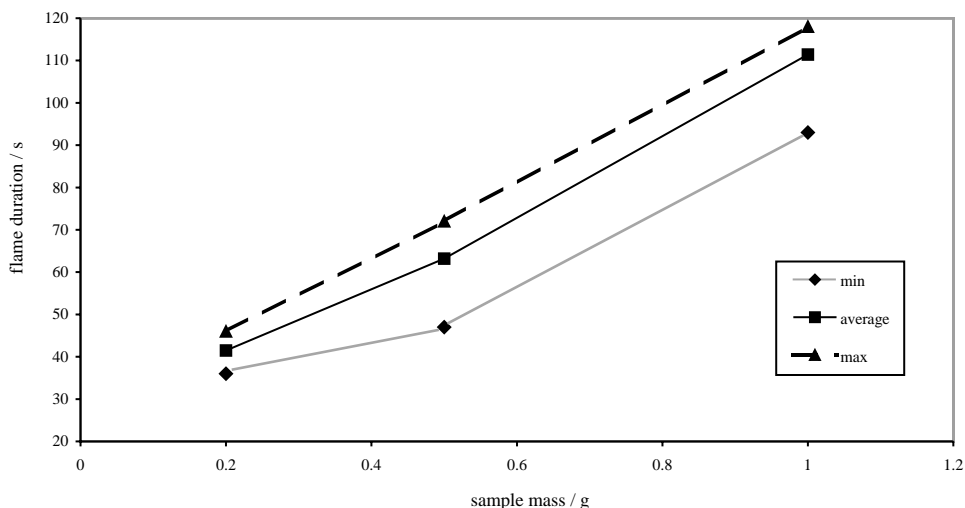


Fig. 5. Flame duration versus sample mass using *Pinus halepensis* samples of 1.0 g and air flow 1.51 min^{-1} .

Finally, it should be noted that some authors have found that the orientation of the specimen can also affect the time to ignition of the solid fuel. However, the changes recorded were negligible [20].

3.4. The influence of fire retardants

Ignition delay and flaming combustion duration data versus temperature in relation to fire retardants applied to forest species are shown in Table 3. The forest samples used were of 1.0 g and the airflow rate was 1.51 min^{-1} . Times and temperatures reported in Table 3 are the average of three replicate tests. The flaming combustion duration is recorded in parentheses.

Fig. 6 shows the effect of $(\text{NH}_4)_2\text{HPO}_4$ (DAP) on the ignitability of *Pinus halepensis* pine needles. As shown in Fig. 6 the presence of DAP increases significantly the ignition delay of the forest specie, particularly at high temperatures, i.e. above 550°C , when high concentration levels of the retardant (i.e. 25%) were applied to the samples. A maximum increase of up to 330% was recorded as shown in Table 3. In addition, the fire point values increased from 510°C to 540°C , while the fire combustion duration, was slightly increased, Table 3.

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

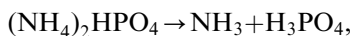
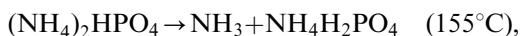
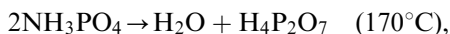


Table 3

The effect of fire retardants on the flaming combustion properties of 1 g *Pinus halepensis* samples in the presence of fire retardants under 1.51 min^{-1} air flow

Retardant	Temperature (°C)	Ignition delay (flaming combustion time) (s)				
		Retardant content per g of forest fuel specie (mg)				
		0	50	100	150	250
DAP						
	500	NI	NI	NI	NI	NI
	510	51 (93)	NI	NI	NI	NI
	520	34 (105)	NI	NI	NI	NI
	530	31(110)	36 (111)	45 (116)	49 (130)	NI
	540	27 (120)	30 (116)	31(115)	38 (116)	45 (142)
	550	24 (109)	27(123)	24 (119)	36 (121)	44 (134)
	560	19 (117)	18 (114)	29 (114)	26 (128)	43 (130)
	570	15 (117)	18 (129)	18 (128)	28 (128)	40 (120)
	580	14 (118)	17(140)	20 (138)	20 (140)	40 (115)
	590	10 (107)	10 (114)	12 (119)	15 (123)	38 (113)
	600	8 (118)	9 (127)	14 (133)	19 (151)	30 (129)
AS						
	500	NI	NI	NI	NI	NI
	510	51 (93)	NI	NI	NI	NI
	520	34 (105)	42 (110)	43 (123)	NI	NI
	530	31(110)	33 (115)	36 (121)	49 (115)	NI
	540	27 (120)	35 (119)	32 (131)	36 (132)	NI
	550	24 (109)	26 (121)	29 (131)	31(144)	36 (131)
	560	19 (117)	20 (122)	23 (135)	25 (151)	26 (156)
	570	15 (117)	22 (132)	17 (147)	16 (139)	22 (145)
	580	14 (118)	13 (134)	16 (154)	17 (150)	18 (165)
	590	10 (107)	13 (136)	12 (134)	15 (153)	16 (174)
	600	8 (118)	10 (122)	12 (141)	13 (138)	12 (137)

NI = no ignition.



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 [13].

Similarly, the presence of $(\text{NH}_4)_2\text{SO}_4$ (AS) affects the ignitability characteristics. However, the effect of AS is more pronounced at low temperatures (i.e. below 540°C) and at high concentration levels of retardant (i.e. 25%), as is shown in Fig. 7. An increase, up to 60%, was recorded for ignition delay times (see Table 3). In addition, the fire point increased from 510°C to 550°C , as the fire combustion duration slightly increased. The retardation effect of $(\text{NH}_4)_2\text{SO}_4$ can be explained similarly as that of $(\text{NH}_4)_2\text{HPO}_4$ given above.

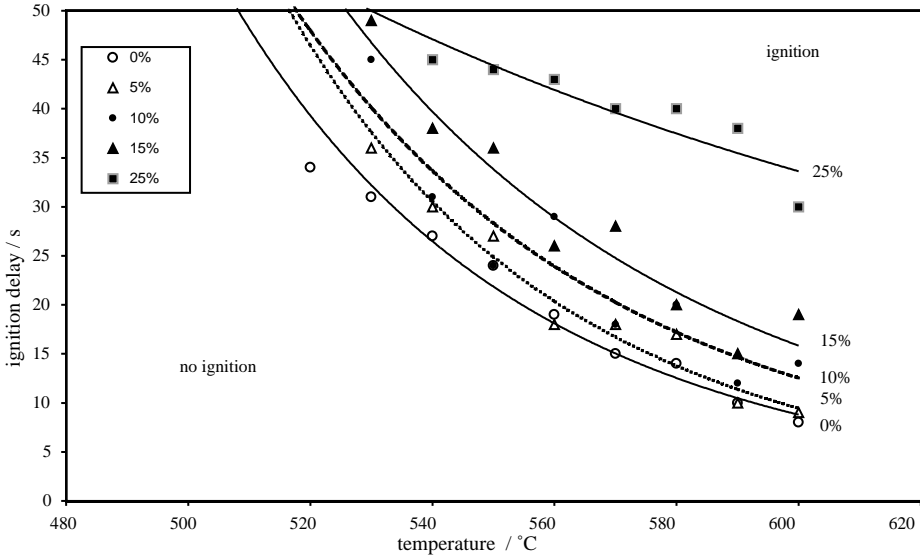


Fig. 6. The effect of DAP on the ignitability (ignition delay versus temperature) of *Pinus halepensis*, using samples of 1.0 g and air flow of 1.51 min^{-1} .

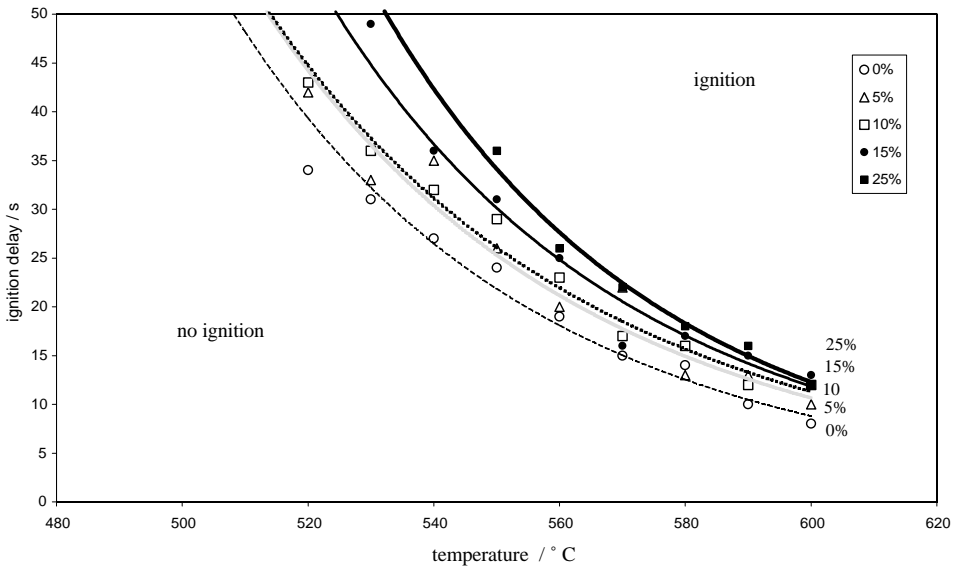


Fig. 7. The effect of AS on the ignitability of *Pinus halepensis* samples.

4. Conclusions

An experimental apparatus has been developed to investigate the effect of various variables, such as airflow, mass size and fire retardant additives, on the ignition properties (ignition delay, fire point, flame combustion duration) of *Pinus halepensis* pine needles. This simple, low cost, apparatus has the potential to be used as a screening device, to compare the fire extinguishing capabilities of various fire retardants. The most interesting conclusions are:

1. The airflow rate affects significantly ignition delay, as well as the fire points values of the fuel examined. The sample size affects mainly the flaming combustion duration as discussed earlier.
2. The retardants tested, reduced considerably the ignition properties of the forest species, affecting their ignition delay and fire point values. The performance of both retardants, $(\text{NH}_4)_2\text{HPO}_4$ (DAP) and $(\text{NH}_4)_2\text{SO}_4$ (AS) increases with their concentration in the samples, in the present range of tests. However, DAP has shown an overall better performance than AS, in terms of increasing the times to ignition. In addition, it was found that DAP has better fire retardant behavior at high temperatures (above 560°C). AS has better performance at low temperatures (below 540°C). It seems therefore that a combination mixture of the above chemicals could prove more beneficial for forest fire retardation. The synergic effect of AS and DAP should be studied.

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