

The retardancy effect of $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{SO}_4$ on six dominant Mediterranean forest species

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Abstract – The fire retarding performance of $(\text{NH}_4)_2\text{HPO}_4$ (DAP) and $(\text{NH}_4)_2\text{SO}_4$ (AS) in various concentration levels (5%, 10%, 15% w/w) was tested by measuring the relative particle fire hazard properties of various forest species samples treated with these chemicals. The forest species selected: *Cupressus sempervirens* (Italian cypress), *Olea europaea* (Olive tree), *Pinus brutia* (Calabrian pine), *Pinus halepensis* (Aleppo pine), *Pistacia lentiscus* (Mastic tree), *Quercus coccifera* (Holly oak), are very common in the Mediterranean region which is frequently devastated by forest fires. The tests were performed using a new method, based on a specifically designed apparatus for monitoring the forest species temperature, under precisely controlled temperature and static air atmosphere conditions. The relative ignition and smoldering combustion properties determined were: the relative self ignition temperature, the combustion duration, and the heat content of forest samples. The key elements for the effectiveness of fire retardants were the delay of ignition and the reduction of heat and combustion rate. Both retardants were found to be efficient on different flammability properties during the smoldering combustion of the forest species examined.

I. INTRODUCTION

Wildfires burn thousands of hectares all over the world each year and fire retardant studies of forest species are very important to forest fire management.

The flammability can be defined as the easiness of a material to catch fire both spontaneously or through exposition to certain ambiances. The flammability of forest species, according to Anderson aspects [1], includes three components: ignitability, combustibility and sustainability. The ignitability determines how easily the fuel ignites. Combustibility is the rate of burn after ignition. Sustainability counts the stability of burning rate, or how well the fuel continues to burn.

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 main purpose of this work is to evaluate the fire extinguishing effectiveness of these two main chemical retardants, using a new simple bench-scale laboratory apparatus constructed for this purpose. The method is based on comparing the relative flammability properties (ignition delay time,

combustion duration, heat content, etc.) of 6 common in the Mediterranean region forest species with those obtained after treatment of the species with DAP and AS at various concentration levels. In addition, this research may lead to a better understanding of the mechanisms of fire retardancy which will facilitate the development of new wildfire retardant products.

II. EXPERIMENTAL

A. Sampling data collection

The forest species foliage was mature, collected after a long drought period in order to avoid moisture effects. The collection site was the mountainside Kalopoula of Ymittos near Athens, located W-NW with dominated rock limestone, geographic coordinates $37^\circ 58' 13''$ N and $23^\circ 48' 20''$ E, height 487 m and average slope 70%. The date of collection was 26 August 2004. According to previous reports, the composition of a forest species depends on various factors: part of plant (bark, wood, leaves), plant age, type of soil, climate, etc. As a consequence, a special care was taken to ensure that the bulk samples collected were representative to the forest species examined [2].

B. Sample preparation

The collected forest species samples were placed into firmly closed polyethylene bags, taken immediately to the laboratory and dried into a vacuum oven for 24 hours under 10 Torr pressure and at a temperature of 60°C .

The flammability tests were performed after reducing plant leaves into a fine, uniform substance (particle foliar flammability). Thus, the study eliminates the influence of plant structure and the external characteristics of combustion (i.e., weather, climate and location) and counts the intrinsic components of the fuel (i.e., chemical composition). The dried samples were ground and the size fraction from $315\ \mu\text{m}$ to $200\ \mu\text{m}$ was selected, in order to have satisfactory repeatability (Figure 1) [2].

The forest species were stored into a conditioning box, at 32°C and relative humidity 12.5%. Thus, the equilibrium moisture content of forest samples retained 2.8 %, according to the insertion tables given in literature [3].

The fire retardant samples were prepared by adding and mixing well certain quantities of chemical retardant in fine powdered form to a certain quantity of ground forest sam-

ples. The concentration levels chosen (5%, 10% and 15% w/w) were similar to that applied by Hellenic Fire Service in real forest fires. The retardants were selected according to results of previous works [4,5], which show that DAP and AS are very efficient chemical retardants, in comparison to other inorganic chemicals. The 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.

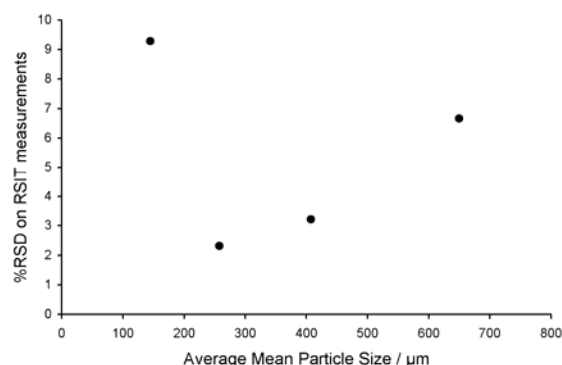


Fig. 1. The influence of particle size on the repeatability of the results.
RSIT: Relative Self Ignition Temperature
RSD: Relative Standard Deviation

C. Apparatus for relative flammability and heat content measurements

The apparatus used for the relative particle foliar flammability and heat content measurements shown in Fig.1 was designed according to 79/831 European Commission Directive [6].

The apparatus consisted of a vertical cylindrical furnace chamber with internal diameter 38 mm and length 300 mm (Fig. 3) heated by coil electric resistance heaters. Temperature control accuracy was $\pm 2\text{ }^\circ\text{C}$ in the range ambient to $1200\text{ }^\circ\text{C}$, whereas a precise programming system was used to control the heating rate between 0.1 and $100\text{ }^\circ\text{C min}^{-1}$. A set of three Chromel / Alumel thermocouples, 0.05 mm diameter, was used to monitor sample, oven and ambient temperatures with an accuracy higher than $0.3\text{ }^\circ\text{C}$ and a response time of 2-4 ms. An analog thermocouple input module, Advantech model Adam-4018, stored up all temperature measurements, taken every 0.01-5 min, and converted them into digital for data handling.

The sample holder was made from stainless wire mesh with 0.045 mm openings folded into open topped 20 mm cube (Fig. 2).

The 8 cm^3 cube was filled with each treated sample and then suspended into the center of the oven with a thermocouple located at the center of the cube (Fig. 2,3). The sample mass was almost 2.5 g, although in each experiment it varied slightly due to the fact that each forest species has a different apparent density.

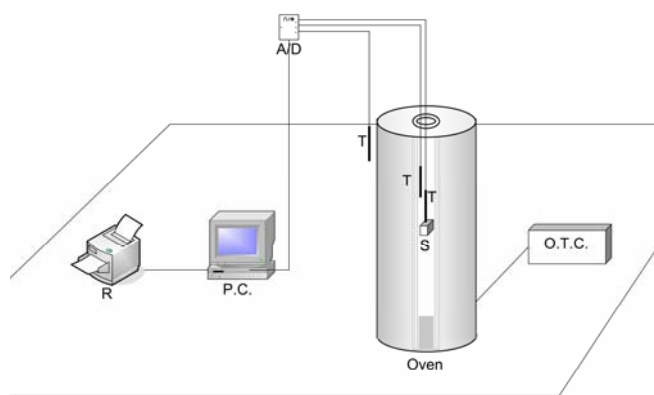


Fig. 2. Schematic diagram of the apparatus used for testing the effectiveness of chemical retardants. T: Thermocouples; S: Sample Holder; O.T.C.: Oven Temperature Controller; A/D: Analog-to-Digital Converter; P.C.: Personal Computer; R: Recorder.

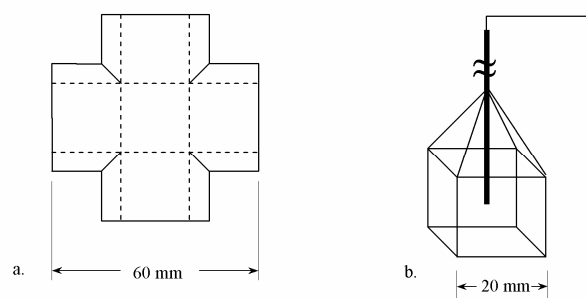


Fig 3. a. Pattern of 20 mm cubic sample holder.
b. The position of thermocouple in the sample holder.

The oven and sample temperatures were measured every 5 s, while the oven temperature was increased to $500\text{ }^\circ\text{C}$, at a rate of $0.5\text{ }^\circ\text{C min}^{-1}$ under static air atmosphere. The heating rate was selected, in order to give satisfactory detail on the decomposition reactions taking place during the heating.

The temperature of the oven at which the sample temperature reaches $400\text{ }^\circ\text{C}$ is defined as relative self-ignition temperature (RSIT – Fig. 4).

By monitoring the forest sample temperature, the temperature profiles were recorded. From their graphical representations, the maximum combustion temperature and the peak area were determined (Fig.5). According to previous experimental work employing a bomb calorimeter [2], the maximum combustion temperature can be related to the sustainability of the burning rate and the peak temperature area is proportional to the heat content of the forest species.

III. RESULTS & DISCUSSION

Under the experimental conditions employed in this study (very low heating rate and static air atmosphere) a smoldering type of combustion took place.

The relative data determined (Relative Self Ignition Temperature, Initial Combustion Temperature, Combustion duration, Maximum Combustion Temperature and Peak Area) provide a simple screening test on the fire hazard properties of forest species [2]. By comparing the relative ignition properties of forest prior and after treatment with chemical retardants, the fire extinguishing efficiency of each retardant was evaluated.

We have sorted the results into 6 tables (Tables I to VI), based on each forest species examined.

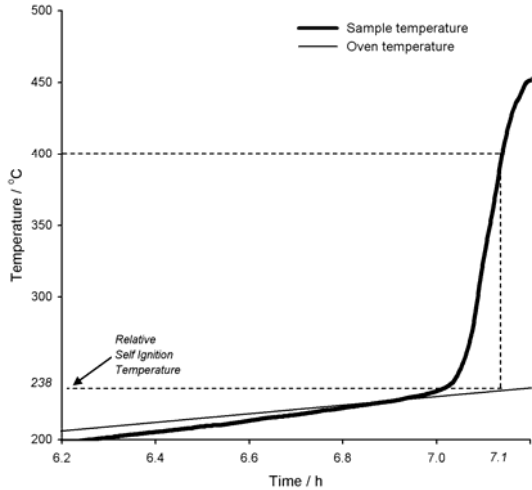


Fig. 4. Measurement of the Relative Self Ignition Temperature

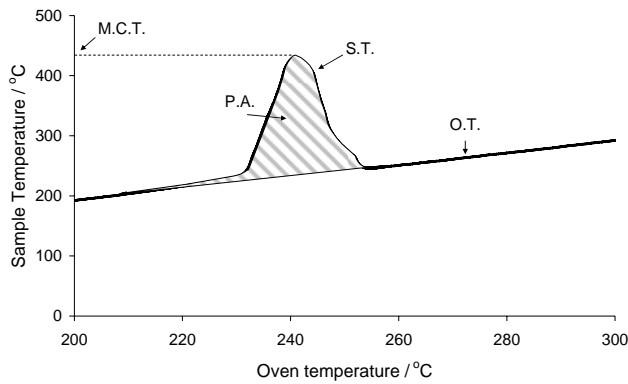


Fig. 5. Measurement of the Maximum Combustion Temperature (MCT) and of the Peak Area (PA). O.T.: Oven temperature; S.T.: Sample temperature

Last, the start point of the burning reaction (Initial combustion temperature) and the Combustion duration were determined), using the first derivative curve of the temperature profile, as seen on Fig. 6. [2].

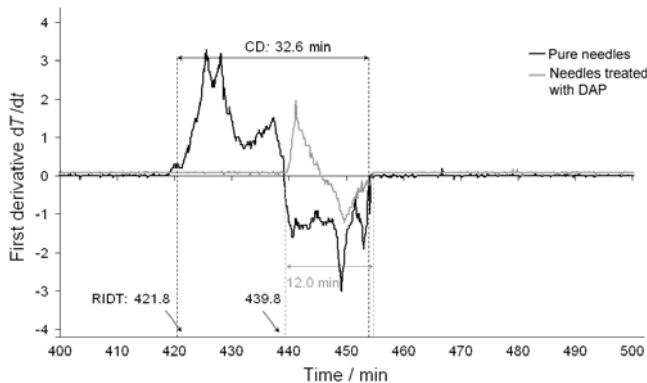


Fig. 6. *Pinus halepensis* needles prior and after treatment with DAP 10% as a typical example of first derivative curves of temperature profiles, showing the measurement of the following flammability properties: CD: Combustion duration; RIDT: Relative ignition delay time.

TABLE I
RELATIVE FLAMMABILITY PROPERTIES OF *Cupressus sempervirens* BEFORE AND AFTER TREATMENT WITH DAP AND AS.

Retardant	w/w	RSIT	ICT	CD	MCT	PA
	%	°C	°C	min	°C	°C s
AS	0	232	227	33.4	483	287 520
	5	242	235	34.2	458	174 425
	10	246	236	37.4	417	142 705
	15	250	238	41.2	406	164 525
DAP	0	232	227	33.4	483	287 520
	5	238	234	31.8	468	264 060
	10	N/A	236	34.2	394	213 390
	15	N/A	236	30.9	366	176 805

TABLE II
RELATIVE FLAMMABILITY PROPERTIES OF *Olea europaea* BEFORE AND AFTER TREATMENT WITH DAP AND AS.

Retardant	w/w	RSIT	ICT	CD	MCT	PA
	%	°C	°C	min	°C	°C s
AS	0	225	222	27.4	514	237 475
	5	227	224	30.8	501	256 000
	10	228	223	34.4	490	213 390
	15	230	225	34.4	475	257 990
DAP	0	230	226	30.0	471	192 943
	5	230	225	28.6	419	145 920
	10	N/A	227	29.6	395	130 685
	15	N/A	226	28.6	349	90 445

RSIT: Relative Self Ignition Temperature; ICT: Initial Combustion Temperature; CD: Combustion duration; MCT: Maximum Combustion Temperature; PA: Peak Area

TABLE III
RELATIVE FLAMMABILITY PROPERTIES OF *Pinus brutia*
BEFORE AND AFTER TREATMENT WITH DAP AND AS.

Retar-dant	w/w	RSIT	ICT	CD	MCT	PA
	%	°C	°C	min	°C	°C s
AS	0	242	239	29.8	514	248 575
	5	245	242	30.8	509	236 490
	10	248	242	36.2	453	232 620
	15	254	245	44.8	425	216 010
DAP	0	247	243	38.4	463	307 121
	5	248	244	30.4	447	229 735
	10	250	245	24.0	406	145 995
	15	N/A	248	16.6	342	91 555

TABLE IV
RELATIVE FLAMMABILITY PROPERTIES OF *Pinus halepensis*
BEFORE AND AFTER TREATMENT WITH DAP AND AS.

Retar-dant	w/w	RSIT	ICT	CD	MCT	PA
	%	°C	°C	min	°C	°C s
AS	0	233	229	30.4	472	230 355
	5	244	239	32.8	467	186 085
	10	249	244	32.6	461	171 265
	15	255	248	38.2	456	166 135
DAP	0	231	227	26.2	444	128 613
	5	240	235	24.0	414	127 015
	10	242	237	21.4	407	100 410
	15	N/A	239	21.2	343	43 730

TABLE V
RELATIVE FLAMMABILITY PROPERTIES OF *Pistacia lentiscus*
BEFORE AND AFTER TREATMENT WITH DAP AND AS.

Retar-dant	w/w	RSIT	ICT	CD	MCT	PA
	%	°C	°C	min	°C	°C s
AS	0	226	221	44.4	441	279 910
	5	N/A	223	38.0	398	170 820
	10	N/A	226	41.2	382	169 785
	15	N/A	229	51.0	391	215 135
DAP	0	226	221	44.4	441	279 910
	5	228	224	36.4	434	239 010
	10	234	227	27.8	405	209 770
	15	N/A	226	29.0	347	91 985

TABLE VI
RELATIVE FLAMMABILITY PROPERTIES OF *Quercus coccifera*
BEFORE AND AFTER TREATMENT WITH DAP AND AS.

Retar-dant	w/w	RSIT	ICT	CD	MCT	PA
	%	°C	°C	min	°C	°C s
AS	0	234	230	38.2	461	324 554
	5	247	241	44.4	420	238 595
	10	N/A	242	52.8	397	221 755
	15	N/A	247	60.6	377	212 260
DAP	0	238	233	45.8	415	266 455
	5	N/A	233	39.0	381	185 805
	10	N/A	236	26.0	373	82 130
	15	N/A	238	18.6	348	29 625

RSIT: Relative Self Ignition Temperature; ICT: Initial Combustion Temperature; CD: Combustion duration; MCT: Maximum Combustion Temperature; PA: Peak Area

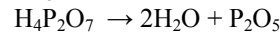
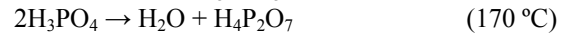
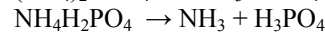
An efficient chemical additive for wood is expected to cause an increase in the relative self-ignition temperature and the initial combustion temperature and a decrease in the maximum combustion temperature, the peak combustion area and the combustion duration. The higher the deviation values are, the most efficient the retardant is.

To note that the calculation of the relative self-ignition temperature was not possible in specific cases, since the applied retardant decreases the maximum combustion temperature at a temperature lower than 400 °C. In such cases, only the Initial Combustion Temperature property was used for the evaluation of the ignition delay time of the retardant.

Careful examination of the aforementioned results confirms previous experimental work [4,5,7,8] concerning the retarding effect of DAP and AS on wood materials.

Ammonium phosphates and ammonium sulphates act via a dehydration mechanism of acids (phosphoric or sulphuric acid) and ammonia, formed during their thermal decomposition, directing the degradation pathway of cellulose toward more char production and fewer volatiles [2,9]. The disadvantage of these chemicals is that easily leach out [10].

The retardancy 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 could also facilitate the decomposition by reacting with intermediate carbonyl compounds to form glycosylamines or Schiff bases.

The retardancy effect of $(\text{NH}_4)_2\text{SO}_4$ (AS) can be explained similarly to $(\text{NH}_4)_2\text{HPO}_4$ (DAP) [9].

IV. CONCLUSIONS

Using a relatively inexpensive but reliable and accurate method, we have tested the retardancy effect of DAP and AS on smoldering combustion of 6 common Mediterranean forest species. The device used to rank those chemical substances is advantageous over other common thermal analysis techniques.

In comparison to other lab-scale flammability tests, the suggested one is both sensitive and reproducible. It is based on a low cost, simple operated apparatus, counting various flammability parameters (i.e., heat content, self ignition temperature, time to ignition, combustion duration, etc), whereas other devices have the potential of determining one sole parameter. In comparison to Thermal Analysis (TA) methods, TA have the drawback of using small samples (i.e., 5 mg) which can lead to erroneous interpretations in terms of forest fuel flammability performance in actual situations.

Careful evaluation of the results can lead to the following conclusions, concerning the retardancy effect of DAP and AS on the various forest species examined:

1. The chemicals had different retardation effect on each forest species examined.
2. The chemicals studied had different influence on the different flammability properties examined. Their effect increased as the retardant concentration levels increased.
3. More specifically, AS appears to be more effective than DAP, as far as the Initial Combustion Temperature and the Relative Self-Ignition Temperature are concerned. AS tends to increase the ICT and RSIT, thus delaying the combustion. The maximum relative increase on the RSIT or ICT property, was recorded by AS applied on *Pinus halepensis* (22 °C or 9.44%).
4. DAP is more effective, in respect to the combustion duration property. DAP efficiently reduces the combustion duration proportionally to its concentration. The maximum relative decrease on the CD property, was recorded by DAP applied on *Quercus coccifera* (27 min or 59.39%).
5. DAP seems to reduce more efficiently than AS the Maximum Combustion Temperature, with the exception of *Quercus coccifera* and *Pistacia lentiscus*, that present the lower values at this property. The maximum relative decrease on the MCT property, was recorded by DAP applied on *Pinus brutia* (121 °C or 26.13%).
6. DAP is more effective in respect to the Peak Area property. An exception can be found in the *Cupressus sempervirens* species, which has the higher value at this property. The maximum relative decrease on the PA property, was recorded by DAP applied on *Quercus coccifera* (236 830 °C s or 88.88%).
7. In respect to all flammability properties examined, AS is most effective on *Cupressus sempervirens* and *Quercus coccifera*, whereas DAP is most effective on *Pinus brutia* and *Quercus coccifera*.

8. DAP and AS are least effective on *Olea europaea*, under the experimental conditions examined.

On the whole, DAP seems to be more efficient retardant than AS in smoldering combustion, since it affects more flammability properties. Combining the observations regarding the Peak Area and the Maximum Combustion Temperature, DAP efficiently reduces the heat release rate of a forest species [2]. However, according to literature [10], AS affects primarily flaming combustion, which is not examined in this study. The above observations lead to the conclusion that the highest overall retardant efficiency can be obtained from chemical mixtures.

Moreover, the efficiency of each retardant depends on the applied forest species. Thus, in real forest fire conditions, successful selection of a retardant should be made according to the forest species involved.

In further work, chemical mixtures of DAP and AS should be studied, in order to examine synergistic mechanisms affecting the flammability of wood or forest species. Furthermore, the retardants effect on flaming combustion of forest species should be studied, using oxygen atmosphere and higher heating rate conditions. In addition, the retardancy effect on each intrinsic component of wood (i.e. lignin, cellulose, extractives, etc.) should be studied for a better understanding of the mechanisms of fire retardancy. This will facilitate the development of new fire retardant products.

V. ACKNOWLEDGMENT

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