

Evaluating the fire retardation efficiency of diammonium phosphate, ammonium sulphate and magnesium carbonate minerals on *Pistacia lentiscus* L.

Stylios Liodakis, Ioannis Antonopoulos
Laboratory of Inorganic and Analytical Chemistry,
Department of Chemical Engineering, Sector I
National Technical University of Athens (NTUA)
9 Iroon Politechniou, St.
Athens 157 73, Greece
liodakis@central.ntua.gr

Abstract – The retardation properties of diammonium phosphate (DAP), ammonium sulfate (AS) and a mixture of huntite/hydromagnesite minerals were studied on particle foliar combustion of *Pistacia lentiscus* L. (Mastic tree) collected from wildland/urban zones near Athens. Two methods were employed for this study. The first is thermal analysis (TG, DTG, SDTA), that uses samples of 15-17 mg under oxygen atmosphere conditions to ensure flaming combustion. The second is a laboratory-scale method (similar to the one described by the 79/831 European Commission Directive for testing relative self ignition properties of solid materials), that uses samples of 2.5 g under static air conditions and low heating rate to ensure smoldering combustion. Both methods concluded that DAP and AS are the most effective retardants, with each presenting better performance at different properties, while the minerals are the least efficient ones.

I. INTRODUCTION

In forests there are three major fuel types: (a) crown fuel (foliage and branches in the overstory), (b) fine fuel in ground vegetation and litter (living vegetation and twigs, leaves and needles) and (c) duff in the ground layer (layers of decomposing litter and decomposed organic soil) [1-3].

Exposing a forest fuel to a sufficiently high heat flux, results to its thermal degradation, which can be considered as two consecutive steps. The first is pyrolysis, which is an endothermic process and breaks down the forest material into low molecular mass gases known as volatiles, tars, carbonaceous char and mineral ash. The second step is exothermic, known as combustion.

Wildland fires consume biomass through flaming or smoldering combustion. Flaming combustion is a gas oxidation phase, accompanied by emission of flames and occurs over short time periods in localized areas. It typically occurs in the crown and fine fuel (surface) layers. Smoldering (or else glowing or surface) combustion is associated with surface oxidation of the char and can last long after flaming combustion has occurred. It typically consumes ground layer fuels. Crown and surface fires usually occur in conjunction with smoldering ground fires.

Forest fire retardant systems are divided in two categories: short-term and long-term. Short-term retardants are suppressants, basically water or water with additives that reduce its surface tension or increase its viscosity. These retardants lose their effectiveness when removed from the fuel by evaporation.

Long-term retardants are chemicals dissolved in water that

remain effective even after the water evaporation. There are four main theories describing the action of fire retardants on cellulosic materials: (1) Chemical theory, in which the active ingredients of fire retardants alter the pyrolysis mechanism, promoting the formation of char and water; (2) Thermal theory, in which the fire retardant has an insulating or a thermal conductivity action; (3) Coating theory, which states that the formation of an impervious coating around the fuel at combustion temperatures effectively reduces the oxygen supply necessary for complete combustion; (4) Gas theory, which states that combustion can be halted by the emission of non-combustible gases from the fire retardant.

Among long-term fire retardants, DAP and AS have a primary place in market, while the minerals huntite and hydromagnesite have been used as retardants in polymer mixtures [4,5]. The use of minerals has been reviewed in previous reports [6-9]. Moreover, their extraction from Greek mines, where they are found in quantities [10-13], supports, on the one hand the potential of commercial fire retardant production in Greece and on the other hand, the introduction of new raw materials in the existing fire retardant industry.

Among methods used for evaluating the effectiveness of a fire retardant, thermogravimetry has a primary place [14-17]. Combustion is usually studied under air flow conditions, in order to simulate open-air fire conditions [18,19]. However, the small samples used in thermogravimetric methods and the rapid removal of combustion products can lead to an erroneous interpretation in terms of forest fuel ignitability performance in field conditions. Therefore, the information provided by thermogravimetry should be supported by large-scale tests, thus approaching actual wildland fire conditions.

This particular study aims to evaluate the forest fire retardation performance of the inorganic substances DAP, AS and the mineral mixture huntite/hydromagnesite on foliar combustion properties of forest material *Pistacia lentiscus* L. (Mastic tree), collected from wildland/urban interface zones. The experiments were performed employing both analytical and lab-scale tests, after having reduced plant leaves and fire retardants into a fine, uniform substance in powder form.

II. EXPERIMENTAL

A. Instruments

Thermogravimetric analysis (TGA), differential thermo-

gravimetry (DTG) and differential thermal analysis (DTA) were conducted using a Mettler TGA/SDTA 851 apparatus.

The lab-scale flammability test method consists of a specifically designed apparatus for monitoring the forest species temperature, under precisely controlled temperature and static air atmosphere conditions. A detailed description of this apparatus is given in a previous report [20].

The particle foliar combustion properties determined from thermal analysis were: ignition delay time, start and end of active combustion, temperature of maximum weight loss rate, combustion duration and mass residue.

Properties determined from the lab-scale flammability method were: relative self ignition temperature, ignition delay time, initial combustion temperature, maximum combustion temperature, final combustion temperature, combustion duration, temperature peak area and mass residue.

B. Methods

B.1 Thermal analysis test

Each sample weighed around 15-17 mg and was put in an open type alumina sample holder. The experiments were carried out under non-isothermal conditions (25 °C to 600 °C) with a linear heating rate of 10 °C/min in oxygen atmosphere with a flow rate of 100 mL/min. All runs were conducted in oxygen atmosphere at a flow rate of 100 ml/min, in order to approach to the extent possible actual combustion conditions.

B.2 Lab-scale flammability test

The sample weighed around 2.5 g and filled up a 20 mm cubic sample holder. The oven temperature was increased from 20 °C to 500 °C with a heating rate of 0.5 °C/min. Temperatures of oven and sample were recorded every 5 sec. A detailed description of the apparatus and used operating conditions are given elsewhere [20,21].

C. Materials

The samples of *Pistacia lentiscus* L. leaves were collected from a wildland/urban interface area (WUI) named Thrakomacedones, which is an area located at the foothill of mountain Parnitha, northern of Athens. The sampling site had: geographical coordinates 38° 07' 50'' N, 23° 46' 22'' E, altitude 323 m, average inclination 10%, exposition E (97 °) and dominating petrologic formation: Coarse-grained fluvio-lacustrine formation on Parnitha piedmont. The samples were collected after a long drought period in order to avoid moisture effects. The collected foliage samples were placed into firmly closed polyethylene bags, brought immediately to the laboratory, dried into a vacuum oven for 48 h under pressure of 10 Torr and temperature of 60 °C and then ground. A fraction between 100 and 200 µm was separated and used for the tests.

The used fire retardants DAP [(NH₄)₂HPO₄] and AS [(NH₄)₂SO₄] were both Merck laboratory reagents. The natural mixture of minerals huntite [Mg₃Ca(CO₃)₄] and hydromagnesite [Mg₅(CO₃)₄(OH)₂·4H₂O] was mined from the Kozani basin, located in northern Greece [22,23]. All these re-

tardant powders were ground and a fraction of less than 20 µm was used for the tests.

The forest material was then mixed with the retardant powders and the samples were placed into a conditioning box, set at temperature of 31.3 °C and relative humidity of 8%. The equilibrium moisture content of samples tested was found 2% by linear insertion, according to the tables given in the standard method ASTM D 4933 [24].

III. RESULTS AND DISCUSSION

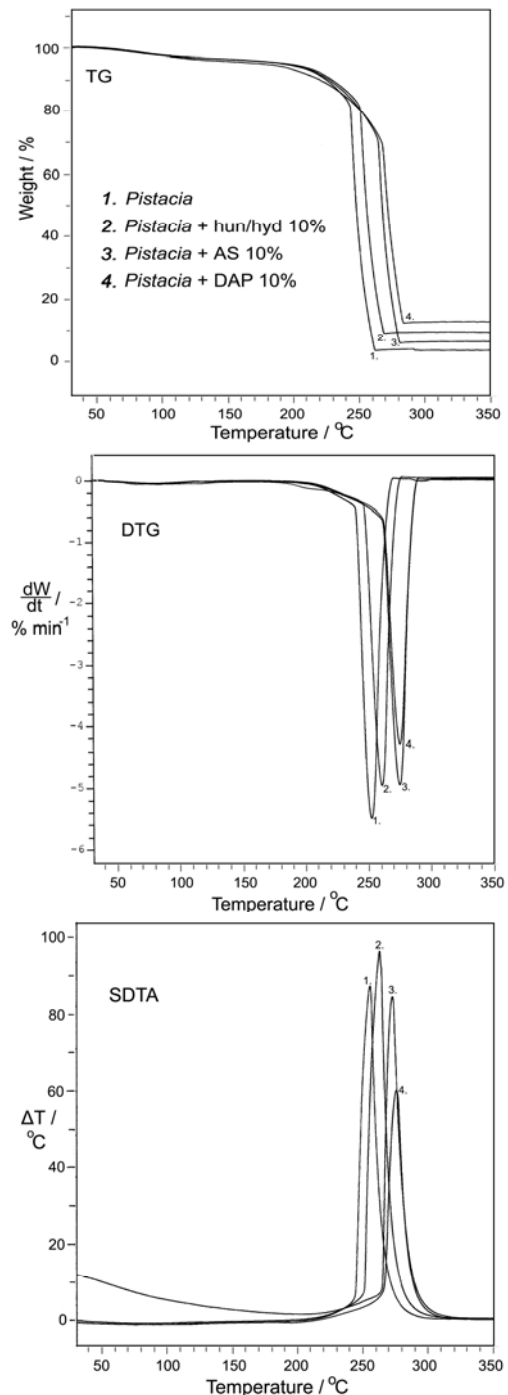


Fig. 1. TGA, DTG and SDTA curves of *Pistacia lentiscus* treated with DAP, AS and huntite/hydromagnesite

TABLE I
THERMOGRAVIMETRIC ANALYSIS OF *Pistacia lentiscus* SAMPLES

Sample	Ignition delay time (min)	Start of active combustion (°C)	Temperature of maximum weight loss rate (°C)	End of active combustion (°C)	Combustion duration (min)	Mass residue (% o.d.w)
<i>Pistacia lentiscus</i> pure	25.91 (0.29)	259.05 (2.94)	297.10 (1.12)	317.06 (5.34)	5.80 (0.24)	3.7642 (0.0093)
<i>Pistacia lentiscus</i> + AS 10%	27.90 (0.31)	279.00 (3.05)	310.64 (2.78)	335.56 (5.42)	5.66 (0.24)	3.7063 (0.1152)
<i>Pistacia lentiscus</i> + DAP 10%	27.56 (0.30)	275.60 (3.01)	305.37 (1.47)	334.98 (1.82)	5.94 (0.48)	9.5104 (0.5555)
<i>Pistacia lentiscus</i> + huntite/hydromagnesite 10%	26.41 (0.10)	264.13 (0.97)	299.49 (0.95)	336.95 (1.57)	7.28 (0.06)	9.8260 (0.0589)

Note: The data given in Table are the mean values of three replicate measurements and in parenthesis are the corresponding RSD values

TABLE II
LAB-SCALE TESTS OF *Pistacia lentiscus* SAMPLES

Sample content	Relative Self Ignition Temperature (°C)	Ignition delay time (min)	Initial combustion temperature (°C)	Maximum combustion temperature (°C)	Final combustion temperature (°C)	Combustion duration (min)	Temperature Peak area (°C s·10 ⁹)	Mass residue (% o.d.w)
<i>Pistacia lentiscus</i> pure	229.17 (1.32)	410.51 (2.35)	225.25 (1.57)	457.12 (2.76)	244.29 (1.98)	38.08 (2.43)	2.33 (0.09)	5.58 (0.12)
<i>Pistacia lentiscus</i> + AS 10%	252.29 (1.78)	454.52 (1.47)	247.25 (1.62)	468.89 (2.03)	260.67 (3.43)	26.83 (2.12)	1.20 (0.31)	5.97 (0.32)
<i>Pistacia lentiscus</i> + DAP 10%	250.75 (2.02)	455.75 (2.35)	247.87 (3.59)	444.73 (3.04)	262.75 (2.56)	29.75 (1.23)	1.12 (0.42)	16.59 (0.89)
<i>Pistacia lentiscus</i> + huntite/hydromagnesite 10%	246.05 (0.98)	443.25 (0.72)	241.62 (2.91)	419.37 (1.32)	257.33 (2.05)	31.42 (1.07)	1.15 (0.21)	11.71 (1.19)

Note: The data given in Table are the mean values of three replicate measurements and in parenthesis are the corresponding RSD values

In Fig. 1 are presented the TG, DTG and SDTA curves of thermal analysis of *Pistacia lentiscus* samples treated with the fire retardants (DAP, AS, huntite/hydromagnesite).

In Table I are presented the particle foliar combustion properties derived from thermal analysis, i.e. ignition delay time, start and end of active combustion, temperature of maximum weight loss rate, combustion duration and mass residue.

In Fig. 2 are presented the temperature profile curves of forest samples, derived from the lab-scale flammability test. In Table II are presented the relative particle foliar combustion properties data measured by the lab-scale method, i.e. self ignition temperature, ignition delay time, initial and final combustion temperature, maximum combustion temperature, temperature peak area, combustion duration and mass residue.

Each value in Tables I and II is the average of three replicate tests and in parenthesis is shown the corresponding relative standard deviation value.

The key elements for evaluating the fire retardation effectiveness of the three examined chemicals were: the increase of ignition temperature (start of active combustion), increase of mass residue, decrease of smoldering combus-

tion peak area and decrease of smoldering combustion duration.

Both Fig. 1 and Fig. 2 show that all examined fire retardants shift the ignition temperature to higher values. Thus, they increase the forest species ignition temperature, with AS being the most effective retardant in this criterion.

Mass residue also increases by the presence of the chemical retardants, with DAP and huntite/hydromagnesite being more effective.

The peak area of smoldering combustion criterion was drastically reduced by the presence of all three chemical retardants, with DAP being the most effective.

Based on the combustion duration of smoldering combustion, the most effective chemical retardant is AS, followed by DAP.

The chemicals studied had different influence on the particle foliar combustion properties examined. Thus, AS and DAP seem to have a better overall performance, with huntite/hydromagnesite following. This leads to the conclusion that the highest overall retardant efficiency can be obtained with chemical mixtures.

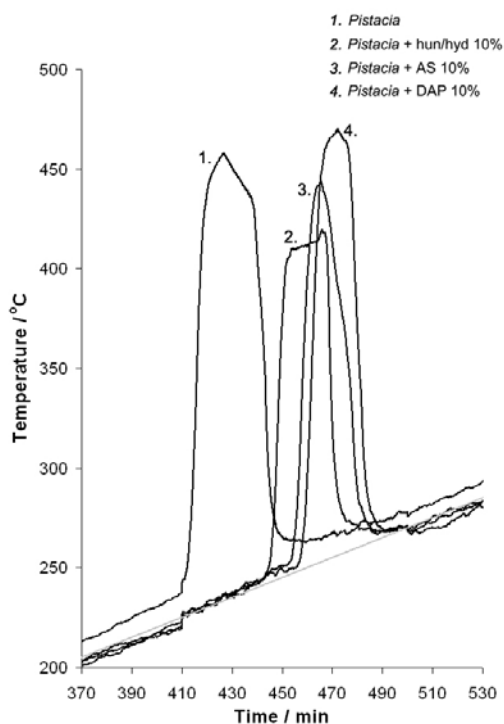


Fig. 2. Oven temperature vs time profiles of *Pistacia lentiscus* treated with DAP, AS and huntite/hydromagnesite

IV. ACKNOWLEDGMENT

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