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Characterization of the thermal degradation and heat of combustion of *Pinus halepensis* needles treated with ammonium-polyphosphate-based retardants

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Abstract The thermal degradation behavior of *P. halepensis* needles treated with two ammonium-polyphosphate-based commercial retardants was studied using thermal analysis (DTG) under nitrogen atmosphere. Moreover, for the same experimental material, the heat of combustion of the volatiles was estimated based on the difference between the heat of combustion of the fuel and the heat contribution of the charred residue left after pyrolysis. The heat of combustion of the volatiles was exponentially related to the retardant concentration of the samples. In the range of retardant concentrations from 10 to 20% w/w the mean reduction percentage of the heat of combustion of the volatiles, with respect to untreated samples, was 18%.

Keywords Bomb calorimeter · Char · Forest fires · Heat of combustion · Long-term retardants · Thermal analysis · Volatiles

List of symbols

APP	Ammonium polyphosphate
DTG	Differential thermogravimetry
DR	DTG peak decomposition rate (10^3 s^{-1})
EHC	Effective heat of combustion (MJ kg^{-1} fuel consumed)
FT1	Fire-Trol 931
FT4	Fire-Trol 934
HC	Heat of combustion (MJ kg^{-1})
HHC	High heat of combustion (MJ kg^{-1})
HY	Heat yield (MJ kg^{-1})
$(\Delta h_c/r_0)$	Heat of combustion released per kg of oxygen consumed (13.1 MJ kg^{-1})
$\Delta h_{dsp\,\mathrm{H_2O}}$	Heat of desorption of bound water in the fuel (MJ kg^{-1})
$\Delta h_{v\,\mathrm{H_2O}}$	Latent heat of vaporization of water at 100 °C (MJ kg^{-1})
LHC	Low heat of combustion (MJ kg^{-1})
$\dot{m}_{\mathrm{O_2},\infty}$	Oxygen mass flow at ambient conditions (kg s^{-1})
$\dot{m}_{\mathrm{O_2}}$	Instaneous oxygen mass flow (kg s^{-1})
PH	*Pinus halepensis*
$\dot{q}$	Heat rate (kW)
Q_{inc}	Heat loss due to incomplete combustion (MJ kg^{-1})
Q_{rad}	Heat loss due to radiation losses (MJ kg^{-1})
R_{550}	Percentage of residual mass at 550 °C to initial mass at 150 °C (% w/w)
PT	DTG peak temperature (°C)
X_c	Char yield (% w/w)
X_H	Percentage of hydrogen (% w/w)
X_r	Retardant concentration (% w/w)
X_w	Moisture content on a dry basis (% w/w)

Subscripts/superscripts

c	Charred residue
f	Fuel
r	Retardant
vol	Volatiles
1, 2, 3	Peak number in DTG graphs

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Introduction

Thousands of forest hectares burn every year in wildfires. Fire prevention and fire suppression are two fundamental management tactics used to protect wildland from fires. In suppression operations, two different extinguishing methods may be applied, depending primarily on the fire's behavior: direct or indirect attack. Direct actions are usually taken during the initial stages of a fire or when, due to the fire's characteristics, it is possible to prepare control lines near its active edge. Indirect operations are generally done in cases of fast-spreading or high-intensity fires, or to use natural or constructed fire-breaks or fuel-breaks. In indirect operations, the control line is located away from the fire's active edge.

Long-term retardant products are used as an indirect attack tool for wildland fire management. After being mixed with water in a prescribed ratio, retardants can be applied from aerial or ground application equipment to slow the spread and reduce the intensity of a fire. They continue to be effective after the water they contain has evaporated [1]. The main active compounds of commercial long-term retardants are ammonium phosphate and sulfate salts. These compounds alter the thermal decomposition (pyrolysis) of forest species. Acids generated during the thermal degradation of the salts catalyze pyrolysis dehydration reactions of forest fuels and promote the appearance of char at the expense of volatiles or flammable tars [2]. Long-term forest fire retardants have been studied for more than 20 years. Analytical trials and tests of flame-front propagation have been carried out to quantify the effectiveness of different products and to gain knowledge about their chemical action mechanisms. Most analytical research has been performed with diammonium phosphate salts and less attention has been paid to commercial products based on ammonium polyphosphates. Only a few studies have modeled fire behavior in areas treated with long-term retardants [3].

The general goal of this study is to obtain data that can be used to predict the behavior of forest fires that propagate in fuel treated with long-term retardants. This study is guided by the hypothesis that in real extinction operations retardants alter the burning behavior of the species rather than the extrinsic characteristics of the structure of the forest fuel (surface-area-to-volume ratio, bulk density, packing ratio, etc.). Based on this idea, the heat of combustion of a forest species (*P. halepensis* needles) treated with two commercial long-term retardants containing ammonium polyphosphate (APP) [Fire-Trol 931 (FT1) and Fire-Trol 934 (FT4)] was examined. Heat of combustion is generally used to calculate the calorific power of propagating forest fires.

A prior thermogravimetric analysis was carried out to characterize the pyrolytic behavior of *P. halepensis* needles treated with the two retardants. Thermogravimetric analyses are used to evaluate the performance of fire retardants [3–5] and to analyze differences in the thermal decomposition characteristics. The retardants used in this study are both APP-based. FT1 only differs from FT4 in that it contains a small amount of coloring agent (iron oxide) and attapulgite clay to suspend the color. According to George et al. [6], small percentages of iron can tie up phosphates to form insoluble compounds that may be ineffective fire retardants. Based on this statement, both products were used and thermogravimetric analyses were performed to determine whether this is the case.

Heat of combustion background in forest fires

The heat of combustion is the energy released when a species undergoes complete combustion with oxygen, and as such it gives an estimate of the amount of energy available per mass of fuel involved in a forest fire. When this term is used, it is important to specify whether it refers to the: high heat of combustion (*HHC*), low heat of combustion (*LHC*), heat yield (*HY*), heat of combustion of the volatiles (HC_{vol}) or effective heat of combustion (*EHC*).

The *HHC* value of a dried sample can be obtained with an oxygen bomb calorimeter. It is a maximum value because the sample burns under complete combustion conditions (high pressure and pure oxygen inside the bomb) and it contains the heat given up when the water vapor of the combustion reaction condenses and cools to the temperature of the bomb. In forest fires, this water vapor escapes as steam, so it is more accurate to subtract this energy contribution and instead consider the *LHC*. The *LHC* value can be obtained by subtracting from the *HHC* the latent heat of vaporization of water multiplied by the amount of water generated during the combustion reaction per amount of fuel. This proportion can be obtained by considering the hydrogen percentage of the dried sample. Thus, if a given amount of forest fuel is completely combusted, the *LHC* can be obtained according to Eq. 1.

$$LHC = HHC - \Delta h_{v\,\mathrm{H_2O}}\; 9\, X_{\mathrm{H}} \qquad (1)$$

The *HY* value was defined by Byram [7] as being numerically equal to the *HHC* value minus the heat losses associated with the vaporization of the water formed during combustion, the presence of moisture in the fuel, the incomplete combustion and the radiation losses (see Eq. 2). The heat loss associated with the vaporization of the water of reaction was equal to the reduction term used to compute the *LHC* value. The heat loss associated with the presence of moisture in the fuel included both the heat of vaporization and the heat of desorption. The term of incomplete combustion remained a matter of subjective judgment, since only a rough guideline was given for its estimation based on visual inspections of smoke and fire intensity [7]. In a later report [8] it was pointed out that the last term, associated with radiation losses, should not be considered because radiation contributes greatly to fire behavior.

$$HY = HHC - \Delta h_{v\,\mathrm{H_2O}}\, 9\, X_{\mathrm{H}} - \left(\Delta h_{v\,\mathrm{H_2O}} + \Delta h_{dsp\,\mathrm{H_2O}}\right) X_w - Q_{inc} - Q_{rad} \quad (2)$$

Susott [9] determined HC_{vol} as shown in Eq. 3. He did not specify whether the heat of combustion of the fuel (HC_f) and char (HC_c) had been computed as *HHC* or *LHC*. However, the use of *LHC* is more suitable because it is closer to real fire conditions.

$$HC_{vol} = HC_f - X_c\, HC_c \quad (3)$$

The HC_{vol} term was basically introduced to consider rapidly spreading forest fires, which propagate primarily by flaming combustion of volatiles, with residual smoldering combustion of char contributing little to propagation [10].

The effective heat of combustion (*EHC*) is normally computed from data obtained by oxygen consumption calorimeters. The primary data taken from this type of equipment are a heat-release rate curve and a mass-loss rate curve [11]. The heat-release rate is obtained by considering the heat of combustion per mass of oxygen consumed nearly constant and equal to 13.1 MJ kg^{-1} [12], and by measuring the consumption of oxygen due to combustion (see Eq. 4).

$$\dot{q} = (\Delta h_c / r_0)\left(\dot{m}_{\mathrm{O}_2,\infty} - \dot{m}_{\mathrm{O}_2}\right) \quad (4)$$

On the basis of the terminology introduced in the previous paragraphs, two test methods are clearly distinguished for use in determining heats of combustion: oxygen bomb calorimetry and oxygen consumption calorimetry.

Ground samples of the test material are used in oxygen bomb calorimetry, so considerations of vegetation structure are avoided. Wood *LHC* values obtained by bomb calorimetry tests have been reported in the range of 16–18 MJ kg^{-1} [11].

Oxygen consumption calorimeters basically differ from one another in two ways: apparatus design (ignition/heating system, weighing system and dimensions) and gas analysis instruments. For instance, in [9, 13], the authors designed an oxygen consumption calorimeter by adapting a gas chromatograph detector for thermal analysis. Another type of oxygen consumption calorimeter was used in [14]. These authors used an intermediate-scale calorimeter consisting basically of equipment for measuring $\mathrm{O_2}$, $\mathrm{CO_2}$ and CO concentrations, two platforms of load cells, a propane line burner and a three-sided ceramic board enclosure. However, the most widely used oxygen consumption calorimeter is the cone calorimeter [15], which is a bench-scale heat-release-rate apparatus that is commonly used to evaluate the combustion characteristics of building materials. It can also be used to test foliage and twig samples and rank vegetation flammability. In [11], the authors reported cone calorimetry *EHC* values of 12–13 MJ kg^{-1} for wood.

Weise et al. [14] indicated that the main distinction between the effective heat of combustion found by cone calorimeters and the heat of combustion found by oxygen bomb calorimeters is the residual charred material. For instance, 20–30% of a wood sample is not consumed in a cone calorimeter [14]. As a result, cone calorimeter values are normally lower than oxygen bomb calorimeter values.

Dibble et al. [11] pointed out certain methodological matters that need further refinement before the cone calorimeter can be widely used to measure forest fire behavior characteristics. In [14], the authors showed that further work should be done to clarify the effect of the physical characteristics of the test sample (e.g. mass and thickness), heat flux level and sample holding system on the flammability properties measured. Because of all these open questions related to cone calorimetry, and because it is actually a more standardized methodology, a bomb calorimeter was used in this study.

Ammonium-phosphate-based retardants reduce the amount of fuel available in the gas phase and act against smoldering combustion [2, 16, 17]. Thus, the energy contribution of char combustion is not available when fuel treated with the above retardants is burning. In particular, the heat of combustion of the volatiles (HC_{vol}) is therefore the most suitable term for studying flame-front propagation after fuel treatment with ammonium-phosphate-based retardants.

The HC_{vol} term has been used in several studies to describe the flame properties of either spreading [18] or static [19] fires. In [18], the authors used this value to compute the fireline intensity of a flame front spreading through an untreated and homogeneous fuel bed. They then used the fireline intensity value to model flame characteristics (angle and height) and the radiation heat transfer mechanism. In [19], the authors studied the properties of flames stemming from the combustion of a simulated isolated small shrub. They calculated the maximum rate of heat release from the maximum rate of mass loss and the value of heat of combustion of the volatiles.

In this study, the term was computed for samples with different retardant concentrations. This value was determined by subtracting the heat of combustion of the charred residue left after pyrolysis from the total heat of combustion of the fuel. The char was prepared in a pyrolytic furnace, and the samples and the corresponding char were burned in an oxygen bomb calorimeter.

Methods

Samples

The forest species used was *P. halepensis*. Mature needles were collected on October 4, 2006 in an area of Thrakomakedones, a wildland-urban interface area in the foothills of Mount Parnitha, north of Athens (Greece). The needles were immediately brought to the laboratory and dried in a vacuum oven for 24 h under 1,333 Pa of pressure at a temperature of 60 °C. Afterwards, they were ground and a size fraction ranging from 0.1 to 0.2 mm was separated and used for the tests.

Two commercial long-term forest fire retardants were used: Fire-Trol 931 (FT1) and Fire-Trol 934 (FT4). To ensure a homogeneous treatment of the ground pine needles, the retardant liquid concentrate was converted into powder by evaporation of the water solvent. It was dried in a vacuum oven for 72 h under 1,333 Pa of pressure at a temperature of 60 °C. The resulting solid was ground and a size fraction of less than 0.02 mm was used for the experimental tests.

The retardant treated samples were prepared by thoroughly mixing the pine needle powder with the retardant powder at three treatment levels: 10, 15 and 20% w/w. Pure pine needle powder was also tested.

Thermogravimetric analysis (TGA)

TG/DTG experiments were performed using a Seteram thermobalance (1200 model). Measurements were carried out using nitrogen gas, with a flow rate of 200 mL min^{-1}. Powder samples of 7 mg were placed in an open platinum crucible and heated from 23 to 600 °C with a low heating rate of 10 °C min^{-1}. Low heating rates make it possible to distinguish DTG peaks, whereas high heating rates may cause peaks to overlap. Four replicates were performed with each sample.

Char preparation

To prepare char, the samples were heated under a 400 mL min^{-1} flow of nitrogen. In forest fires, fuel is heated in the presence of air, so pyrolysis and combustion reactions are in fact simultaneous processes. In our experiments, however, it was necessary to prepare char under pyrolytic conditions because the two processes were simulated separately.

A horizontal, electrically heated cylindrical furnace (30 cm long) containing a Pyrex tube (3.8 cm diameter) was used to produce the char. The inlet of the furnace was connected to a compressed nitrogen cylinder via a rubber tube. Volatile pyrolysis products were released to the environment, whereas the tarry pyrolyzate fraction was condensed into a funnel located at the outlet of the horizontal furnace.

A 24 cm^3 (2 × 2 × 6 cm^3; height × width × length) open sample holder made from stainless wire mesh was used to accommodate 3 g of powder sample into the tube furnace. A thermocouple was also placed in the furnace to monitor the oven temperature. The following heating steps were programmed by a controller device to control the furnace temperature:

- *First step*: Ramp rate of 10 °C min^{-1}, from ambient temperature to 350 °C
- *Second step*: Constant temperature (350 °C) for 5 min
- *Third step*: Heating is stopped and the cooling period begins

During the cooling period to room temperature, nitrogen was flowed into the furnace to avoid the oxidation of the char prepared.

Some preliminary tests were performed to adjust the minimum flow of nitrogen. Five different values were tested. The products obtained using 60, 250, 300 and 350 mL min^{-1} contained little amount of ash (grey residue). However, with a flow of 400 mL min^{-1}, a deep black residue was observed.

The initial mass of pure or treated pine and the residual mass of char in the sample holder were recorded to compute the char yield value (X_c). Residual masses of char were later burned in a bomb calorimeter.

Bomb calorimetry

Bomb calorimetry tests were conducted using a plain jacket bomb calorimeter (Parr Instrument, model 1341) and powder samples (1 g) of pure and treated *P. halepensis* needles, and of the corresponding char. Before performing tests on the samples, the bomb calorimeter was standardized with benzoic acid pellets and its energy equivalent factor was determined (mean value 10.15 kJ °C^{-1}; relative standard deviation 0.64%). The experimental procedure followed to determine the high heat of combustion of the samples (HHC_f and HHC_c according to Eqs. 6 and 7) was specified in the operating instructions provided by the manufacturer and a fuse wire correction was applied.

Heat of combustion of the volatiles

To estimate the heat of combustion of the volatiles (HC_{vol}) of samples treated with retardants, Eq. 3 was modified to express this value on an initial mass of pine basis (MJ kg^{-1}

of *P. halepensis*) (see Eq. 5). It is better to use these units, instead of MJ kg^{-1} of pine and retardant, because the results are easier to interpret. The terms HC_f, HC_c and X_c of Eq. 5 are expressed on an initial mass of the sample basis.

$$HC_{vol} = \left(HC_f - X_c\,HC_c\right)\,(100/(100 - X_r)) \tag{5}$$

The terms HC_f and HC_c were computed as shown in Eqs. 6 and 7. These equations are based on the definition of low heat of combustion. The differences are due to the presence of moisture and retardants in the samples used in this study.

$$HC_f = HHC_f - \Delta h_{v\,\mathrm{H_2O}}\left[9\,X_{\mathrm{H}}^f + X_w^f + 9\;1/3X_{\mathrm{H}}^r\,X_r\right] \tag{6}$$

$$HC_c = HHC_c - \Delta h_{v\,\mathrm{H_2O}}\;\left[9\,X_{\mathrm{H}}^c + X_w^c\right] \tag{7}$$

The term associated with the vaporization of the water generated during the combustion reaction was quantified based on the hydrogen content of the fuel and char samples (X_{H}^f and X_{H}^c, respectively). Carbon, hydrogen and nitrogen analyses were performed with elemental analyzers (Flash Thermo Finnigan 1112 and Carlo Erba 1108) and Table 1 shows the corresponding percentages.

Table 1 Elemental composition (C, H and N) of dried samples of pine (PH), retardants (FT1 and FT4) and char of untreated and treated pine. The data obtained are the mean values of two measurements, with relative standard deviation values lower than 5%

Sample	C (% w/w)	H (% w/w)	N (% w/w)
PH	51.82	6.68	0.84
FT1	0.81	4.62	11.30
FT4	0.53	5.19	12.27
PH char	64.94	3.73	1.50
PH + 10% FT1 char	56.18	3.10	2.62
PH + 15% FT1 char	52.24	2.79	2.93
PH + 20% FT1 char	47.73	2.84	3.34
PH + 10% FT4 char	56.19	3.11	2.91
PH + 15% FT4 char	51.51	2.92	3.25
PH + 20% FT4 char	48.56	2.82	3.66

A term associated with the vaporization of the water present in the samples as moisture was also included. The mean X_w value of the samples was 2.8%. It is worthwhile to notice that the energy associated with the moisture of the samples was much lower than that of the water of the combustion reaction. For instance, for the untreated *P. halepensis* sample, 0.061 MJ kg^{-1} were associated with the water present as moisture, whereas 1.3 MJ kg^{-1} were associated with the water of reaction.

Since water is generated during the decomposition of the retardants, another term was included to compute HC_f. The amount of water generated due to the degradation of the retardants was estimated based on the hydrogen percentage present in the retardants (X_{H}^r) (see Table 1) and the stoichiometry of the diammonium phosphate decomposition reaction [20]: 4 $(NH_4)_2HPO_4$ (*s*) → 8 NH_3 (*g*) + 6 H_2O (*g*) + 2 P_2O_5 (*s*)

This water contribution was not considered in Eq. 7 because it was assumed that the retardant residue present in the char samples was basically P_2O_5 and, thus, water from the retardants was not generated during char combustion. This assumption is based on the fact that diammonium phosphate decomposition reactions take place at approximately 200 °C, which is lower than the char preparation temperature (350 °C).

Results and discussion

Thermogravimetric analyses

Table 2 shows thermal analysis data taken from pyrolysis TG/DTG experiments carried out with *P. halepensis* needles before and after treatment with retardants. Percent mass loss was recorded after a temperature of 150 °C to assure that the water in the sample had been driven off. According to the literature [21], APP begins to decompose at temperatures higher than 150 °C. Thus, the assumption of recording the percent mass loss after a temperature of

Table 2 DTG parameters of *P. halepensis* needles before and after treatment with FT1 and FT4 in N_2 atmosphere (200 mL min^{-1}) at a heating rate of 10 °C min^{-1}

Sample	PT_1 (°C)	DR_1 (10^3 s^{-1})	PT_2 (°C)	DR_2 (10^3 s^{-1})	PT_3 (°C)	DR_3 (10^3 s^{-1})	R_{550} (%)
PH	344	1.00	–	–	406	0.29	26
PH + 10% FT1	302	0.69	349	0.58	406	0.31	34
PH + 15% FT1	300	0.70	347	0.52	–	–	38
PH + 20% FT1	301	0.71	348	0.53	–	–	40
PH + 10% FT4	299	0.72	348	0.52	385	0.30	35
PH + 15% FT4	296	0.72	349	0.52	–	–	37
PH + 20% FT4	299	0.73	349	0.57	–	–	40

The data obtained are the mean values of four measurements, with relative standard deviation values lower than 3%

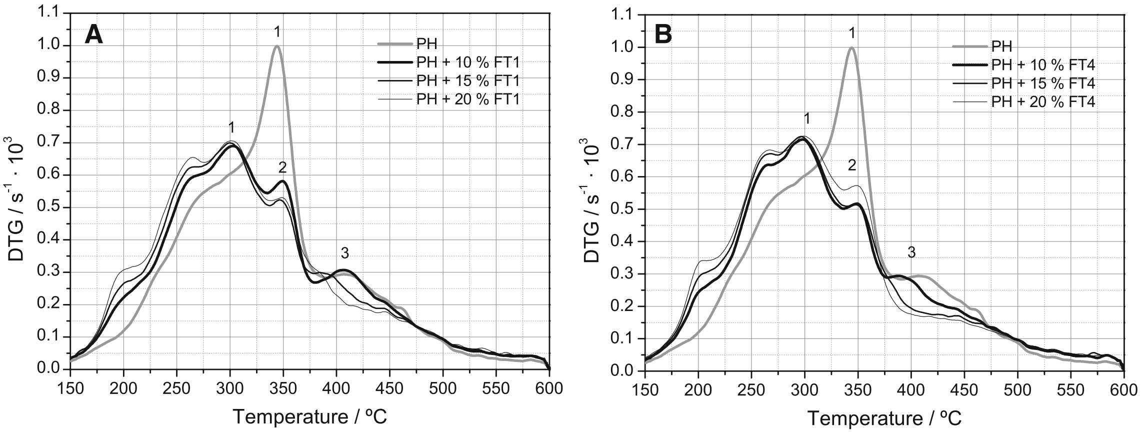

Fig. 1 DTG curves of *P. halepensis* needles (PH) before and after treatment with FT1 (**a**) and FT4 (**b**) at three concentration levels (10, 15 and 20% w/w) in N_2 atmosphere (200 mL min^{-1}) at a heating rate of 10 °C min^{-1}

150 °C is appropriate when working with APP-treated samples.

Biomass pyrolysis can be represented as a simple superposition of the behavior of its three components (hemicellulose, cellulose and lignin). In biomass decomposition curves, the main DTG peak is dominated by the decomposition of cellulose, while the shoulder at a lower temperature can mainly be attributed to hemicellulose decomposition. Lignin decomposes at a lower rate in a wide temperature range (200–600 °C) [22]. This characteristic profile is clearly shown in the sample PH in Fig. 1. Retardant decomposition reactions were also visible in Fig. 1 as shoulders on the DTG curves of the treated samples at approximately 200 °C.

Based on the results shown in Table 2 and visual inspection of Fig. 1, the decomposition profiles were found to be different for untreated pine and pine treated with retardants. Much of the difference between the pure and treated pine needle profiles had to do with the peak at high temperatures associated with lignin decomposition (peak 3), which is not visible at high retardant concentrations. Moreover, for both retardants, in the temperature range of 225–375 °C, multiple separate peaks were obtained (Fig. 1). In pure PH samples, only a peak associated with cellulose decomposition and a shoulder associated with hemicellulose decomposition were recorded. This means that the decomposition mechanism is getting more complex when retardants are applied on fuel.

In comparison with untreated samples, it was also found that treated samples started decomposing earlier, the primary DTG peak occurred at a lower temperature (reduced on average by about 13% with both retardants), the maximum rate of decomposition was considerably smaller (reduced on average by about 30% with FT1 and 28% with FT4), and the residual mass at 550 °C was increased by the presence of retardants (on average by about 44% with both retardants).

Comparing both retardant products, it was observed that the profiles, peak temperatures and residual masses were similar, and the only distinction between them was a slight difference in the primary rate of decomposition (0.70×10^{-3} s^{-1} and 0.72×10^{-3} s^{-1} for FT1 and FT4, respectively). Thus, our results seem to be contrary to the statement pointed out by George et al. [6], who supported that small percentages of iron can tie up phosphates to form insoluble compounds that may be ineffective fire retardants.

Based on our results, both retardants were used as a unique group representing APP-based commercial products and in the following sections data from the two products are not differentiated.

Char yield

The char yield (X_c) of the samples was obtained from char preparation experiments. The computed values of char yield are plotted in Fig. 2. As expected, the char yield was higher for samples containing retardants than for untreated samples. The experimental data initially showed a fairly steep increase, but they leveled off to a more gradual increase. They were fitted using a rational model and the R-square fit result was 0.95 according to the equation shown in Fig. 2.

The char obtained from treated samples was more compact than the char from untreated pine. Phosphorus oxide, the solid decomposition product of APP, has been shown to form a viscous fluid coating [20], which may have contributed to the char's compactness at room temperature.

Bomb calorimetry results

Experimental heat of combustion values obtained in bomb calorimetry tests were corrected according to Eqs. 6 and 7.

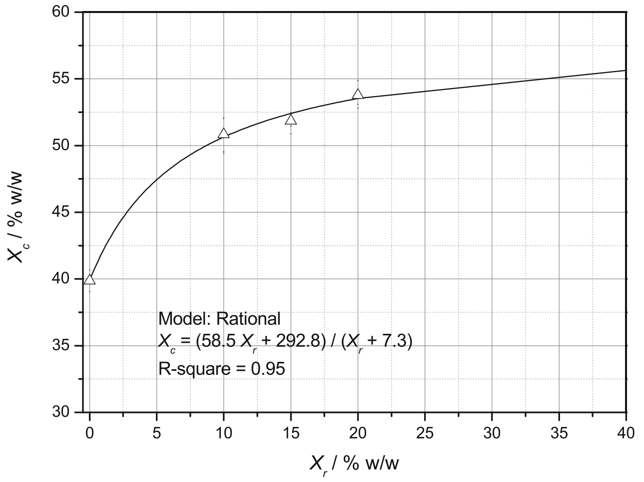

Fig. 2 Char yield evolution of *P. halepensis* needles before and after treatment with retardants (FT1 and FT4) at three concentration levels (10, 15 and 20% w/w). The data obtained are the mean values of four measurements, with relative standard deviation values lower than 3%

Table 3 Mean heat of combustion values of pure and treated *P. halepensis* needles (pure and treated samples contained 4 and 8 observations, respectively) and of the corresponding char (2 and 4 observations were used for pure and treated char samples, respectively)

X_r (% w/w)	HC_f (MJ kg^{-1})[a]	HC_c (MJ kg^{-1})[a]
0	20.7 (0.6)	25.1 (0.3)
10	18.9 (1.3)	21.3 (1.0)
15	17.6 (0.4)	19.5 (2.1)
20	16.7 (0.5)	18.1 (1.7)

HC values are expressed on an initial mass of the sample basis

[a] Dry basis. The moisture content was obtained after drying two pellets per retardant concentration in a vacuum oven under 1,333 Pa of pressure and at a temperature of 60 °C until constant mass. The relative standard deviation values are shown in parenthesis in percent units

The mean values, expressed on a dry initial mass of the sample basis, decreased as the retardant concentration in the samples increased (Table 3). This reduction simply reflects the smaller proportion of organic matter in the sample, since the tests were performed using a constant total mass and, thus, the amount of retardant increased as the amount of pine decreased.

The total heat of combustion of the samples expressed on a mass of dry fuel basis [according to Eq. 5, the term $HC_f\,(100/(100 - X_r))$] was found to be approximately equal for untreated pine samples (20.7 MJ kg^{-1}) and samples treated with retardants (mean value 20.9 MJ kg^{-1}; mean relative standard deviation 0.7%). This is a result that might be expected since the main energetic processes in the complete combustion of all the samples are the oxidation of carbon-carbon and carbon-hydrogen bonds and the energetic of these processes is independent of the presence of retardants.

The mean heat of combustion obtained for untreated pine samples was very comparable with the values reported in the literature. For instance, Liodakis et al. [23] obtained a high heat of combustion of 21.7 MJ kg^{-1} for *P. halepensis* needles using the same apparatus employed in this study. Based on the hydrogen content of the *P. halepensis* needles in this study, which in turn is in agreement with the value presented in [24] (6.68% in this study and 6.72% in [24]), this high heat of combustion corresponds to a heat of combustion value of 20.3 MJ kg^{-1}.

The heat of combustion of the untreated char sample (25.1 MJ kg^{-1} char) was lower than the values found in the literature for char from *P. ponderosa* needles. No references on *P. halepensis* char were found. In [25], a low heat of combustion value of 26.3 MJ kg^{-1} was obtained after heating 1 g dried fuel samples at 15 °C min^{-1} to 400 °C. This higher value may be due to the different composition of the species or to the different heating treatment temperature. In [26], it was reported that the carbon percentage of the residual char of cellulose samples was 59.9% w/w when they were pyrolyzed in a preheated furnace at a treatment temperature of 350 °C for 5 min, whereas 76.5% w/w was computed at a treatment temperature of 400 °C. Thus, since the heat content of the char depends on the available carbon in the char sample, it also depends on the treatment temperature. If these considerations are taken into account, the experimental value presented in this study appears to be consistent with those reported previously.

Heat content of the volatiles

The heat content of the volatiles (HC_{vol}) was calculated using Eq. 5. Mean HC_{vol} values were plotted against retardant concentration in Fig. 3. They were found to decrease according to an exponential decay model; Fig. 3 shows the expression obtained. R-square fit results were very good (0.99).

In [19], for *P. pinaster* needles, the authors reported a mean value of the heat of combustion of the volatiles of 15.9 MJ per kg of volatiles. This value corresponded to a heat of combustion of the volatiles per unit mass of pine of 11.5 MJ kg^{-1}, taking into consideration that the mean char yield was 27.5% w/w. Thus, the heat of combustion of the volatiles obtained in our study for untreated *P. halepensis* needles (10.6 MJ kg^{-1}) is similar in order of magnitude to the value reported in [19].

Figure 3 shows that the heat of combustion of the volatiles was kept practically constant for retardant concentrations above 10% w/w. This is a consequence of the char yield profile that was obtained and is consistent with the results of [27]. These authors stated that diammonium

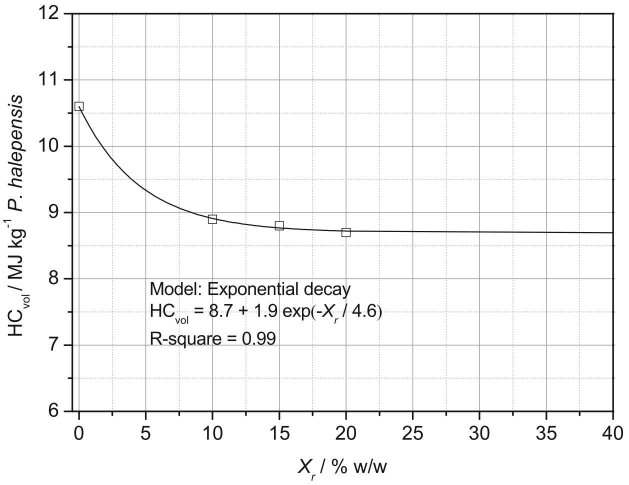

Fig. 3 Heat of combustion of the volatiles versus retardant concentration (mean values)

phosphate concentrations above 10% w/w appeared to be sufficient to exercise nearly the maximum action on the yield of the main classes of fir wood pyrolysis products.

Conclusions

The pyrolytic degradation profiles (DTG graphs) of *P. halepensis* needles treated with FT1 and FT4 were different from the profiles of pure *P. halepensis* needles. The primary rates of decomposition were lowered and shifted to lower temperatures, and the mass residue was increased. Also the DTG peak associated with lignin decomposition found in pure samples was not obtained when high retardant concentrations were applied. The thermal degradation profiles of FT1-treated samples were similar to those of FT4-treated samples. Thus, both products were studied in this work as a single group, representing APP-based commercial retardants.

The heat of combustion of the volatiles in retardant-treated samples was computed by subtracting the heat contribution of the char fraction from the total heat of combustion of the sample. The heat of combustion of the volatiles did not vary significantly for retardant concentrations in the range of 10–20% w/w. The mean reduction percentage with respect to the untreated sample was 18% in this range of retardant concentrations. An exponential decay model fitted data on heat of combustion of the volatiles as a function of the retardant concentration, and a rational model fitted char yield data.

A mean value of heat of combustion of the volatiles of 8.8 MJ kg^{-1} (on a dry fuel basis) was determined for *P. halepensis* needles treated with polyphosphate-based retardants in the treatment range of 10–20% w/w. This value could be used to predict the calorific power of a spreading flame front that propagates through fuel treated with polyphosphate-based retardants. Corrections for incomplete combustion should not be applied to this value because they are already taken into account since only the calorific contribution of the volatiles is considered.

Further work should be done with other species to explore the tendency of the heat of combustion of the volatiles as a function of retardant concentration.

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