Ash properties of *Pinus halepensis* needles treated with diammonium phosphate

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Abstract

The ash properties of *Pinus halepensis* (Aleppo pine) needles before and after treatment with diammonium phosphate $(NH_4)_2HPO_4$ (DAP) have been investigated, using thermogravimetric analysis (TG), differential thermal analysis (DTA), titrimetry, inductively coupled plasma-emission spectrometry (ICP-ES), X-ray diffraction (XRD) and scanning electron microscopy (SEM). DAP is extensively used as active component in wildland fire retardants.

The following crystalline compounds have been identified in ashes prepared at $600\,°C$ before treatment with DAP: KCl, $Ca(OH)_2$, MgO, $(CaMg)CO_3$, $K_2CO_3·CaCO_3$, K_2CO_3, K_2SO_4, CaO and $CaCO_3$, whereas CaO, MgO, K_2SO_4, K_2CO_3, $CaCO_3$, KCl and CaO, MgO, K_2SO_4 and K_2CO_3 at 800 and $1000\,°C$, respectively. The presence of DAP alters the composition of ashes converting, almost completely at high temperatures, the metallic oxides into phosphate salts. Thus, decreasing their alkalinity. The micrographs obtained by SEM indicate that pine needles ashes contain large porous particles of carbon compounds and several inorganic particles of irregular shape <1.0 mm, whereas after treating the needles with DAP an amorphous rigid structure was formed.

To facilitate our investigation model mixtures of $CaCO_3 + DAP$, $MgCO_3 + DAP$, $K_2CO_3 + DAP$ were heat treated under the same conditions used for preparing the ashes. The chemical transformations taken place during heating were studied by analysing the reaction products using thermal analysis and XRD.

The physical, mineralogical and chemical forest ash properties determined could be used to evaluate the environmental risk of the use of fire retardants on soils, plants and aquatic systems as well as to investigate the mechanism of combustion of forest fuels in the presence of DAP.
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1. Introduction

The term "wood ash" refers to all inorganic constituents of wood that remain after burning. During the combustion of wood, organic compounds are mineralized and the basic cations are transformed to oxides, which are slowly hydrated and subsequently carbonated under atmospheric conditions. The wood ash is a highly alkaline matter (pH 9–13.5) and its disposal is a growing problem, as environmental regulations become more stringent. A number of studies has been carried out on the utilization of wood ash in agriculture and forestry as an alternative method for disposal [1]. Wood ash, as an excellent source of potash (potassium), lime and other plants nutrients, can been used either as a soil amendment in agriculture [2] or to correct forest nutrient deficiencies or unbalances due to acid deposition and leaching [3]. Furthermore, it has been used as a binding agent, a glazing agent in the ceramic industry, a road base, an additive in cement industry and an alkaline material for the neutralization of wastes [4].

Earlier studies [5–11] have shown that the dominant elements of wood ash are calcium, potassium, magnesium, silicon, manganese, aluminium, phosphorous, sulphur, iron, sodium and zinc.

Etiegni and Campbell [5] have found that the ash yield and its chemical composition change with combustion temperature. Thus, the ash yield is decreased by approximately 45%, potassium, sodium, zinc and carbonate content are also decreased, silicon and aluminum are remained almost constant,

and calcium, magnesium, manganese, iron and phosphorous are increased as the combustion temperature is increased (i.e., from 538 to 1093 °C). They have also suggested, based on X-ray diffraction (XRD) patterns that calcium silicate may be responsible for some of the swelling that occurs when ash and water react together. Scanning electron microscopy (SEM) analysis has indicated that ash has an average particle size of 230 μm and contains large porous particles and many irregularly shaped inorganic particles.

Similarly, Misra et al. [6] have investigated the elemental and molecular composition of ash of various wood species as a function of combustion temperature, using thermogravimetric analysis (TG), differential thermal analysis (DTA), inductively coupled plasma emission spectroscopy (ICP-ES), and X-ray diffraction (XRD). At 600 °C ash contained mainly $CaCO_3$ and $K_2Ca(CO_3)_2$, whereas at 1300 °C CaO and MgO were the main compounds. Olanders and Steenari [7] have characterized ashes from wood and straw using XRD, TG and SEM analyses for determining the main crystalline compounds formed. Erich and Ohno [8] have applied a procedure suggested by the Association of Official Analytical Chemists (AOAC) for the titrimetric determination of calcium carbonate equivalence of wood ashes.

However, the data published on the composition of forest species ashes were not as detailed as for the ashes of coal. According to several authors [12,13], the composition of forest ashes depends on various factors: type of forest species, part of plant combusted (bark, wood, leaves), plant age, type of soil, climate, conditions of combustion, etc. As a consequence available data on the properties of forest species ashes are very variable and generalizations are therefore difficult to be made. Furthermore, the application of fire retardants during forest fires is expected to alter the physical and chemical characteristics of ash formed.

The use of *long-term fire retardants* is very important to forest fire management. These are applied ahead of a wildfire front for reducing the rate of fire spread or combustion intensity. In most cases the active ingredients of forest fire retardants are ammonium salts of phosphoric (or sulphuric) acid, i.e. diammonium phosphate (DAP). The above compounds alter the thermal decomposition (pyrolysis) mechanism of forest species, usually by acid catalyzed dehydration reactions. Thus, promoting the formation of H_2O, CO_2 and char, at the expense of flammable gases [14]. In particular the high effectiveness of ammonium phosphates is attributed to the synergistic effects of nitrogen and phosphorus [15].

In this paper, the physical and chemical properties of *Pinus halepensis* needles ash prepared at 600, 800 and 1000 °C, before and after treatment with DAP have been examined using thermogravimetric analysis (TG), differential thermal analysis (DTA), inductively coupled plasma emission spectrometry (ICP-ES), X-ray diffraction (XRD), titrimetry and scanning electron microscopy (SEM). The objectives of this research were to evaluate the yield, chemical composition and mineralogy of wood ash produced by intense burning during forest fires in the presence of fire retardants and to predict its effects on soil properties, on the availability of nutrient elements, as well as its impact on the environment.

2. Experimental

2.1. Thermal analysis

Thermal analysis was carried out using a Mettler TGA/SDTA 851 module supported with a PC and software for control and data handling. The pine needles ash samples, approximately 10 mg in weight, were introduced into an open 0.07 ml platinum sample pan and were heated from 25 to 600 °C, with a linear heating rate of 50 °C min^{-1}, and then up to 1300 °C with a linear heating rate of 10 °C min^{-1}. To avoid sticking of sample pan on the sample holder we inserted between them a sapphire disk of 7 mm diameter, according to the manufacturer's instructions. All runs were carried out in nitrogen atmosphere at a flow rate of 50 ml min^{-1}. Heat-up temperatures were limited to a maximum of 1300 °C according to the TG instructions. The same conditions were employed for the thermal analysis of the selected model mixtures: $CaCO_3$/DAP 3.15/10.0 (w/w), $MgCO_3$/DAP 1.26/10.0 (w/w), K_2CO_3/DAP 1.08/10.0 (w/w).

2.2. Elemental analysis

Analysis samples were prepared by dissolving approximately 50 mg of the dried ash (or heat treated model mixtures) in 10.0 ml hydrochloric acid 20% (w/w). The solution was heated, filtered and the precipitate was washed with deionised water. The filtrate was diluted to 100.0 ml and analyzed using a Jobin Yvon inductively coupled plasma emission spectrometer (ICP-ES).

2.3. Titration for measuring the alkalinity (or acidity) of ash leachate

0.10 g of ash, formed before or after treating the pine needles with DAP, were mixed with 50.0 ml of distilled water and agitated for 48 h. The mixture was centrifuged, filtered through a 0.2 μm membrane filter, and the soluble fraction was titrated either with 0.01 M HCl (samples before DAP treatment) or with 0.01 M NaOH (samples after DAP treatment) [5]. The titration was carried out with an Orion, model 950 Ross FASTQC, automatic potentiometric titrator. The sensor was a pH electrode, type Orion-72 BN. Based on the titration curves (pH versus *V*) the soluble alkalinity, due to the hydroxides and carbonates ions content (or the soluble acidity due to the phosphoric acid content), was determined.

2.3.1. X-ray diffraction analysis (XRD)

The samples (ashes or heat treated model mixtures) were analyzed in a Siemens D-5000 X-ray diffractometer using a copper target to generate the X-rays (wavelength = 1.5405×10^{-10} m). The samples were first finely ground and then mounted on the sample holder. The powder was ground fine to ensure random orientation of the crystals so that there are sufficient amount of crystals to generate detectable signals of all angles and minimum background noise.

2.4. Scanning electron microscopy (SEM)–energy dispersive X-ray fluorescence spectrometer (ED-XRF) analysis

The samples were examined by a FEI Quanta 200 scanning electron microscope (SEM) combined with an EDAX energy dispersive X-ray fluorescence spectrometer, giving the elemental composition at chosen points on the sample surface.

The instrument was operated at low vacuum mode at a pressure of 90 Pa with a high voltage of 10 kV. Samples were deposited on a sample holder and were secured with a conductive carbon tape. No pretreatment or coating of the samples was required.

A number of 15–20 analyses were performed for each "class" of samples covering different magnifications and surface areas to improve the credibility of the reported data.

2.5. Samples

Tests were conducted on *P. halepensis* needles before and after treatment with diammonium phosphate (DAP). The selected forest species is very common in the Mediterranean region and DAP is one of the most often used retardant in forest fires.

The sample collection site was the mountainside Kalopoula of Imitos, near Athens, located W–NW with dominated rock limestone, with geographic coordinates $37°58'13''$N and $23°48'20''$E, height 487 m and average slope 70%. The sampling date was the 26 August 2005. All samples were mature foliage, collected after a long drought period in order to avoid moisture effects. The pine needles were washed twice with deionised water, dried at 60 °C for 48 h under vacuum of 100 mmHg. Then, the samples were ground and a fraction between 100 and 200 μm was separated and used for the tests. The preparation of DAP treated samples was performed by well mixing a certain quantity (5 or 10%, w/w) of Merck laboratory reagent DAP with the forest material powder. The concentration level chosen (5% or 10%, w/w) was similar to that applied by Hellenic Fire Service in real forest fires.

The forest species samples were dry ashed at 600, 800 and 1000 °C for 24 h, according to standard methods [16,17].

The model mixtures were artificially prepared by mixing the necessary pure components, purchased from Merck, and grinding them in a mortar. They had composition ($CaCO_3$/DAP 3.15/10.0, w/w; $MgCO_3$/DAP 1.26/10.0, w/w; K_2CO_3/DAP 1.08/10.0, w/w) similar to the one of ash samples treated by DAP. The model compounds were heat treated under the same conditions which were used for dry ashing the forest species. The composition chosen for the model mixtures was similar to that found in ashes of pine needles treated with DAP.

3. Results and discussion

3.1. Thermal analysis

The TG, DTG (differential thermogravimetric analysis) and SDTA (simultaneous differential thermal analysis) graphs of *P.*

halepensis needles ash prepared at 600 °C before and after treatment with 5% and 10% (w/w) DAP are presented in Fig. 1, under the operating conditions described in section 2.1. Similarly, the TG/DTG/SDTA graphs of the model substances (DAP, $Ca_3(PO_4)_2$, $MgCO_3$ + DAP, $CaCO_3$ + DAP and K_2CO_3 + DAP), are presented in Fig. 2. The peaks shown in Figs. 1 and 2 are numerated using the same numbers with those indicated in the following chemical equations. To note that variables such as sample mass, heating rate and gas flow rate have a marked effect on the profile of TG and DTG curves [18,19].

The mass loss observed in the temperature range 380–500 °C (peak 1, Fig. 1) is attributed to the decomposition of $Ca(OH)_2$ and $Mg(OH)_2$, according to the following equations with the respective TG peak temperatures (T_p) given in the literature [20,21]:

$$Mg(OH)_2 \rightarrow MgO + H_2O \quad 390–420\,°C \tag{1a}$$

$$Ca(OH)_2 \rightarrow CaO + H_2O \quad 420–520\,°C \tag{1b}$$
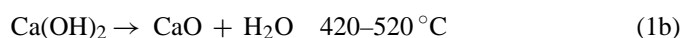
The above hydroxides were formed, after the thermal treatment of forest species, by the reaction of the respective oxides with the ambient moisture.

The mass loss observed at the temperature range 560–650 °C (peak 2, Fig. 1) is attributed to the decomposition of $MgCO_3$, according to the following equation with the respective TG peak temperatures (T_p) given in the literature [19]:

$$MgCO_3 \rightarrow MgO + CO_2 \quad 580–630\,°C \tag{2}$$
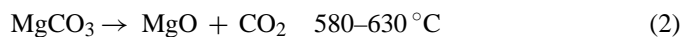
The mass loss observed in the temperature range 650–710 °C (peak 3, Fig. 1a) is attributed to the decomposition of dolomite [22], according to the equation:

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \tag{3}$$
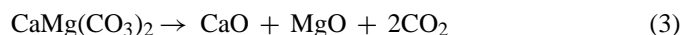
The mass loss observed in the temperature of 740–850 °C (peak 4, Fig. 1) is due to the decomposition of $CaCO_3$, according to the equation and the respective TG peak temperature (T_p) given in the literature [18,21,23–25]:

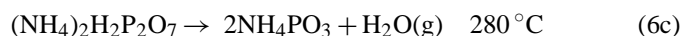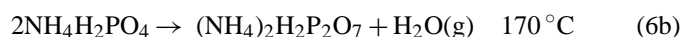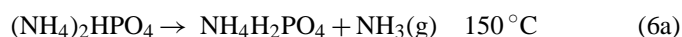$$CaCO_3 \rightarrow CaO + CO_2 \quad 720–840\,°C \tag{4}$$
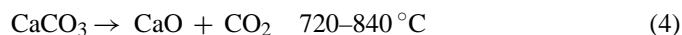
Finally, the mass loss recorded above 1100 °C (peak 5, Fig. 1) is mainly due to the decomposition of K_2CO_3, according to the equation with the respective decomposition temperature range (T_i–T_f) reported in literature [26]:

$$K_2CO_3 \rightarrow K_2O + CO_2 \quad 1100–1400\,°C \tag{5}$$

Similar results were obtained by TG/DTG analysis of *P. halepensis* ashes prepared at 800 and 1000 °C.

The presence of DAP alters the thermal degradation route of ash samples, because of the decomposition of DAP according to the equations [27]:

$$(NH_4)_2HPO_4 \rightarrow NH_4H_2PO_4 + NH_3(g) \quad 150\,°C \tag{6a}$$

$$2NH_4H_2PO_4 \rightarrow (NH_4)_2H_2P_2O_7 + H_2O(g) \quad 170\,°C \tag{6b}$$

$$(NH_4)_2H_2P_2O_7 \rightarrow 2NH_4PO_3 + H_2O(g) \quad 280\,°C \tag{6c}$$

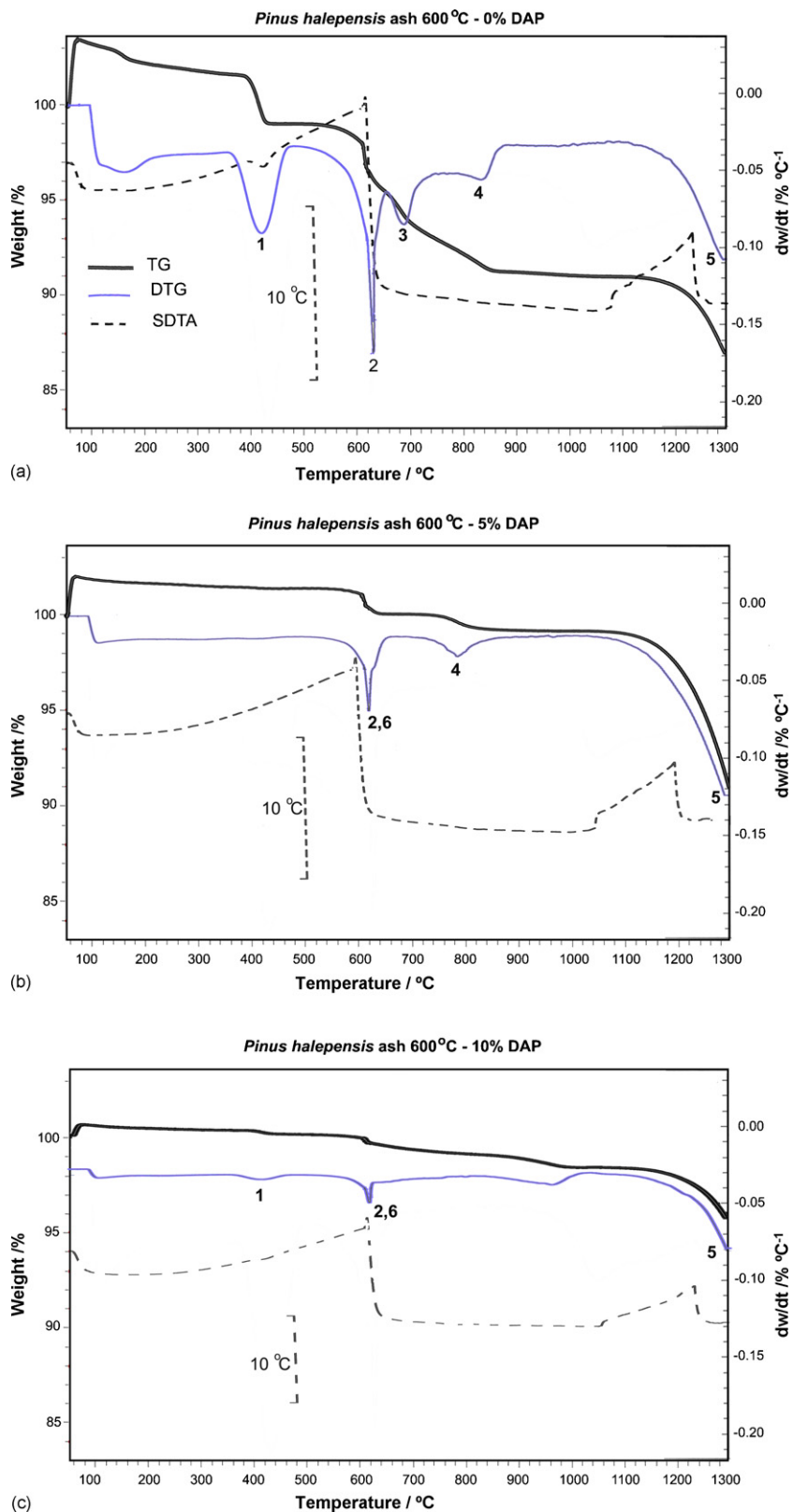$$2NH_4PO_3 \rightarrow P_2O_5(g) + 2NH_3(g) + H_2O(g) \quad 660\,°C \tag{7}$$

Fig. 1. TG, DTG and SDTA curves of *Pinus halepensis* needles ash prepared at 600 °C, before and after treatment with 5% and 10% (w/w) DAP, under nitrogen atmosphere with flow rate 50 ml min^{-1} and heating rate 50 °C min^{-1} from 25 to 600 °C and 10 °C min^{-1} from 600 to 1300 °C. Decomposition reactions: 1. Ca(OH)$_2$ and Mg(OH)$_2$; 2. MgCO$_3$; 3. CaMg(CO$_3$)$_2$; 4. CaCO$_3$, 5. K$_2$CO$_3$ and phosphate salts to P$_2$O$_5$(g); 6. NH$_4$PO$_3$.
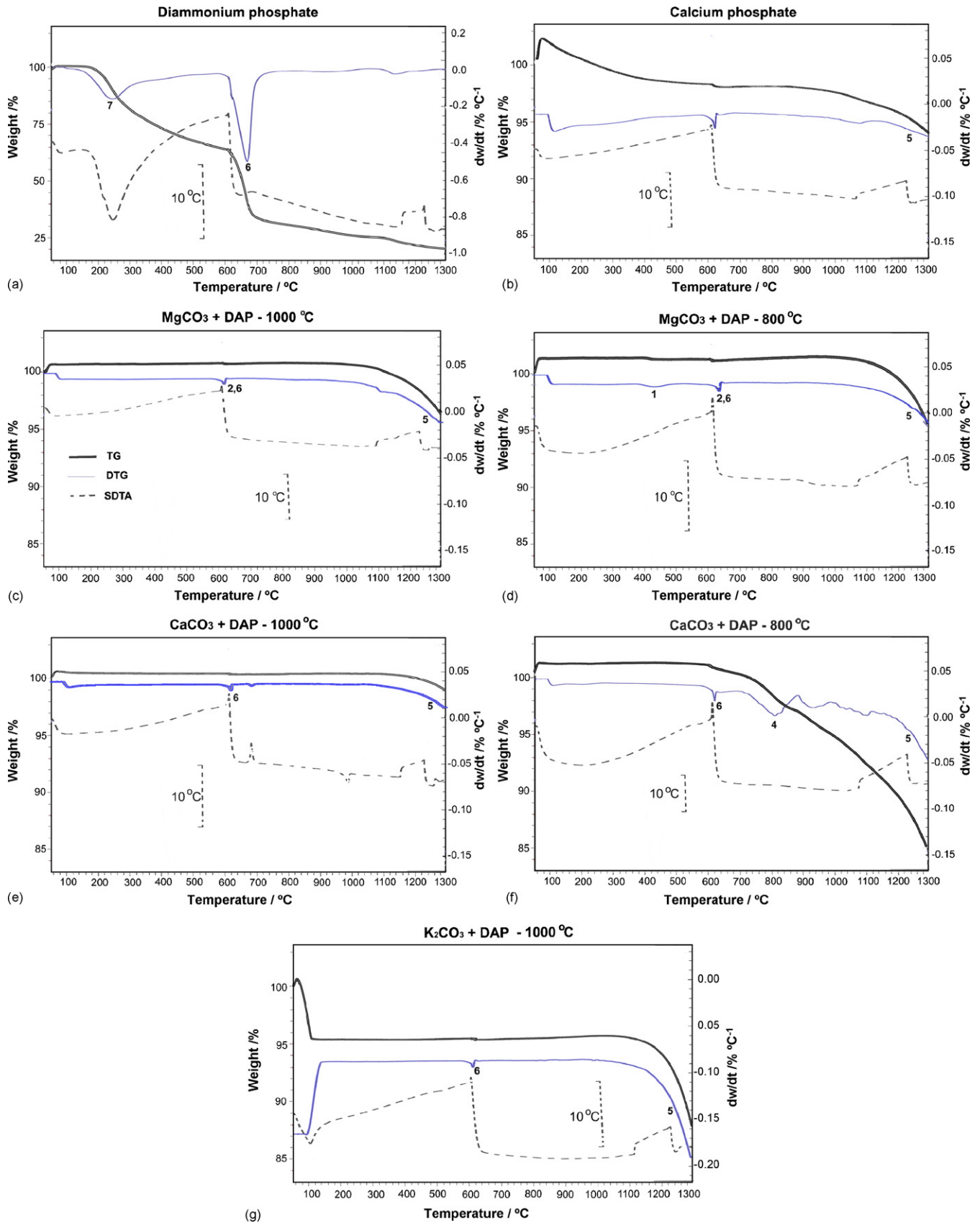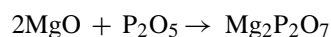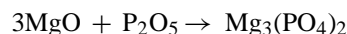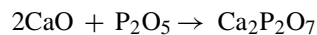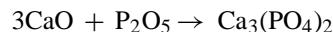
Fig. 2. TG, DTG and SDTA curves of model substances, under nitrogen atmosphere with flow rate 50 ml min^{-1} and heating rate 50 °C min^{-1} from 25 to 600 °C and 10 °C min^{-1} from 600 to 1300 °C. Decomposition reactions: 1. Mg(OH)$_2$; 2. MgCO$_3$; 4. CaCO$_3$; 5. K$_2$CO$_3$ and phosphate salts to P$_2$O$_5$(g); 6. NH$_4$PO$_3$; 7. (NH$_4$)$_2$HPO$_4$ and NH$_4$H$_2$PO$_4$.

In addition, the metallic oxides MgO and CaO, formed in the temperature range of 400–850 °C, are almost completely converted to phosphates, according to the following equations:

$$3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$$

$$2CaO + P_2O_5 \rightarrow Ca_2P_2O_7$$

$$3MgO + P_2O_5 \rightarrow Mg_3(PO_4)_2$$

$$2MgO + P_2O_5 \rightarrow Mg_2P_2O_7$$

Also, $Ca_7Mg_2(PO_4)_6$ is formed on heating to the temperature range 900–1000 °C [28], whilst at higher temperatures (above 1100 °C) the phosphate salts start decomposing to $P_2O_5(g)$.

The above findings were confirmed by thermal analysis of model substances (pure components: DAP; calcium phosphate and mixtures: $CaCO_3 + DAP$; $MgCO_3 + DAP$; $K_2CO_3 + DAP$. The model mixtures ($CaCO_3 + DAP$; $MgCO_3 + DAP$; $K_2CO_3 + DAP$) were first heated at 800 and 1000 °C for 24 h. The TG/DTG/SDTA graphs of the model substances were taken under the same operating conditions used for the analysis of ashes (Fig. 2). Some short comments on the analysis data of model substances are given below:

1. DAP (Fig. 2a). Diammonium phosphate follows the thermal decomposition route described earlier to $NH_3(g)$ and $P_2O_5(g)$.
2. $Ca_3(PO_4)_2$ (Fig. 2b). In the region of 20–680 °C the phosphate ions (PO_4^{3-}) are partially converted to pyrophosphates ($P_2O_7^{4-}$), in the range of 680–1000 °C crystallization of phosphates takes place as well as the formation of $Ca_8P_2O_7(PO_4)_4$ and above 1000 °C starts the decomposition of phosphates and pyrophosphates to $P_2O_5(g)$ [29].
3. $MgCO_3 + DAP$ (Fig. 2c and d). The reaction $3MgO + P_2O_5 \rightarrow Mg_3(PO_4)_2$ is almost completed after heating the mixtures at 1000 °C. $Mg_3(PO_4)_2$ starts decomposing to $P_2O_5(g)$ at 1200 °C (Fig. 2c). On the contrary, by treating the mixture at 800 °C, the reaction between $MgCO_3 + DAP$ is incomplete (Fig. 2d). As is shown in Fig. 2d, the mass loss in the temperature range 350–450 °C represents the decomposition of $Mg(OH)_2$ which is formed after the thermal treatment of model mixture through the reaction between MgO and ambient moisture [11]. The mass loss in the temperature range 600–640 °C represents the decomposition of $MgCO_3$ which is also formed by reacting MgO with ambient CO_2.
4. $CaCO_3 + DAP$ (Fig. 2e and f). The reaction $3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$ is almost completed after heating the mixtures at 1000 °C. $Ca_3(PO_4)_2$ starts decomposing to $P_2O_5(g)$ at temperatures above 1100 °C (Fig. 2e). On the contrary, by treating the mixture at 800 °C, the reaction between $CaCO_3 + DAP$ is incomplete (Fig. 2f). As it is shown in Fig. 2f the mass loss in the temperature range 550–650 °C represents the decomposition of $Ca(OH)_2$, which is formed after thermal treating the samples via the reaction of CaO with ambient moisture. Also the mass loss in the temperature range 720–840 °C represents the decomposition of $CaCO_3$.

Table 1
Ash content, elemental and titrimetric analysis data of *Pinus halepensis* needles ash prepared at 600, 800 and 1000 °C before and after treatment with DAP

	Ash content (%, w/w)	Ca (%, w/w)	Mg (%, w/w)	Na (%, w/w)	Si (%, w/w)	K (%, w/w)	P (%, w/w)	Fe (%, w/w)	Al (%, w/w)	Zn (%, w/w)	Cu (%, w/w)	Mn (%, w/w)	Pb (%, w/w)	S.A. (mmol HCl/g ash)	S.A. (mmol NaOH/g ash)
Pi-ha-600 °C-0% DAP	3.60	26.34	7.56	1.22	0.84	12.7	2.68	0.79	0.05	0.05	0.01	0.13	0.02	2.10	–
Pi-ha-600 °C-5% DAP	4.99	15.28	4.46	0.58	0.09	8.70	22.18	0.44	0.03	0.20	0.01	0.08	0.02	0.07	
Pi-ha-600 °C-10% DAP	7.59	13.34	3.18	0.70	0.24	7.30	19.84	0.39	0.02	0.01	0.01	0.04	0.02	–	0.14
Pi-ha-800 °C-0% DAP	2.88	29.82	8.68	2.00	1.93	6.90	3.18	0.95	0.03	0.02	0.04	0.16	0.02	6.05	–
Pi-ha-800 °C-5% DAP	5.30	16.16	4.66	0.86	0.33	6.80	17.85	0.43	0.02	0.01	0.02	0.09	0.02	0.17	
Pi-ha-800 °C-10% DAP	7.32	8.94	2.78	0.68	0.40	5.40	22.2	0.26	<0.01	<0.01	0.01	0.06	0.02	–	1.84
Pi-ha-1000 °C-0% DAP	2.79	29.86	9.12	1.91	2.21	1.60	3.94	0.88	<0.01	<0.01	0.04	0.16	0.02	5.90	–
Pi-ha-1000 °C-5% DAP	5.22	14.00	4.30	1.73	0.12	6.80	20.53	0.47	0.02	0.01	0.02	0.09	0.02	1.02	
Pi-ha-1000 °C-10% DAP	6.50	10.46	3.70	1.64	0.35	8.10	22.03	0.38	0.01	0.01	0.02	0.01	0.02	–	2.52

Pi-ha: *P. halepensis*; S.A.: soluble alkalinity-neutralization to pH 7.

5. K_2CO_3 + DAP (Fig. 2g). No reaction between K_2CO_3 and DAP has taken place. K_2CO_3 starts decomposing at temperatures higher than 1100 °C.

3.2. Elemental analysis

Table 1 lists the concentrations of the major elements (K, Na, Ca, Mg) and minor elements (Si, P, Fe, Al, Zn, Cu, Mn, Pb), determined by ICP-ES. The measurements recorded are the average values of four replicate tests and have a relative standard deviation below 10%. In Table 1 is also shown the influence of temperature and DAP treatment on the elemental composition of pine needles ashes.

The increase of 13.21% in calcium, 14.81% in magnesium and 63.93% in sodium content of ashes with temperature, from 600 to 800 °C, is primarily due to the decomposition of calcium and magnesium carbonates (peaks 2 and 4 in Fig. 1, Fig. 2). Contrary the % w/w content of potassium decreased by 45.67% when increasing the ash preparation temperature from 600 to 800 °C and by 76.8% from 800 to 1000 °C,

due to the partial volatilization of potassium oxide formed after the decomposition of K_2CO_3 (peak 5 in Figs. 1 and 2). Similarly, the minor compounds (Si, Fe, P, Cu) content is increased with temperature, whereas Zn and Al is decreased with increasing temperature and Pb, Mn is remained constant. The above results are in good agreement with previous works [5,6].

In general, the presence of DAP decreases the content of Ca, Mg, Na, Si, Fe, Al and Mn in all ash samples examined due to the formation of phosphate salts which are decomposed to P_2O_5 at temperatures above 1100 °C (peak 5 in Figs. 1 and 2), whereas the content of Cu and Pb remains almost constant.

3.3. Titration for measuring the alkalinity (or acidity) of ash leachate

The titration curves of ash leachates with 0.01 M HCl or 0.01 M NaOH were prepared according to the procedure described in Section 2.3 and are shown in Fig. 3.
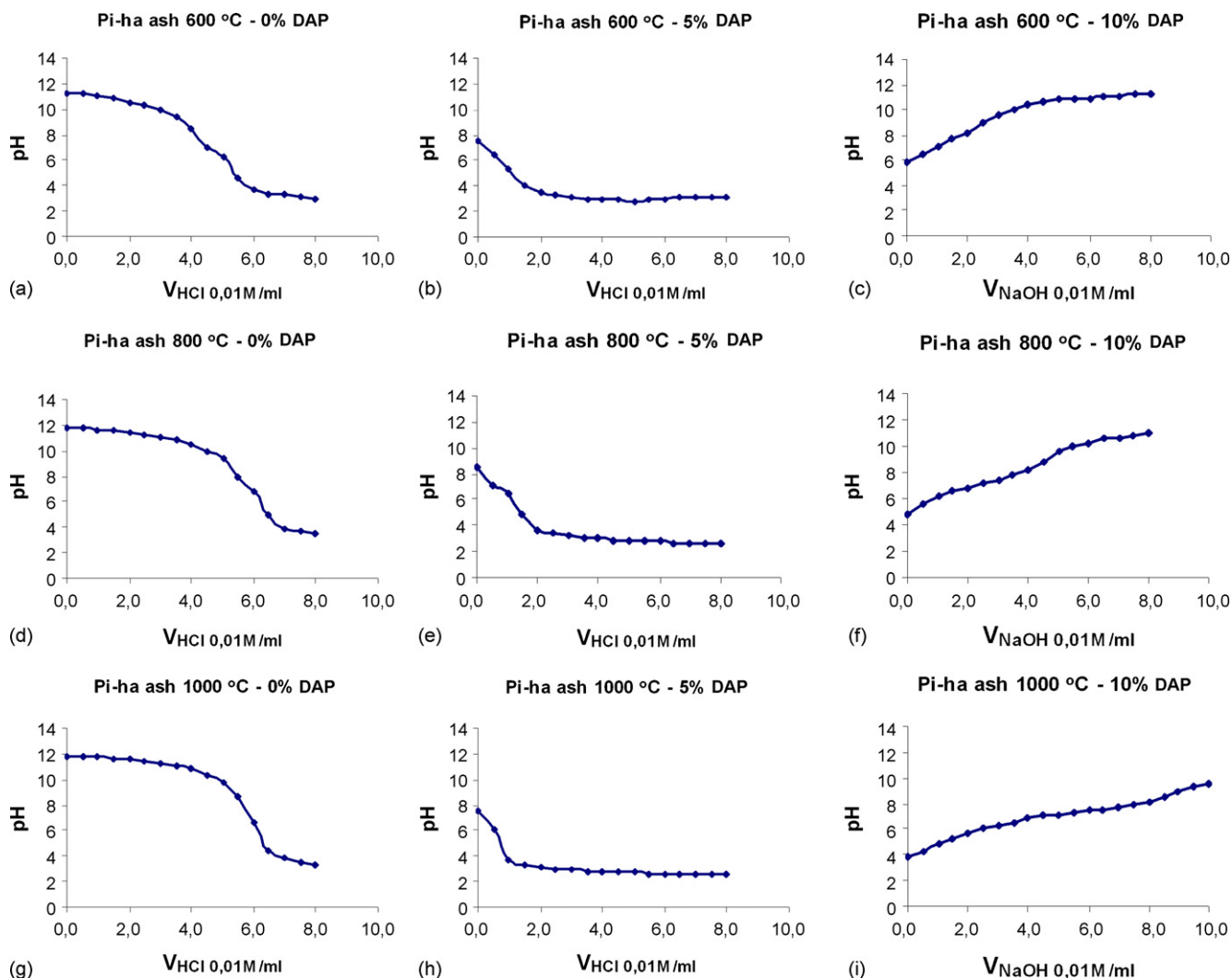

Fig. 3. Titration curves of *P. halepensis* needles ash leachate with 0.01 M HCl or 0.01 M NaOH. Ashes were prepared at 600, 800 and 1000 °C before and after treating pine needles with 5% and 10% (w/w) DAP.

The soluble alkalinity was determined by measuring the number of mmoles of HCl or NaOH required to neutralize 1.0 g of ash leachate to pH = 7 and the results are presented in Table 1. The data reported in Table 1 are the average values of three replicate titrations, with a relative standard deviation below 5%.

The ash temperature preparation affects its alkalinity properties, with the soluble alkalinity increasing (188.10%) from 600 to 800 °C (Table 1) due to the decomposition of $CaCO_3$ and $MgCO_3$ to oxides (peaks 2 and 4 in Figs. 1 and 2) and faintly decreasing (2.48%) from 800 to 1000 °C due to the partial volatilization of K_2O (peak 5 in Figs. 1 and 2).

As it shown in Table 1, the presence of DAP increases dramatically the acidity of ashes, especially at high temperatures, because P_2O_5 is formed via decomposition of phosphate salts, especially DAP, according to the thermal analysis data exhibited in Section 3.1 (Fig. 2a).

3.4. X-ray diffraction analysis (XRD)

The crystalline compounds in all ash samples examined, were identified by X-ray diffraction analysis and can be seen in Table 2.

Fig. 4 presents the XRD patterns for *P. halepensis* needles ash prepared at 600 °C before and after treatment with DAP.

The main type of compounds identified in the ash samples before treatment with DAP were oxides of Ca and Mg, hydroxide of Ca (peak 1 in Fig. 1), carbonates of Ca, Mg and K (peaks 2,3,4 in Fig. 1), sulphates and chlorides of K. Ashing at high temperatures ($T > 600$ °C) promotes the decomposition of carbonates, i.e. $(CaMg)CO_3$ (dolomite), $K_2CO_3 \cdot CaCO_3$ (fairchildite) and the sublimation of chlorides, i.e. KCl. The only salts identified at high temperatures ($T = 1000$ °C) were K_2SO_4 and K_2CO_3 (peak 5 in Fig. 1a and Table 2).
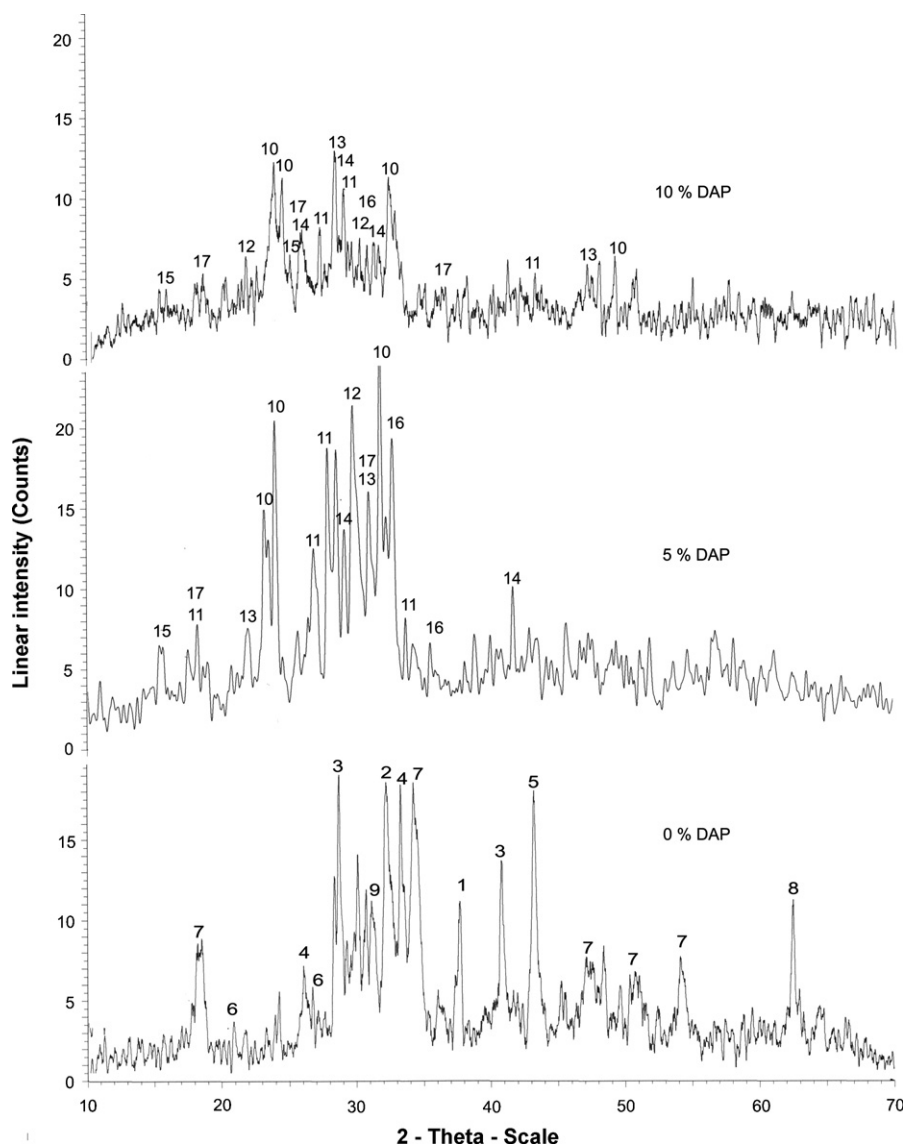

Fig. 4. X-ray diffraction patterns of *P. halepensis* needles ash prepared at 600 °C before and after treatment with 5% and 10% (w/w) DAP: (1) CaO; (2) K_2CO_3; (3) KCl; (4) $K_2CO_3 \cdot CaCO_3$; (5) $MgCO_3$; (6) $CaCO_3$; (7) $Ca(OH)_2$; (8) MgO; (9) $(Ca,Mg)CO_3$; (10) $Ca_4Mg_5(PO_4)_6$; (11) $Ca_2P_2O_7$; (12) $Mg_2P_2O_7$; (13) $Ca_3(PO_4)_2$; (14) $Ca_7Mg_2P_6O_{24}$; (15) P_2O_5, (16) K_3PO_4, (17) $K_4P_2O_7$.

Table 2
Crystalline compounds in *P. halepensis* needles ash identified by X-ray diffraction analysis

Ash samples	DAP content (%, w/w)	Compounds in ashes
P. halepensis at 600 °C	0	**K₂CO₃ CaCO₃** (fairchildite), **CaO, MgO, MgCO₃, KCl, Ca(OH)₂, K₂CO₃**, K₂SO₄, (CaMg)CO₃, CaCO₃
	5	**Ca₄Mg₅(PO₄)₆, Ca₂P₂O₇, Mg₂P₂O₇, Ca₃(PO₄)₂**, Ca₇Mg₂P₆O₂₄, P₂O₅, K₃PO₄, K₄P₂O₇
	10	**Ca₇Mg₂P₆O₂₄, Ca₄Mg₅(PO₄)₆, Ca₂P₂O₇, Ca₃(PO₄)₂**, Mg₂P₂O₇,P₂O₅, K₃PO₄, K₄P₂O₇
P. halepensis at 800 °C	0	**CaO, MgO, K₂CO₃**, CaCO₃, K₂SO₄, KCl
	5	**(CaMg)P₂O₇, Ca₄Mg₅(PO₄)₆, Ca₂P₂O₇, Mg₂P₂O₇**, P₂O₅, Ca₃(PO₄)₂, CaO, Mg₃(PO₄)₂, K₃PO₄, K₄P₂O₇
	10	**(CaMg)P₂O₇, Ca₄Mg₅(PO₄)₆, Ca₂P₂O₇, Mg₂P₂O₇**, P₂O₅, Ca₃(PO₄)₂, CaO, Mg₃(PO₄)₂, K₃PO₄, K₄P₂O₇
P. halepensis at 1000 °C	0	**CaO, MgO**, K₂SO₄, K₂CO₃
	5	**Ca₇Mg₂P₆O₂₄, (CaMg)P₂O₇, Ca₂P₂O₇, Ca₃(PO₄)₂, Mg₃(PO₄)₂, Mg₂P₂O₇**, CaO, MgO, P₂O₅, K₃PO₄,K₄P₂O₇
	10	**Ca₇Mg₂P₆O₂₄, (CaMg)P₂O₇, Ca₂P₂O₇, Ca₃(PO₄)₂, Mg₃(PO₄)₂**, CaO, MgO, P₂O₅, K₃PO₄, K₄P₂O₇

Ashes were prepared at 600, 800 and 1000 °C before and after treating pine needles with 5% and 10% (w/w) DAP. Compounds in bold are the main constituents of the corresponding ash.
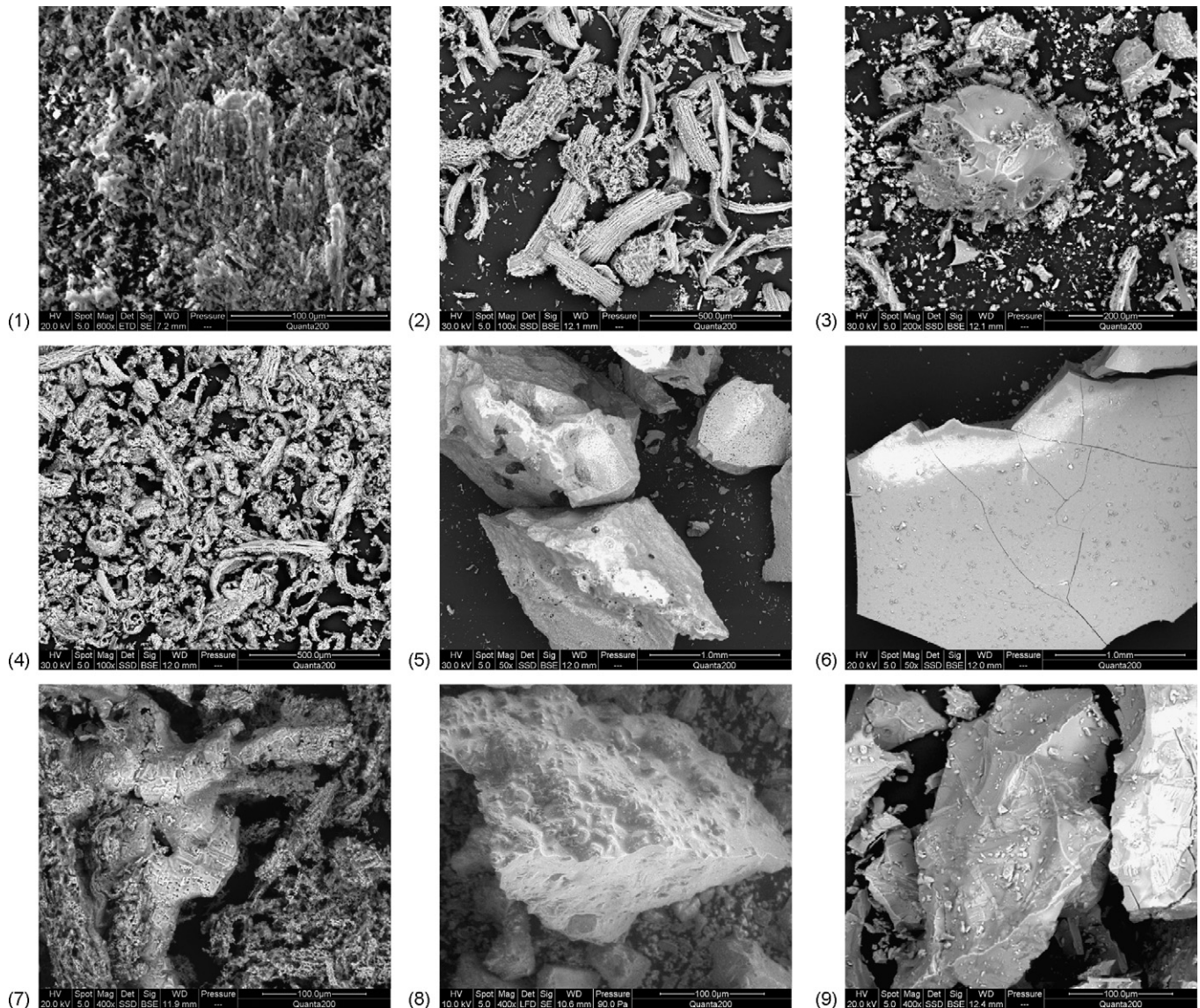

Fig. 5. Morphological features of *P. halepensis* needles ash. Ash prepared at 600, 800 and 1000 °C and before and after treating pine needles with 5% and 10% (w/w) DAP.

Calcium, magnesium and in a lesser extend potassium, were the main elements in all ash samples studied. Calcium and magnesium were found mainly as oxides and potassium as potassium carbonate or calcium–potassium carbonate (fairchildite). The above results are consistent with those obtained by TG and ICP analysis (Sections 3.1 and 3.2).

The oxides MgO and CaO detected at $600\,^{\circ}C$ were probably formed via the combustion of magnesium and calcium organic matter rather than via the decomposition of $MgCO_3$ and $CaCO_3$, which takes place at higher temperatures. Also, the $Ca(OH)_2$ (portlandite) detected at $600\,^{\circ}C$ is probably formed after the thermal treatment via the reaction between CaO and ambient moisture.

After treating *P. halepensis* needles with DAP, the ash samples were found in a glassy state due to the conversion of metal oxides and carbonates to phosphates (Fig. 1). The ash samples prepared at $600\,^{\circ}C$ after treatment with 5% DAP have similar mineral composition with those treated with 10% DAP. Also, as is shown in Table 2, no significant variation in mineral composition was recorded for the DAP treated ash samples prepared at higher temperatures (800 and $1000\,^{\circ}C$).

The main compounds identified in the DAP treated ash samples were: $(CaMg)P_2O_7$, $Ca_4Mg_5(PO_4)_6$, $Ca_2P_2O_7$, $Mg_2P_2O_7$, P_2O_5, $Ca_3(PO_4)_2$, $Mg_3(PO_4)_2$, $Ca_7Mg_2P_6O_{24}$ (Fig. 4). Also, peaks of XRD patterns of the ash samples treated with 10% (w/w) DAP are lower than the ash samples treated with 5% (w/w) DAP (Fig. 4). It seems that the addition of DAP favours the partial vitrification of the ashes.

3.5. Scanning electron microscopy analysis (SEM-EDX)

P. halepensis needles ash samples were examined with SEM/EDX in order to determine the influence of temperature and DAP concentration on their morphology and chemical composition. The results are presented in Fig. 5.

Prior to the DAP treatment, the morphological analysis of the samples prepared at $600\,^{\circ}C$ shows large porous fibrous particles with holes and voids (Photo 1). The EDX elemental analysis reveals that the main elements are Ca, Mg, K, P, C and O. Almost the same surface morphology was observed for the ash samples prepared at $800\,^{\circ}C$ (Photo 4). In both cases the particles have a fibrous texture, a diameter smaller than $10\,\mu m$ and seem to be loosely bonded. These particles do not fuse or sinter together after having been heated up to $800\,^{\circ}C$. On the contrary, for the ash samples prepared at $1000\,^{\circ}C$, sintering becomes apparent (Photo 7). The surface of this sample's particles starts to soften and contact. The EDX analysis of all ash samples prior to DAP treatment suggests that Mg, Na and Si content tends to increase as the temperature increases, whereas the K content shows a decreasing tendency. That is in accordance with the results obtained by ICP analysis and reported in Table 1.

The SEM/EDX analyses of the ash samples after DAP treatment, revealed a significant change in the morphology and composition. The particles appear to be attached to each other forming large aggregates with smooth glassy surface. This process starts with 5% (w/w) DAP at $600\,^{\circ}C$ (Photo 2) and completes at $1000\,^{\circ}C$ (Photo 8). By raising the percentage of DAP added, up to 10% (w/w), amorphous glassy shards are developed at all temperatures (Photo 3). The EDX analyses of the DAP treated samples suggest the decrement of Ca, Mg and K concentration as the DAP concentration increases.

4. Conclusions

The mineralogical and chemical properties of ash prepared from pine needles, before and after treatment with a fire retardant (DAP), have been determined by thermal analysis, ICP, XRD, SEM and titrimetric analytical techniques.

The main conclusions drawn by this study are:

1. The ash temperature preparation affects significantly its chemical composition. The content of Ca, Mg, Na, Si, Fe, P, Cu, tends to increase, K, Zn, Al to decrease and Pb, Mn to retain constant as ash preparation temperature rises. The soluble alkalinity first increases, as the temperature increases from 600 to $800\,^{\circ}C$ and then faintly decreases from 800 to $1000\,^{\circ}C$. Ashing at low temperatures ($T = 600\,^{\circ}C$) promotes the formation of metal carbonates, whereas at high temperatures ($T = 800$ and $1000\,^{\circ}C$) oxides are mainly formed. The only salts identified by XRD at high temperatures ($T = 1000\,^{\circ}C$) were K_2SO_4 and K_2CO_3. The above results were confirmed by thermal analysis. SEM analysis of ash samples has shown large porous fibrous particles with holes and voids with sintering taking place at high temperatures ($T = 1000\,^{\circ}C$).
2. The presence of DAP decreases the ash content in Ca, Mg, Na, Si, Fe, Al and Mn because of the formation of phosphate salts and P_2O_5, whereas K content increases since the volatilization of K_2O is avoided. Also the presence of DAP reduces dramatically the soluble alkalinity of ashes due to the excess of P_2O_5 formed in ashes. XRD and thermal analysis confirmed the conversion of metal oxides and carbonates to phosphates into a glassy state form.
3. The reported data can be used to evaluate the yield, chemical composition and mineralogy of ash produced by intense burning during forest fires in the presence of fire retardants and to predict its effects on soil properties, on the availability of nutrient elements, as well as its impact on the environment. Furthermore, to investigate the mechanism of combustion of forest species in the presence of fire retardants.

Acknowledgements

References

[1] A. Demeyer, J.C. Voundi Nkana, M.G. Verloo, Bioresour. Technol. 77 (2001) 287.

[2] J.C. Voundi Nkana, A. Demeyer, M.G. Verloo, Bioresour. Technol. 63 (1998) 251.

[3] C.S. Cronan, D.F. Grigal, J. Environ. Qual. 24 (1995) 209.

[4] S.K. Mukherji, T.K. Dan, B.B. Machhoya, Interceram 44 (1995) 31.

[5] L. Etiegni, A.G. Campbell, Bioresour. Technol. 37 (1991) 173.

[6] M.K. Misra, K.W. Ragland, A.J. Baker, Biomass Bioenergy 4 (1993) 103.

[7] B. Olanders, B. Steenari, Biomass Bioenergy 8 (1995) 105.

[8] M.S. Erich, T. Ohno, Analyst 117 (1992) 993.

[9] S.I. Ahonkhai, W.I. Nwokoro, Wood Sci. Technol. 21 (1987) 257.

[10] O.A. Fakankum, C.A. Loto, Wood Sci. Technol. 24 (1990) 305.

[11] S. Liodakis, G. Katsigiannis, G. Kakali, Thermochim. Acta 437 (2005) 158.

[12] A. Wyttenbach, P. Schleppi, L. Tobler, S. Bajo, J. Bucher, Plant Soil 168/169 (1995) 305.

[13] A.L. Ulery, R.C. Graham, C. Amrhein, Soil Sci. 156 (1993) 358.

[14] J. Kalousstian, A.M. Pauli, J. Pastor, J. Therm. Anal. 63 (2001) 7.

[15] K. Kishore, K. Mohandas, Fire Mater. 6 (1982) 54.

[16] American Society for Testing Materials, Standard Test Method for Ash in Wood, ASTM D1102-84, 2001.

[17] TAPPI, Ash in wood, pulp, paper and paperboard: combustion at 525 °C, T211 om-93, 1993.

[18] F.W. Wilburn, J.H. Sharp, D.M. Tinsley, R.M. McIntosh, J. Therm. Anal. 37 (1991) 2003.

[19] R.C. Mackenzie (Ed.), Differential Thermal Analysis, vol. 1, Academic Press, London, 1978, p. 242 and p. 303.

[20] D.T.Y. Chen, P.H. Fong, J. Therm. Anal. 12 (1977) 5.

[21] J. Adams, D. Dollimore, D.L. Griffiths, Thermochim. Acta 324 (1998) 67.

[22] P. Engler, M.W. Santana, M.L. Mittleman, D. Balazs, Rigaku J. 5 (2) (1988) 3.

[23] G. Liptay (Eds.), Atlas of Thermoanalytical Curves, vol. 4, Heyden & Sons Ltd., London, 1976, vol. 1–5, p. 20, p. 136, p. 60 and p. 244.

[24] J.M. Criado, F. Rouquerol, J. Rouquerol, Thermochim. Acta 38 (1980) 117.

[25] J.P. Sanders, P.K. Gallagher, Thermochim. Acta 388 (1988) 115.

[26] S. Arvelakis, P.A. Jensen, K. Dam-Johansen, Energy Fuels 18 (2004) 1066.

[27] A.M. Gadalla, M.F. Abadir, M.Y. Kasem, F.T. Salem, J. AIChE 30 (1984) 50.

[28] V.A. Sinyaev, E.S. Shustikova, L.V. Levchenko, G.A. Tokseitova, D. Griggs, Russ. J. Appl. Chem. 76 (2003) 1375.

[29] A. Lebugle, E. Zahidi, G. Bonel, React. Solid 2 (1986) 151.