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TG-MS ANALYSIS FOR STUDYING THE EFFECTS OF FIRE RETARDANTS ON THE PYROLYSIS OF PINE-NEEDLES AND THEIR COMPONENTS*

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Thermogravimetry-mass spectrometry (TG-MS) was used to study the effect of the inorganic salts $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$, active substances of many commercial forest fire retardants, on the pyrolysis of *Pinus halepensis* needles and their main components (cellulose, lignin and extractives). These salts seemed to affect the pyrolysis of cellulose by increasing significantly the char residue, decreasing the pyrolysis temperature and changing the composition of the evolved gases, that is, increasing levoglucosenone and decreasing oxygen containing volatile products. $(NH_4)_2SO_4$ seemed to have negligible effect on the pyrolysis of lignin, while $(NH_4)_2HPO_4$ increased the char residue and decrease the relative contribution of guaiacols in the evolved gases. No effects of the inorganic salts on the extractives were observed. Finally, the inorganic salts seemed to affect the pyrolysis of pine-needles, mainly the cellulose component, but the effects were not as intense as in the pyrolysis of cellulose.

Keywords: *cellulose, extractives, fire retardants, lignin, pine-needles, TG-MS*

Introduction

Application of fire retardants is a common method used for fighting forest fires. Fire retardants are applied ahead of a fire to reduce the rate of spread or intensity of fire. Several theories attempt to explain the action of fire retardants on the forest fuels. The barrier theory attributes the retardant action to a glassy barrier formed by the retardants. This barrier prevents the escape of volatile products. It also prevents oxygen from reaching the substrate and insulates the forest fuel surface from high temperatures. The dilution by non-combustible gases theory suggests that nonflammable gases, released by the decomposition of the fire retardant chemicals, dilute the combustion gases formed by the pyrolysis of the forest fuel and form a non-flammable gaseous mixture. According to the free radical trap theory fire retardants release free radical inhibitors at pyrolytic temperatures, that interrupt the chain propagation mechanism of flammability. Finally, the increased char/reduced volatiles theory, the most widely accepted theory, suggests that the fire retardants change the pyrolysis mechanism of the forest fuels. They lower the temperature at which pyrolysis occurs, directing the degradation pathway toward more char production and fewer volatiles [1].

The effect of the inorganic salts $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$, active substances of many fire retardants, on the pyrolysis mechanism of *Pinus halepensis* needles, a common forest fuel in the Mediterranean countries, has been studied in previous works by various analytical techniques such as DSC, TG, DI-MS, Py-GC-FID, Py-GC-MSD and optical microscopy and stereoscopy [2–7]. The effects of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ on the pyrolysis of pine needles were not so clear with TG and DSC [4]. That is because the thermal decomposition of lignocellulosic material is considered to be complicated, due to overlapping decomposition of its major constituents [8]. The Py-GC-MSD and Py-GC-FID experiments showed a significant change in the composition of the evolved volatiles, due to the presence of the inorganic salts. They also suggested, that although pine-needles are a complex natural product their main components such as cellulose and lignin preserve their own character under pyrolysis conditions and fire retardants seem to act directly on them [6]. Therefore, it would be useful to investigate the effect of the above chemicals on the pyrolysis of the main components of the pine-needles, which are cellulose, lignin and extractives.

The effects of fire retardants on the pyrolysis mechanism of cellulose have been studied extensively by various analytical techniques [9–11]. The pyrolysis of cellulose proceeds by two alternative pathways. The first pathway, which dominates at temperatures below 300°C, involves dehydration, rearrangement, formation of carboxyl and carbonyl groups, evolution of carbon monoxide and carbon dioxide and forma-

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tion of carbonaceous residue (char). The second pathway, which starts at about 300°C and dominates at higher temperatures, involves depolymerization of cellulose to tarry volatiles containing levoglucosan and other anhydrosugar derivatives. Fire retardant salts, such as $(NH_4)_2HPO_4$ or $(NH_4)_2SO_4$, lower the decomposition temperature of cellulose, enhance the first pathway which produce water, carbon monoxide, carbon dioxide and char at the expense of the combustion volatiles. This occurs because the salts are decomposed to acidic reagents (H_3PO_4 or H_2SO_4) on heating which catalyze hydrolysis and decomposition of the cellulose. NH_3 produced by the thermal decomposition of the retardant salts facilitates decomposition of cellulose by reacting with intermediate carbonyl compounds to form glycosylamines or Schiff bases, that are readily dehydrated by a β-elimination process [10]. The phosphoric acid, produced by the thermal degradation of phosphate-based retardants, cause phosphorylation of glucose especially at the reactive C-6 primary hydroxyl group. This phosphorylation inhibits depolymerisation and promotes char formation by blocking this site. The char produced acts as a diffusion barrier to volatiles leaving the fuel and to reactive oxygen reaching the fuel surface. It also acts as a thermal barrier, reducing heat transfer to fresh portions of the fuel, and so further reducing the extent of pyrolysis [11].

Although the effect of fire retardants on the pyrolysis of cellulose has been studied extensively there is limited information for the effect of the retardants on the pyrolysis of the other two components of pine-needles, lignin and extractives. A previous study using TG and DSC suggested that $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ appear to have negligible effect on the pyrolysis of lignin and not so clear effects on the extractives [3].

In this work, a more informative analytical technique than TG and DSC, that is TG-MS, is used for studying the effects of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ on the pyrolysis of Pinus halepensis needles, as well as, on the pyrolysis of their main components (cellulose, lignin and extractives). TG-MS can monitor simultaneously the thermal behavior of a sample and the evolved gases during heating [12–16]. It has been used in previous works for determining quantitatively H_2O and CO_2 during pyrolysis of commercial cellulose (Avicel Microcrystalline) [15] and pine needles [16] in the presence and absence of fire retardants. The purpose of this work is to investigate which component of the pine-needles (cellulose, lignin and extractives) is mainly affected by the fire retardants. Specifically, the effects of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ on the pyrolysis temperature, on the char residue and on the composition (qualitative changes) of the flammable gases evolved during heating are studied for pine-needles and for each component isolated from them, individually. Inert atmosphere is used in the experiments for avoiding secondary oxidative reactions of the volatile pyrolysis products. Oxidative reactions would lead mainly to the formation of CO, CO_2 and H_2O, making it difficult to explain the influence of fire retardants on the forest fire. Besides, inert atmosphere is adequate for approaching the real conditions of a fire, which takes place in an atmosphere of limited oxygen very close to the fuel.

Experimental

Materials

The $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ used were of p.a. grade from Carlo Erba and BDH, respectively. The pine-needles used were collected from a forest near an urban area. They were washed with deionized water, air dried and cut in pieces of 3 mm. As a more realistic approach for studying the effect of the chemicals on pine-needles components, the components (cellulose, lignin, extractives) were isolated from pine-needles instead of using commercial products. More specifically, cellulose was isolated from pine-needles after processing with a mixture of HNO_3–CH_3COOH [18]. Lignin was isolated from pine-needles according to the ASTM D 1106-96 method after processing with H_2SO_4. The extractives were obtained from pine-needles by soxhlet extraction with a mixture of ethanol-toluene (ASTM D 1107-96).

The following samples were used: cellulose and cellulose treated with $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$, lignin and lignin treated with $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$, extractives and extractives treated with $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ and finally pine-needles and pine-needles treated with $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$. The concentration of the inorganic salts was 10 mass/mass% in all the treatments. For preparing the treatments, 25 cm^3 of an aqueous solution of 0.4 mass/mass% of the inorganic salt was added to 900 mg of the untreated material (e.g. cellulose) and the suspension was dried in an oven at 40°C for 48 h. The same procedure, but with deionized water instead of 0.4% solution of inorganic salts was followed for preparing the untreated samples.

Methods

The used TG-MS system consisted of a thermogravimetric analyzer (TA instrument, TGA 2050) and a mass selective detector (HP-5972). An in-house made interface [17] was used for hyphenating the above instruments. The transfer line of the TG-MS interface was a Chrompack uncoated column (2.17 m×0.15 mm id).

The TG-MS interface temperature was 200°C and the transfer line temperature was 220°C. The inert gas used was helium with a flow rate of 100 mL min^{-1} in the thermobalance. Approximately 10 mg of each sample (4 mg of extractives) were heated in the thermobalance from 50 to 650°C with a heating rate of 50°C min^{-1}. The MS interface was heated at 280°C. The electron impact source was tuned at 70 eV and the scan duration was 0.5 s. The mass range for the MS data acquisition was 2–210 amu.

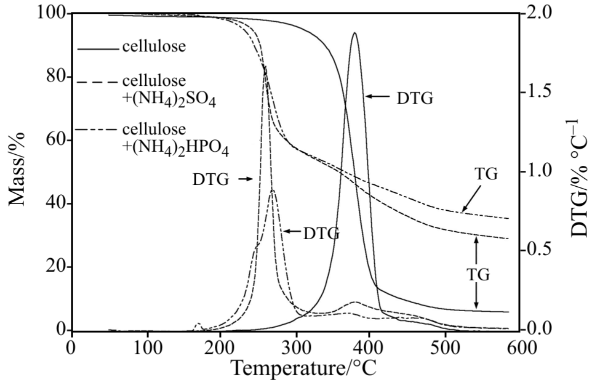

Fig. 1 TG and DTG curves resulted from the TG-MS analysis of cellulose and cellulose treated with $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$

Results and discussion

In Fig. 1 the TG and DTG curves of cellulose and cellulose treated with $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ are presented. It is observed that the pyrolysis temperature is shifted from 380°C for cellulose to 260°C for cellulose treated with $(NH_4)_2SO_4$ and 270°C for cellulose treated with $(NH_4)_2HPO_4$. The char residue (at 580°C) is also increased from about 6% for cellulose to 30% for cellulose treated with $(NH_4)_2SO_4$ and 36% for cellulose treated with $(NH_4)_2HPO_4$.

Changes to the composition of the flammable pyrolysis products, due to the action of $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$, were found by comparing the full mass spectra corresponding to the maximum evolution rate of gases, during the pyrolysis of the three samples of cellulose (Fig. 2). It should be noted, that full mass spectra give a picture of the majority of the gases that evolve during heating. The spectrum of the pyrolysis of cellulose (Fig. 2a) is a complex spectrum consisted of masses attributed to acetic acid (*m*/*z* 60), levoglucosan (*m*/*z* 57, 60, 70, 73), carbonyl compounds, (*m*/*z* 68, 69, 70, 71, 72, 73, 74, 84, 86, 100), pyranone derivatives (*m*/*z* 68, 69, 84, 97, 98, 100), furan derivatives (81, 82, 95, 96, 97, 98, 109, 110) and reduced furans (*m*/*z* 69, 70, 71, 72, 82, 84, 86, 97, 98, 100) [19, 20]. Figures 2b and c indicate that $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ increase *m*/*z* 68, 96, 98 and 126 which can be attributed to levoglucosenone, a dehydration product of levoglucosan. The above chemicals decrease *m*/*z* 73, 74, 84, 86 and 100, which are attributed to carbonyl compounds, pyranone derivatives and reduced furans. Mass 64 in Fig. 2b is due to SO_2 from the decomposition of $(NH_4)_2SO_4$. The observations made in this work about the effects of the inorganic salts on cellulose derived from pine-needles are in good agreement with the results of a previous study on commercial cellulose (Avicel Microcrystalline) [15].

The TG and DTG curves of lignin in Fig. 3 show that lignin decomposes with maximum rate at around 410°C and it has about 33% char residue at 580°C. $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ do not seem to shift the pyrolysis temperature of lignin significantly. Negligible increase of the char residue is observed with $(NH_4)_2SO_4$, while a slight increase is observed with $(NH_4)_2HPO_4$ (48% char residue at 580°C).

In Fig. 4a the mass spectrum of the pyrolysis of lignin corresponding to the maximum decomposition rate is presented. This complex spectrum consists of masses attributed to various guaiacols (*m*/*z* 124, 138, 150, 164), various phenols (*m*/*z* 93, 94, 107, 108, 120) and aromatic hydrocarbons (*m*/*z* 77, 91) [21, 22]. Spectra of the pyrolysis of treated lignin (Figs 4b and c) show great similarity with the spectrum of un-

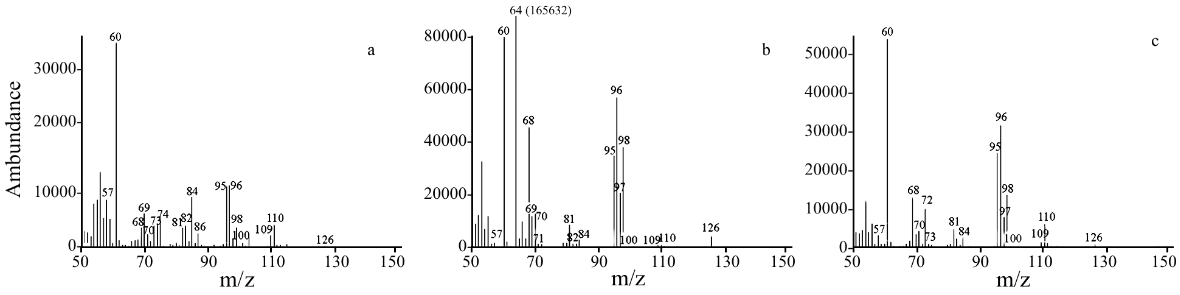

Fig. 2 Mass spectrum of the pyrolysis of a – cellulose, b – cellulose treated with $(NH_4)_2SO_4$ (number in parenthesis is the abundance of *m*/*z* 64) and c – cellulose treated with $(NH_4)_2HPO_4$, at the maximum evolution rate of the gases (380, 260 and 270°C, respectively)

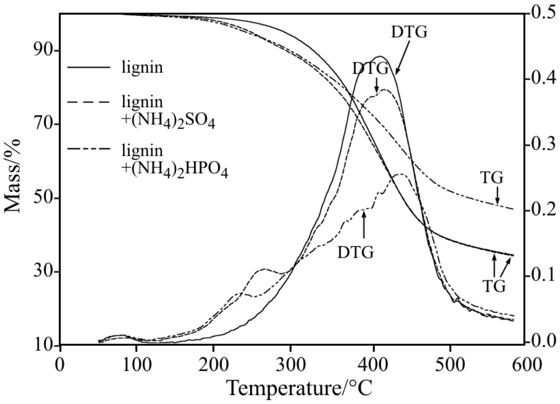

Fig. 3 TG and DTG curves resulted from the TG-MS analysis of lignin and lignin treated with $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$

treated lignin indicating that $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ do not affect significantly the volatile products of lignin thermal degradation. However, the average mass spectrum of lignin treated with $(NH_4)_2HPO_4$ (Fig. 5b) shows a relative decrease of the guaiacol series (*m*/*z* 124, 138, 150, 164) compared to the average mass spectrum of lignin (Fig. 5a), indicating a possible effect of $(NH_4)_2HPO_4$ on the pyrolysis of lignin.

In Fig. 6 the TG and DTG curves of the extractives and the extractives treated with $(NH_4)_2SO_4$ are presented. It is observed that $(NH_4)_2SO_4$ has no significant effect on the pyrolysis temperature and the char residue of the extractives. The average mass spectrum of the extractives pyrolysis is presented in Fig. 7. It consists of masses attributed to fatty acids (*m*/*z* 55, 69, 83, 97, 111) and terpenic compounds (91, 93, 105, 107, 119, 121, 133, 135) [2, 22]. The average spectrum of the pyrolysis of extractives treated with $(NH_4)_2SO_4$ (not shown) shows great similarity with Fig. 7, indicating that $(NH_4)_2SO_4$ has no significant effect on the volatile pyrolysis products of the extractives. However, it should be mentioned that many gases evolved during the pyrolysis of the extractives (like resin acids, or fatty acids of high molecular weight) had not been detected by the MS because they are condensed, either in the TG furnace or in the TG-MS interface.

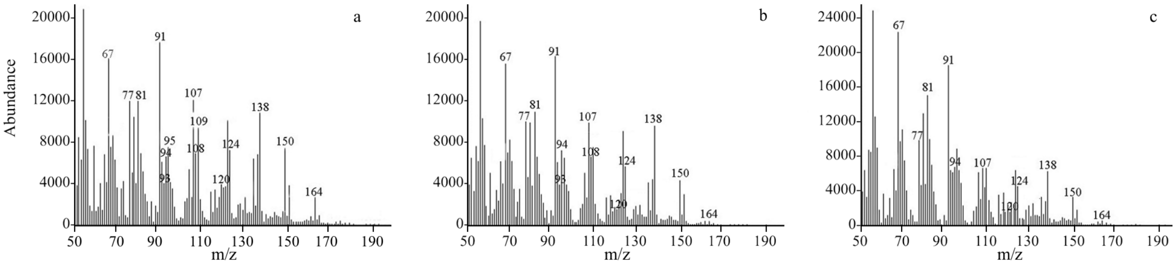

Fig. 4 Mass spectrum of the pyrolysis of a – lignin, b – lignin treated with $(NH_4)_2SO_4$ and c – lignin treated with $(NH_4)_2HPO_4$, at the maximum evolution rate of gases (412, 417 and 439°C, respectively)

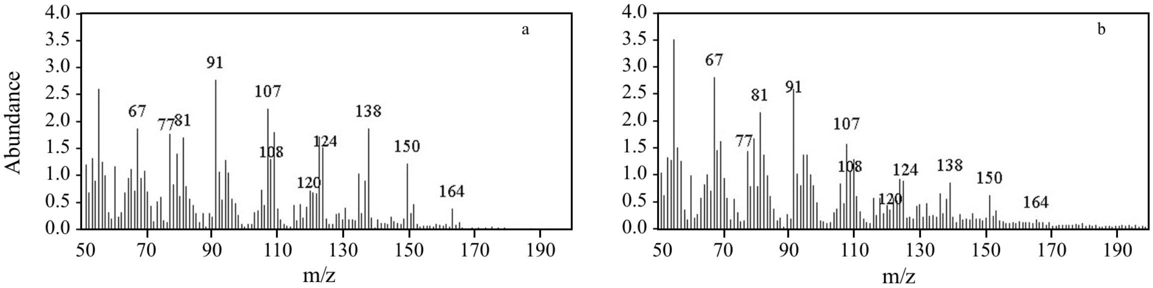

Fig. 5 Average mass spectrum of the pyrolysis of a – lignin and b – lignin treated with $(NH_4)_2HPO_4$

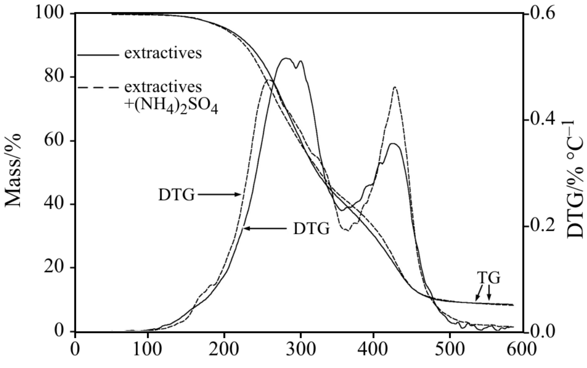

Fig. 6 TG and DTG curves resulted from the TG-MS analysis of extractives and extractives treated with $(NH_4)_2SO_4$

The TG and DTG curves of the pyrolysis of pine-needles are presented in Fig. 8a.The DTG curve shows one maximum at 360°C and a second one at

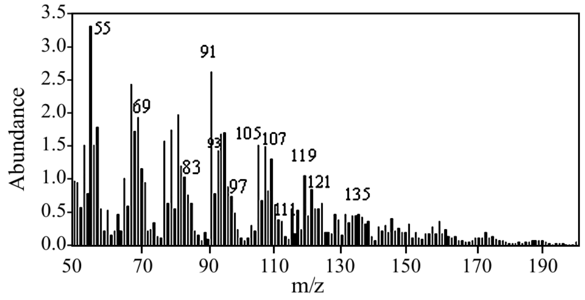

Fig. 7 Average mass spectrum of the pyrolysis of extractives

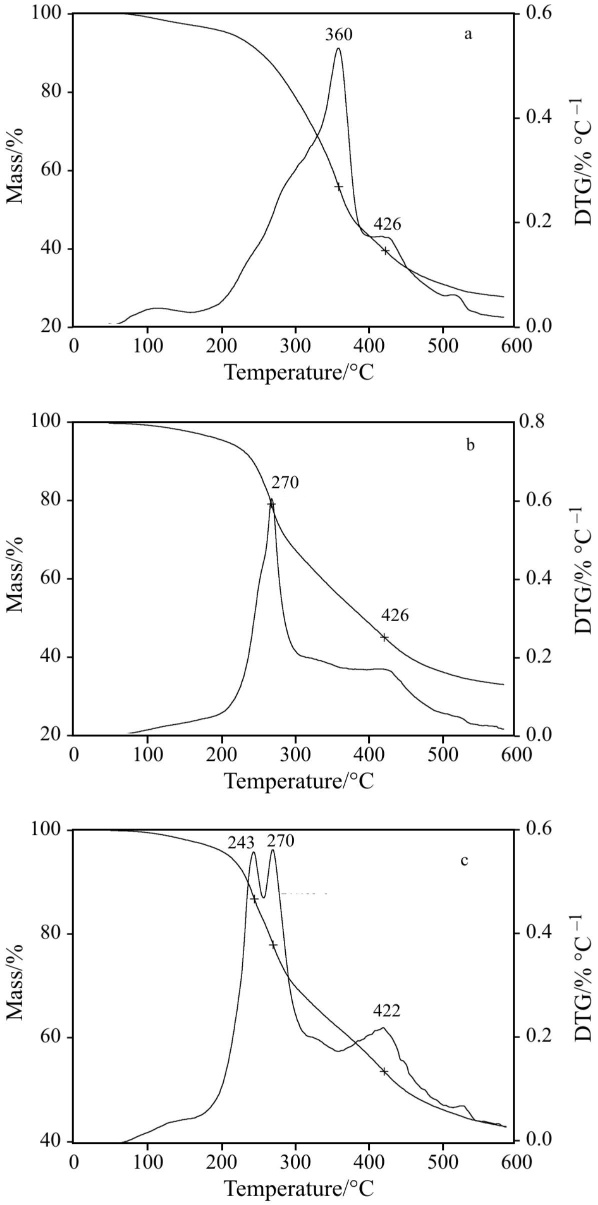

Fig. 8 TG and DTG curves resulted from the pyrolysis of a – pine-needles, b – pine-needles treated with $(NH_4)_2SO_4$ and c – pine-needles treated with $(NH_4)_2HPO_4$

426°C. The mass spectrum corresponding to 360°C (Fig. 9a) presents masses that could be attributed mainly to the pyrolysis of cellulose (*m*/*z* 60, 68, 69, 72, 74, 84, 95, 96, 98, 110) and the pyrolysis of lignin (*m*/*z* 67, 81, 91, 107, 124, 138, 150, 164). The mass spectrum corresponding to 426°C (Fig. 9b) presents masses that could be attributed mainly to lignin (*m*/*z* 67, 77, 79, 81, 91, 107, 108, 120, 150, 164) or to heavier terpenic compounds (105, 107, 119, 121, 133, 135).

Figures 8b and c show the TG and DTG curves of the pyrolysis of pine-needles treated with $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$, respectively. It is obvious that the first maximum of the DTG curve has been shifted for both cases to lower temperatures (around 270°C) compared to Fig. 8a, while the second one is still shown at around 426°C. The maximum at 243°C of the DTG curve in Fig. 8c is attributed to the pyrolysis of $(NH_4)_2HPO_4$ itself. The char residue of pine-needles at 580°C is about 27%. A slight increase of the char residue is observed with $(NH_4)_2SO_4$, while a more significant increase is observed with $(NH_4)_2HPO_4$ (34 and 44% char residue at 580°C, respectively). It should be noted that the increase of char residue and decrease of combustible volatiles in case of treated pine-needles was reported by quantitative TG-MS analysis [16]. In addition, it is reported

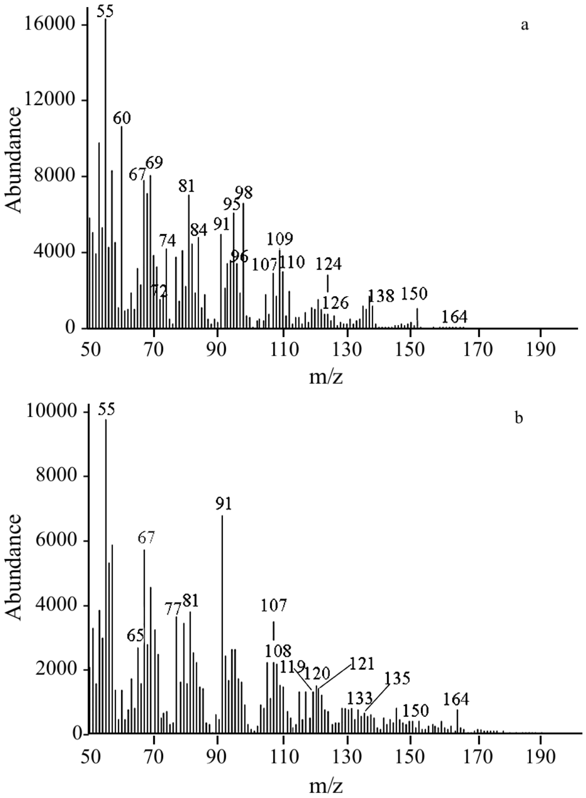

Fig. 9 Mass spectrum a – at 360°C and b – at 426°C of the pyrolysis of pine-needles

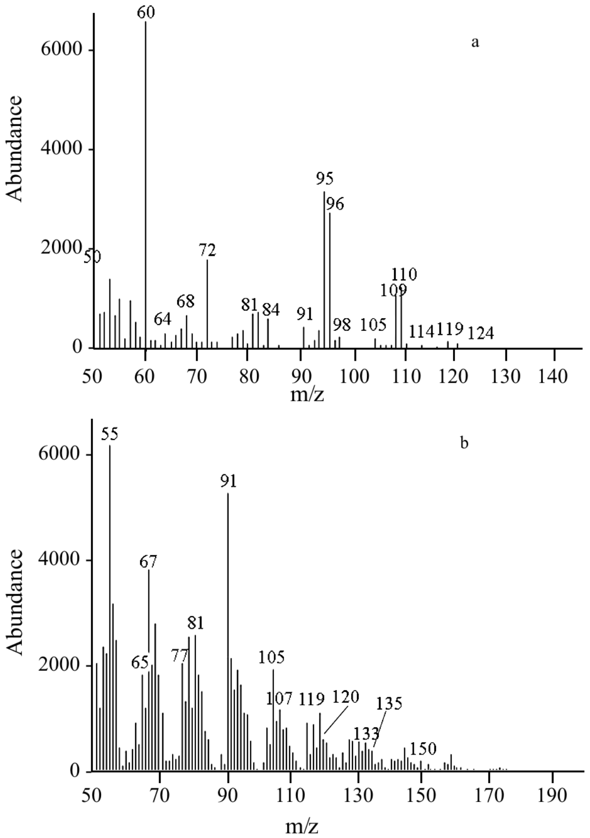

Fig. 10 Mass spectrum a – at 270°C and b – at 422°C of the pyrolysis of pine-needles treated with $(NH_4)_2HPO_4$

that the use of fire retardants causes increase of char residue in the case of wood [23].

The mass spectra of the pyrolysis of pine-needles treated with $(NH_4)_2HPO_4$ at temperatures corresponding to maximum evolution rates of gases, as indicated by the DTG curve (270 and 422°C), are presented in Fig. 10. The mass spectrum at 270°C of the pyrolysis of pine-needles treated with $(NH_4)_2HPO_4$ (Fig. 10a) shows similarity with the spectrum of cellulose treated with $(NH_4)_2HPO_4$ (Fig. 2c), indicating that $(NH_4)_2HPO_4$ affects mainly cellulose during pine-needles pyrolysis. Mass spectrum corresponding to 422°C of the pyrolysis of pine needles treated with $(NH_4)_2HPO_4$ (Fig. 10b) resembles the mass spectrum at 426°C of the pyrolysis of pine-needles (Fig. 9b), indicating that $(NH_4)_2HPO_4$ does not significantly affect lignin or extractives (terpenic compounds) during the pyrolysis of pine-needles. Similar observations are made concerning the effect of $(NH_4)_2SO_4$.

Conclusions

TG-MS proved to be a powerful technique for studying the effect of $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ on the pyrolysis of *Pinus halepensis* needles and their components. These inorganic salts seemed to affect the pyrolysis of cellulose by increasing significantly the char residue, decreasing the pyrolysis temperature and changing the composition of the evolved gases, that is, increasing levoglucosenone and decreasing oxygen containing volatile products such as pyranone derivatives, reduced furans and carbonyl compounds. $(NH_4)_2SO_4$ seemed to have negligible effect on the pyrolysis of lignin, while $(NH_4)_2HPO_4$ seemed to increase the char residue and decrease the relative contribution of guaiacols in the evolved gases. No effects of the inorganic salts on the extractives were observed. Finally, the inorganic salts seemed to affect the pyrolysis of pine-needles, mainly the cellulose component, but the effects were not as intense as in pyrolysis of cellulose.

Acknowledgements

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