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Thermal analysis of *Pinus halepensis* pine-needles and their main components in the presence of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$

A.A. Pappa *, N.E. Tzamtzis, M.K. Statheropoulos, G.K. Parissakis

Laboratory of Inorganic and Analytical Chemistry, Department of Chemical Engineering, National Technical University of Athens, 9 Iroon Polytechniou Str., Athens 157 73, Greece

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Abstract

DSC and TG were used to study the effects of fire retardants on the pyrolysis of *Pinus halepensis* pine-needles and their components (cellulose, lignin and extractives). $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ were used as fire retardants at the 10% w/w concentration level. The TG results showed that the mass loss profile of pine-needles resembles those of lignin and extractives. The DSC curves showed that in the presence of fire retardants there is a shift to lower pyrolysis temperatures for cellulose. In addition, there is an increase in the pyrolysis residue for both cellulose and pine-needles. Minor or negligible effects were observed for lignin and extractives in the presence of the retardants.

Keywords: Cellulose; Extractives; Fire-retardants; Lignin; Pine-needles; Pyrolysis

1. Introduction

Forest fires are a serious problem with devastating consequences. Among the various fire-fighting techniques, is the use of chemicals (fire retardants) in aqueous solutions to prevent or suppress fire spreading. Some of the common fire retardants are mixtures containing mainly ammonium phosphate or sulphate. These retardants produce an acid (phosphoric or sulphuric) prior to the flaming temperatures, which changes the decomposition profile of forest fuels. The main changes are the production of decreased quantities of volatiles and the increase in char residue [1].

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* Corresponding author.

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Forest fuel consists mainly of three groups of chemical components: cellulose, lignin and extractives. Therefore, the study of the thermal behaviour of the forest fuel and its components in the presence of chemicals could contribute to the development of more effective fire retardants.

The thermal behaviour of various forest fuels [2], cellulose, lignin [3,4] and conifer extractives (indirectly) [5], has been studied. The effects of various chemicals on the pyrolysis and combustion of cellulose [6] and lignin [3] have also been reported. The thermal behaviour of *Pinus halepensis*, a frequently found forest species in Mediterranean countries, and its components have not been studied systematically. In this work, DSC and TG have been used to study the thermal behaviour of pine-needles of *Pinus halepensis* and its components in the presence of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$.

2. Experimental

2.1. Instruments

The differential scanning calorimeter (DSC) used was a Stanton Redcroft instrument, model HT1500. The thermobalance (TG) used was a Perkin-Elmer model TG-2.

2.2. Methods

DSC: Approximately 50 mg of the sample were placed in a Pt crucible and heated at a rate of 10°C min^{-1}, from ambient temperature to 500°C. The selected heating rate is representative of the low heating rates reported in the literature. The heating rate does not have a significant effect, at least on the char yield of forest fuels [7]. The carrier gas was N_2 with a flow rate of 50 ml min^{-1}. Pre-cured α-Al_2O_3 was used as reference material. The reproducibility of the temperature measurements by DSC was better than 2% for almost all the experiments.

TG: Each sample used was 6–8 mg. In the case of the extractives, the initial sample mass was close to 45 mg. The thermogravimetric experiments were carried out in a non-isothermal regime at a linear heating rate of 10°C min^{-1}, from 100 to 500°C. The carrier gas used was N_2 with a flow rate of 60 ml min^{-1}.

2.3. Materials

The cellulose used in this study was a Merck reagent with a purity of at least 99.5%. The $(NH_4)_2SO_4$ was a p.a. grade Merck reagent, and the $(NH_4)_2HPO_4$ was a BDH laboratory reagent. The pine-needles used were collected from a forest near an urban area. They were heated at 40°C for 24 h in an oven, ground, and then the fraction between 200 and 500 μm was separated and used for the preparation of the samples. The lignin used was isolated from the pine-needles after processing with H_2SO_4 (Klason method, ASTM D1106-56). The isolated lignin product was dried and used in a powder form. The extractives used were obtained from the pine-needles using the soxhlet extraction apparatus and a mixture of toluene and ethanol (method ASTM

D1107-56). After extraction, the solvent was evaporated in a thin-layer evaporator apparatus (Rotavap ex. Buchi), at 40°C and 19.7 kPa; the remaining solvent residues were flashed off in a vacuum oven at 40°C and 1.31 kPa.

2.4. Samples

Twelve types of samples were prepared: (a) pure cellulose and cellulose treated with $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$, (b) pure pine-needles and pine-needles treated with $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$, (c) pure lignin and lignin treated with $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$, and (d) pure extractives and extractives treated with $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$. The concentration of the above inorganic chemicals was 10% w/w in all the treatments. In a previous work [8], this was found to be an optimum concentration level. The preparation of the above samples is described elsewere [8].

3. Results and discussion

Fig. 1 shows the DSC curves of pure retardants. The endotherms shown are due to the decomposition, and to the melting of the salts [6].

Figs. 2–5 show the DSC curves of untreated and treated samples of cellulose, lignin, extractives and pine-needles, respectively. Table 1 presents the changes in the char residue at 500°C obtained when pine-needles, cellulose and lignin were treated with fire

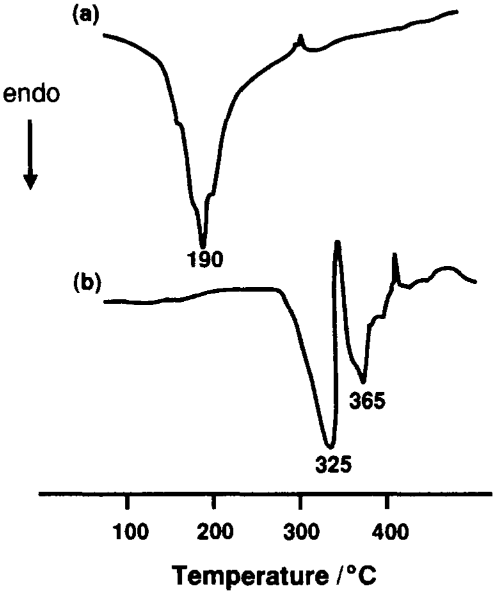

Fig. 1. DSC curves of: (a) pure $(NH_4)_2HPO_4$ and (b) pure $(NH_4)_2SO_4$, heated in N_2 at 10°C min^{-1}.

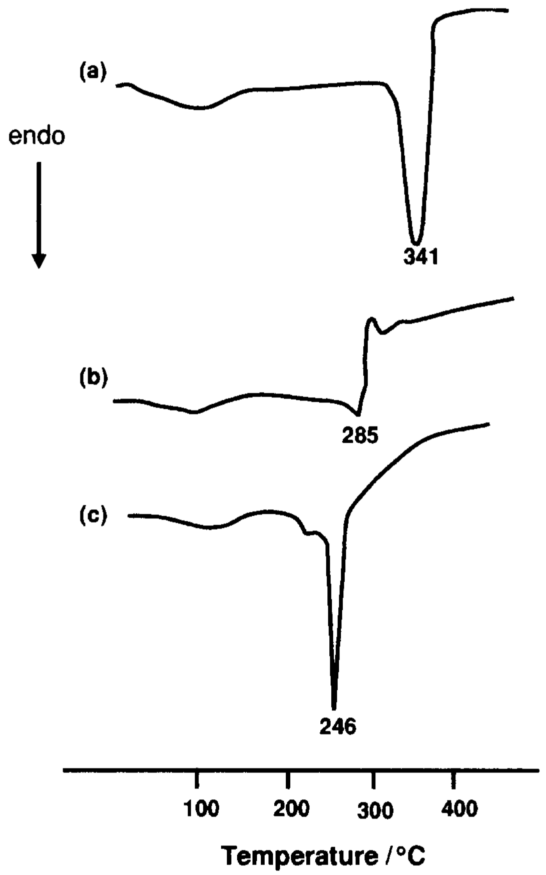

Fig. 2. DSC curves of: (a) cellulose, (b) cellulose treated with 10% w/w $(NH_4)_2HPO_4$ and (c) cellulose treated with 10% w/w $(NH_4)_2SO_4$, heated in N_2 at 10°C min^{-1}.

retardants. In addition, the TG curves of pine-needles and their main components (cellulose, lignin, extractives) are plotted in Fig. 6.

The DSC curve of pure cellulose (Fig. 2(a)) shows a narrow endotherm at 341°C. This is reconfirmed by the steep TG curve of cellulose (Fig. 6) in the temperature range 300–400°C. This corresponds to about 90% mass loss. The above endotherm is correlated to the thermal decomposition of cellulose, which takes place by two competing pathways [8]. The first is a depolymerization process, which leads to an intermediate product, levoglucosan, which further decomposes to various volatiles, e.g. aldehydes, ketones, furans, pyrans [9]. The second pathway is a dehydration process, which mainly produces char residue, water and carbon oxides. In the presence of 10% w/w $(NH_4)_2HPO_4$, the endotherm shifts to 285°C (Fig. 2(b)), whereas in the presence of 10% w/w $(NH_4)_2SO_4$ the pyrolysis endotherm shifts to 246°C (Fig. 2(c)). It should be noted that the above temperature shift may release the volatiles at lower than their

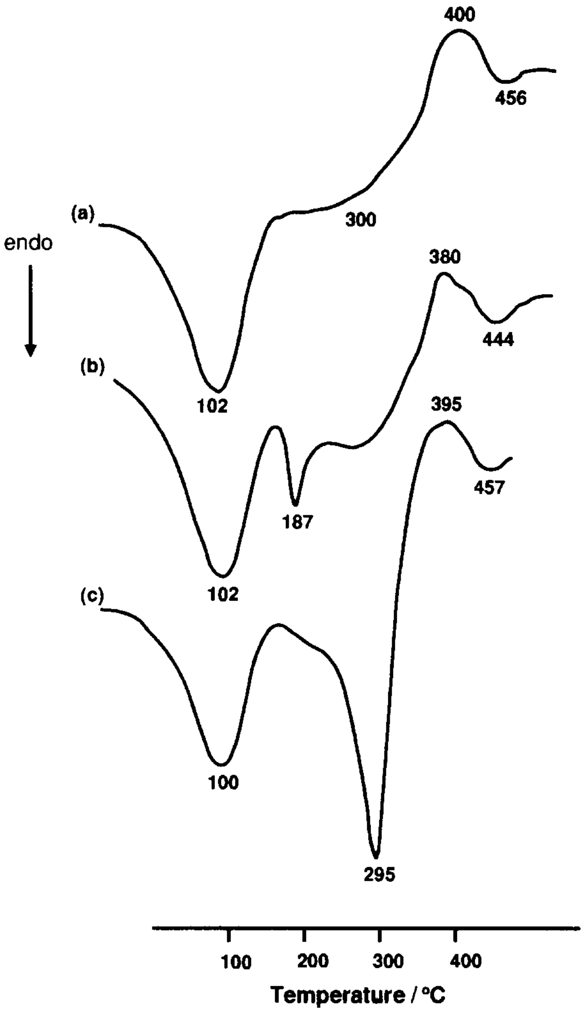

Fig. 3. DSC curves of: (a) lignin, (b) lignin treated with 10% w/w $(NH_4)_2HPO_4$ and (c) lignin treated with 10% w/w $(NH_4)_2SO_4$, heated in N_2 at 10°C min^{-1}.

ignition temperatures, affecting the cellulose combustion. In addition, the treatment with the fire retardants increases by about 2.4 times the char residue of cellulose (Table 1). This shows that these chemicals favour the dehydration process.

The DSC curve of pure lignin (Fig. 3(a)) shows one endotherm at 102°C, due to moisture loss. The exotherm at 400°C is attributed to the recombination of the degradation products of lignin, e.g. phenols and phenolic derivatives, which leads to the char formation. This exotherm peak seems to mask the shallow endotherm of lignin thermal degradation at about 300°C [3]. However, the TG curve (Fig. 6), shows that mass loss begins at about 220°C, due to the thermal degradation of lignin. This mass

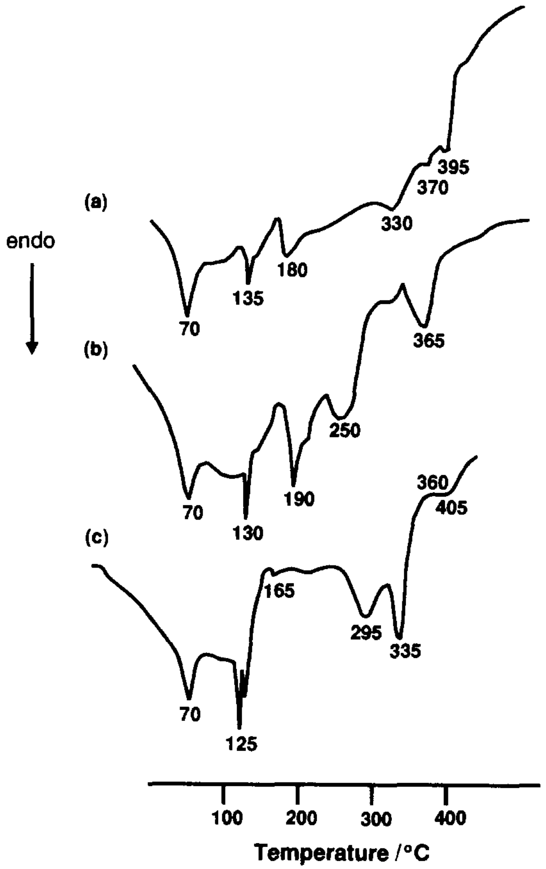

Fig. 4. DSC curves of: (a) extractives, (b) extractives treated with 10% w/w $(NH_4)_2HPO_4$ and (c) extractives treated with 10% w/w $(NH_4)_2SO_4$, heated in N_2 at 10°C min^{-1}.

loss takes place in a broader temperature range compared to cellulose, leaving a relatively higher char residue. In the presence of 10% w/w $(NH_4)_2HPO_4$ (Fig. 3(b)), the exotherm shifts from 400 to 380°C, whilst in the presence of 10% w/w $(NH_4)_2SO_4$ (Fig. 3(c)), no significant shift is noticed. The endotherms at 187°C (Fig. 3(b)) and 295°C (Fig. 3(c)) can be attributed to the inorganic salts. In addition, in the presence of both retardants there are negligible changes in char residues (Table 1). It appears that the examined salts have no significant effect on the pyrolysis of lignin.

The DSC curve of pure extractives (Fig. 4(a)) shows endotherm peaks at 70, 135, 180, 330, 370 and 395°C. It should be emphasized that the extractives are complex mixtures of various compounds, e.g. terpenes, resin acids, phenolic compounds, waxes, fats [10]. The peaks below 200°C are correlated to physical changes in the various constituents. The endotherms at 70 and 180°C are attributed to softening and melting of resinous acids respectively. The endotherm at 135°C is probably due to evaporation of some high volatility constituents. The TG curve of the extractives (Fig. 6) shows a mass loss

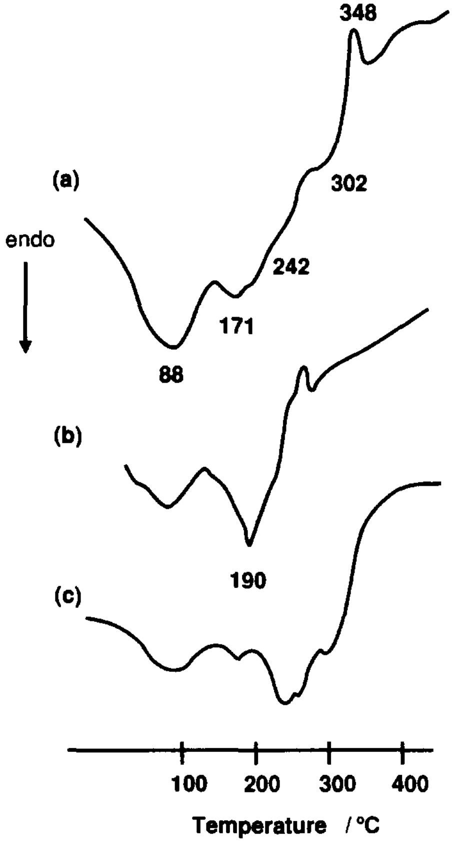

Fig. 5. DSC curves of: (a) pine-needles, (b) pine-needles treated with 10% w/w $(NH_4)_2HPO_4$ and (c) pine-needles treated with 10% w/w $(NH_4)_2SO_4$, heated in N_2 at 10°C min^{-1}.

below 200°C, which reconfirms the above-mentioned evaporation. The endotherms in the region 300–500°C may be attributed to the evaporation and/or to the thermal decomposition of the heavy constituents of the extractives [5]. The DSC curve of the extractives treated with 10% w/w $(NH_4)_2HPO_4$ (Fig. 4(b)), shows no differences in the low-temperature region to that of the untreated sample. The peak at 190°C originates from $(NH_4)_2HPO_4$. The DSC curve profile indicates an effect of the chemical on the heavy constituents of the extractives (in the high-temperature range). This might be possible through the acceleration of hydrolysis reactions. The DSC curve of the extractives treated with 10% w/w $(NH_4)_2SO_4$ (Fig. 4(c)) is also similar to the untreated sample up to 200°C. The peaks at 295 and 335°C are attributed to $(NH_4)_2SO_4$ and mask the pyrolysis endotherm of the extractives in this region.

The DSC curve of the untreated pine-needles (Fig. 5(a)) shows endotherm peaks at 88 and 171°C. Two less prominent endotherm peaks and an exotherm appear at 242, 302 and 348°C, respectively. The endotherm peak at 88°C is attributed to the moisture, to the softening of resinous acids of the extractives, and/or to evaporation of high

Table 1
The char residues of pine-needles and their components in the presence of $(NH_4)_2HPO_4$ and $(NH_4)_2SO_4$ (DSC measurements)[a,b]

Substance	Substance treated with 10% w/w $(NH_4)_2HPO_4$	Substance treated with 10% w/w $(NH_4)_2SO_4$
Pine-needles	1.7	1.6
Cellulose	2.3	2.4
Lignin	1.1	1.0

[a] Numbers corresponding to char residues are expressed as multiples of the quantity of the char residue of untreated substances determined at 500°C.

[b] To estimate the residue of the treated substance, the residue of pure retardant was subtracted from the total residue. The residues found for $(NH_4)_2HPO_4$ and for $(NH_4)_2SO_4$ were 50% w/w and 3% w/w of their initial masses, respectively.

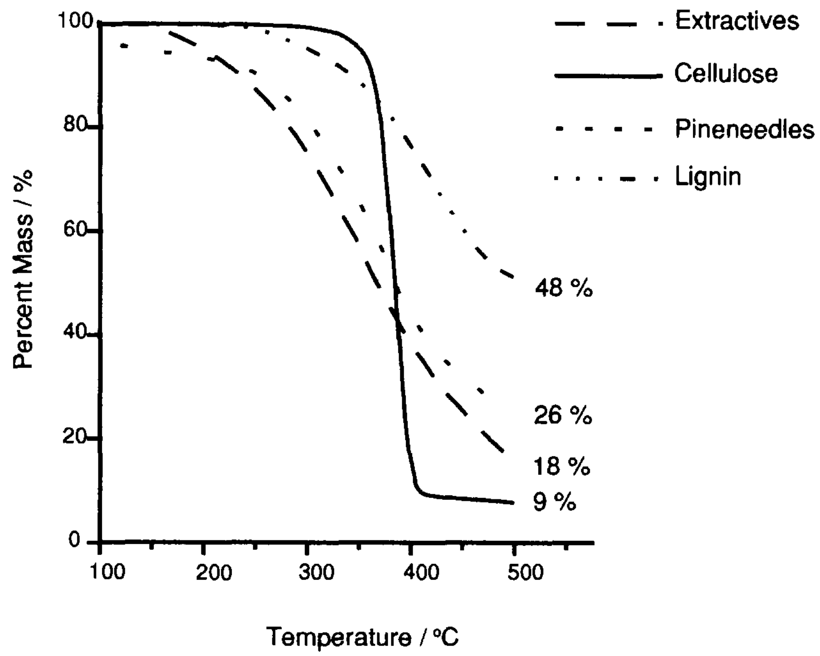

Fig. 6. TG curves of pine-needles and their components (cellulose, lignin, extractives), heated in N_2 at 10°C min^{-1}.

volatility constituents of pine-needles, e.g. terpenes of low molecular masses. This evaporation is reconfirmed by the mass loss observed in the TG curve of pine-needles below 150°C (Fig. 6). It should be noted that no mass loss is observed for the TG curves of the extractives for temperatures lower than 150°C. This could be explained by the loss of these volatile components during the isolation process of the extractives from pine-needles. The endotherm peak at 171°C is attributed to the melting of resinous acids and/or to the continuous evaporation of high volatility components. The less prominent endotherm at 302°C may be correlated with cellulose pyrolysis. A similar observation has been reported for the DSC curve of Ponderosa foliage [2]. The exotherm at 348°C is attributed to the char formation, mainly due to the lignin content [8]. As shown in Fig. 6, the mass loss profile of pine-needles resembles that of the extractives and the lignin. It appears from the same figure that cellulose pyrolysis is quite different. The DSC curves of treated pine-needles are similar to that of the untreated sample for the low-temperature range (Fig. 5). The exotherm at 348°C, which appeared for pure pine-needles, is not present in these curves. However, there is a significant increase in char residue in the presence of both retardants (Table 1). This indicates a retardant effect of both chemicals on the pyrolysis of the pine-needles.

4. Conclusions

The major components of pine-needles (cellulose, lignin, extractives) have different contributions in the pyrolysis of pine-needles. However, cellulose which is frequently used as a model compound for forest fuel pyrolysis studies, appears to have a different degradation profile to pine-needles, at least as shown in the TG measurements. Furthermore, the endotherm of cellulose pyrolysis is not so prominent in the DSC curves of pine-needles. The fire retardants examined have the following effects on the pyrolysis of pine-needles and their components: they lower the pyrolysis temperature of cellulose and increase the char residue for both cellulose and pine-needles. In contrast, they appear to have negligible effects on the pyrolysis of lignin and not so clear effects on the extractives. More information could be provided through the use of hyphenated techniques such as TG-MS and TG/DSC–GC-MS.

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