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## The effect of salt and oxide-hydroxide additives on the pyrolysis of cellulose and *Pinus halepensis* pine needles

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### Abstract

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) were used to study the effects of various salts and oxide-hydroxide additives on the pyrolysis of cellulose and *Pinus halepensis* pine needles.  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaHCO}_3$ ,  $\text{KHCO}_3$ ,  $(\text{COONa})_2$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{O}\cdot\text{CaO}$  were used as additives at concentrations of 4% w/w and 10% w/w. DSC and TGA showed that the addition of  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{NaH}_2\text{PO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  on cellulose causes a significant shift to lower pyrolysis temperatures, i.e. 50°C to 80°C, as well as a significant increase in char residues. The effect of  $\text{NaHCO}_3$ ,  $\text{KHCO}_3$ , and  $(\text{COONa})_2$  on the pyrolysis of cellulose was also found to be significant in terms of the DSC profile, while the increase in char residues was moderate. In contrast the effect of  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{O}\cdot\text{CaO}$  on the pyrolysis of cellulose was found to be minor, under the above-mentioned criteria.

The above chemicals, tested as fire retardants, have shown minor effects on the pyrolysis of *Pinus halepensis* pine needles. Some changes, however, were noticed in the solid pyrolysis residues, particularly when  $(\text{NH}_4)_2\text{HPO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  were used.

**Keywords:** Cellulose; DSC; Fire retardants; Pine needles; Pyrolysis; TGA

### 1. Introduction

Forest fires present a serious problem with devastating consequences. A combination of various techniques is used to fight forest fires, including the use of chemicals, which are used either as fire suppressants, applied directly to a fire, or more commonly,

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as retardants applied ahead of a fire to reduce the rate of spread or intensity. These retardants are mixtures containing mainly ammonium phosphate or ammonium sulphate [1]. The chemical reactions that occur during a forest fire are complicated. However, the thermal degradation of forest fuels can be simplified by considering two consecutive steps. Firstly, pyrolysis takes place, and secondly, the combustion of the volatile products of pyrolysis occurs (flaming combustion), followed by combustion of the carbonaceous residue (glowing combustion). The thermal methods of analysis (DTA, DSC, TGA), are used for studying these processes on a laboratory scale [2–5]. Several inorganic or organic materials which usually contain P, S, B, N or halogens have been tested as fire retardants. However, these studies have mainly been carried out on cellulose, and applications to the retardation of forest fuels are limited [6–12].

In this work the effects of various chemicals, such as  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaHCO}_3$ ,  $\text{KHCO}_3$ ,  $(\text{COONa})_2$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{O} \cdot \text{CaO}$ , on the pyrolysis of cellulose and pine needles have been studied by DSC and TGA. Emphasis is given to pyrolysis which seems to be the most important step for forest fire retardation studies on an analytical scale. This step is related to the flaming combustion, which involves gas phase oxidation of volatile pyrolysis products. The effect of inorganic additives on smouldering combustion is quite different and probably more complex, since some of the additives enhance and others suppress this process. This comparative study could help the systematic understanding of the effects of the various fire retardants on the pyrolysis of cellulose. The use of cellulose as a model compound for pyrolysis of pine needles will be examined, as well as the applicability of DSC and TGA in the study of the pyrolysis of pine needles. The above studies could facilitate the selection of more effective retardants for forest fuel fires.

## 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:* Approx. 50 mg of the sample was placed in a Pt crucible and heated at a rate of  $10^\circ\text{C min}^{-1}$ , from ambient to  $500^\circ\text{C}$ . The carrier gas was  $\text{N}_2$  with a flow rate of  $50 \text{ ml min}^{-1}$ . Precured  $\alpha\text{-Al}_2\text{O}_3$  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 weighed 6–8 mg. The thermogravimetric experiments were carried out in a non-isothermal regime at a linear heating rate of  $10^\circ\text{C min}^{-1}$ , from  $100^\circ\text{C}$  to  $550^\circ\text{C}$ . The carrier gas used was  $\text{N}_2$  with a flow rate of  $60 \text{ ml min}^{-1}$ .

### 2.3. Materials

The cellulose used was a microcrystalline Avicel cellulose (a Merck reagent for column chromatography). Avicel is a trade mark for microcrystalline cellulose, a highly purified particulate form of cellulose with a degree of polymerisation (DP) of about 200. The particle size ranges from <1 to 150  $\mu\text{m}$  and the average varies with grade. The density is  $1.55 \text{ g cm}^{-3}$  [13]. The  $(\text{NH}_4)_2\text{SO}_4$  used was a p.a. grade Merck reagent;  $(\text{NH}_4)_2\text{HPO}_4$  was a BDH laboratory reagent,  $\text{NaH}_2\text{PO}_4$  a Riedel de Haen AG c.p. reagent,  $\text{NaHCO}_3$  a p.a. grade Ferak reagent,  $\text{KHCO}_3$  a Merck extra pure reagent,  $(\text{COONa})_2$  and  $\text{Ca}(\text{OH})_2$  were Carlo Erba c.p. reagents, and  $\text{Na}_2\text{O}\cdot\text{CaO}$  was a Mallinckrodt c.p. reagent. The pine needles used were collected from a forest near an urban area, heated at  $40^\circ\text{C}$  for 24 h in an oven, ground and then a fraction, between 200 and 500  $\mu\text{m}$ , was separated and used for the preparation of the samples.

### 2.4. Samples

The following types of samples were prepared: (a) pure cellulose and cellulose treated with  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaHCO}_3$ ,  $\text{KHCO}_3$ ,  $(\text{COONa})_2$ ,  $\text{Ca}(\text{OH})_2$ , and  $\text{Na}_2\text{O}\cdot\text{CaO}$ ; (b) pure pine needles and pine needles treated with  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaHCO}_3$ ,  $\text{KHCO}_3$ ,  $(\text{COONa})_2$ ,  $\text{Ca}(\text{OH})_2$ , and  $\text{Na}_2\text{O}\cdot\text{CaO}$ . The concentration of the above chemicals was 4% w/w in all cellulose treatments. The concentration of the chemicals was 4% w/w in pine needle treatments for the DSC measurements and 10% w/w in pine needle treatments for the TG measurements. The desired percent by weight of the chemical was obtained by adding a stock solution of known concentration to a preweighed sample of cellulose or pine needles. The volume of the mixture was completed with distilled water up to 10 ml. After mixing, the samples were dried in an oven at  $35^\circ\text{C}$  for 48 h. The same procedure, but without fire retardants, was followed for preparing untreated samples.

## 3. Results and discussion

Cellulose can be used as a model compound for forest fuel degradation. It is generally accepted that cellulose pyrolysis follows two competing pathways. The first is through the production of an intermediate product, levoglucosan, which further decomposes to various volatiles, and the second is a dehydration process which mainly produces char residue, water and carbon oxides [13, 14].

The action of various chemicals as fire retardants on the pyrolysis of cellulose is not quite clear. There is a question whether the fire retardants exert their influence mainly on cellulose directly, or on levoglucosan and other degradation products during secondary reactions. Among the fireproofing mechanism theories, the one concerning the direct dehydration of cellulose by Lewis acids or bases liberated from the fire retardants at the pyrolysis temperatures has the greatest merit.

In this work,  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{NaH}_2\text{PO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  are examined as agents producing Lewis acids, while  $\text{NaHCO}_3$ ,  $\text{KHCO}_3$  and  $(\text{COONa})_2$  are examined as

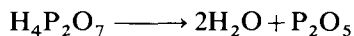
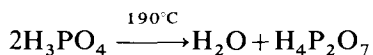
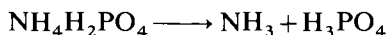
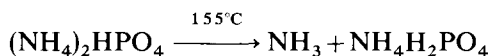
agents producing Lewis bases. In addition,  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{O}\cdot\text{CaO}$  are examined as agents that could promote the dehydration process through the absorption of the evolved  $\text{CO}_2$ .

In order to evaluate the effectiveness of a fire retardant on the pyrolysis of cellulose and pine needles, the following criteria were used: the shift of pyrolysis temperature to lower values (the evolved volatiles could dissipate before their ignition temperature), the alteration of pyrolysis profile in terms of DSC and TG curves, and the increase in char residue. It should be noted that for the estimation of the residue of the treated substance, the residue of pure retardant at the same temperature has been subtracted from the total residue.

### 3.1. Pyrolysis of cellulose

The DSC curve of pure cellulose shows a large endotherm peak at  $327^\circ\text{C}$ , which is in general agreement with the literature (see Fig. 1a). Degradation temperatures referred to in the literature depend on the cellulose grade (crystallinity, molecular weight) and purity used [15]. However, a close correlation between degradation and molecular weight seems to be somewhat tenuous because of the rapid lowering of the molecular weight at the initial stage of the pyrolysis. In addition, the significance of crystallinity is overshadowed by the fact that the crystalline forces are weakened at elevated pyrolysis temperatures [16]. This endotherm is attributed to the decomposition–depolymerisation of the glycosyl units to char and volatile tarry products containing mainly levoglucosan.

A comparison between the DSC curve of pure cellulose and that treated with 4% w/w  $(\text{NH}_4)_2\text{HPO}_4$  (see Fig. 1b) shows the same profile, but an earlier decomposition in the case of cellulose + 4% w/w  $(\text{NH}_4)_2\text{HPO}_4$  ( $284^\circ\text{C}$ ). The presence of  $(\text{NH}_4)_2\text{HPO}_4$  decreases by  $50^\circ$  the temperature at which rapid weight loss commences, and increases by 3.5 times the char residue at  $500^\circ\text{C}$  (see Fig. 2a). This leads to the conclusion that in the presence of  $(\text{NH}_4)_2\text{HPO}_4$ , flame-producing reactions are eliminated in favour of glowing combustion reactions. This may be explained with reference to the  $(\text{NH}_4)_2\text{HPO}_4$  decomposition to phosphoric acid, which takes place according to the scheme



The presence of phosphoric acid now and possibly later of phosphorous pentoxide, would cause an earlier dehydration of cellulose through reaction with hydroxyl groups of glucosan units. Ammonia also could facilitate the decomposition by reacting with intermediate carbonyl compounds to form glycosylamines or Schiff bases, which are

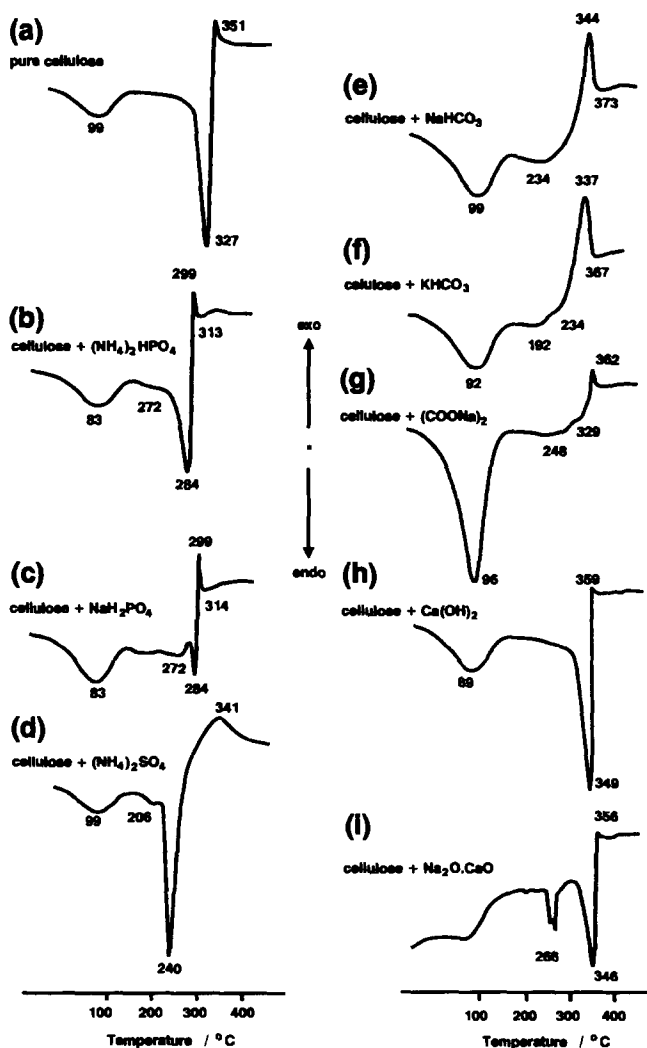


Fig. 1. DSC curves in nitrogen of (a) cellulose and cellulose treated with 4% w/w: (b) (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>; (c) NaH<sub>2</sub>PO<sub>4</sub>; (d) (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; (e) NaHCO<sub>3</sub>; (f) KHCO<sub>3</sub>; (g) (COONa)<sub>2</sub>; (h) Ca(OH)<sub>2</sub>; and (i) Na<sub>2</sub>O.CaO.

readily dehydrated by beta-eliminated process [8]. Similar results in terms of DSC curve profile, endotherm peak shift and char residue were obtained by using NaH<sub>2</sub>PO<sub>4</sub>, instead of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (see Figs. 1c and 2a). This leads to the conclusion that NH<sub>3</sub> has a minor fire retardation effect.

Ammonium sulphate gives comparable results to (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>: the same DSC curve pattern and a temperature shift of the endotherm peak from 327 to 240 °C (see Fig. 1d). In addition, the temperature at which rapid weight loss commences decreased

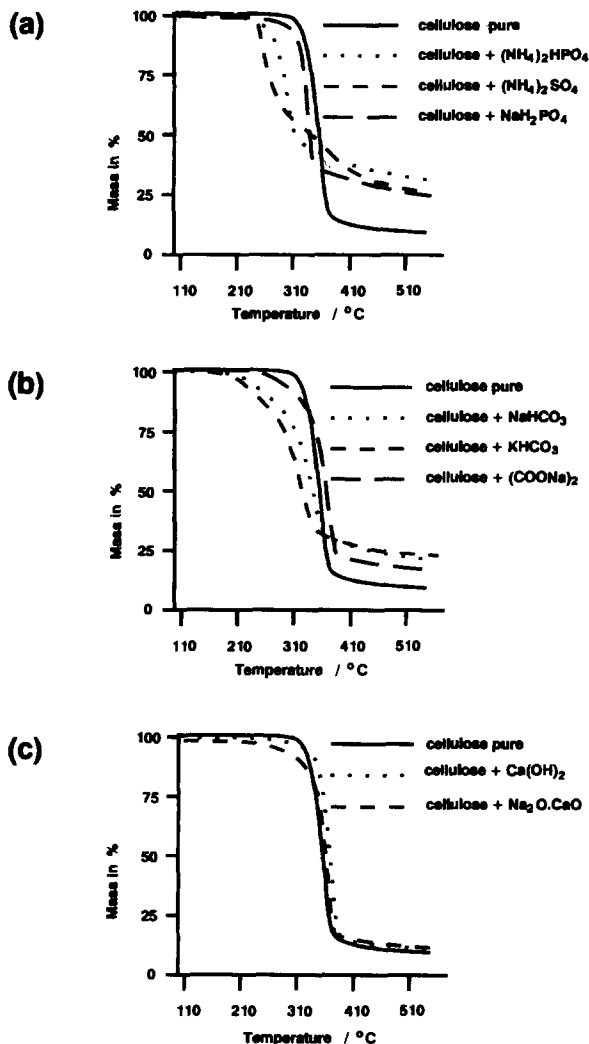
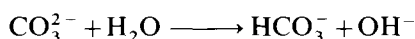
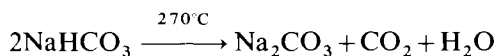


Fig. 2. TG curves of (a) cellulose and cellulose treated with 4% w/w: (b) (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>; (c) NaH<sub>2</sub>PO<sub>4</sub>; (d) (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; (e) NaHCO<sub>3</sub>; (f) KHCO<sub>3</sub>; (g) (COONa)<sub>2</sub>; (h) Ca(OH)<sub>2</sub>; and (i) Na<sub>2</sub>O.CaO. Heating rate 10°C min<sup>-1</sup> under N<sub>2</sub> atmosphere.

by 90°C, while the char residue was 3.0 times more than that of pure cellulose at 500°C (see Fig. 2a). This was expected because (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> acts through a similar mechanism to (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>.

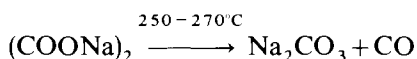
The effect of the bicarbonate salts (NaHCO<sub>3</sub>, KHCO<sub>3</sub>) on the pyrolysis of cellulose was found to be significant. The profile of the DSC curve was notably changed, which indicates that a series of new reactions takes place (see Figs. 1e, 1f). In addition the temperature at which rapid weight loss commences decreased by 30°, while the char

residue was 2.5 times more than that of pure cellulose in the temperature range around 500°C (see Fig. 2b). A mechanism which explains the above behaviour is that the bicarbonate salts are decomposed and then hydrolysed by water formed during pyrolysis, according to the following chemical equations



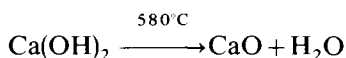
The hydroxyl ions, in accordance with the Lewis electron theory, then cause dehydration of the cellulose molecule through the formation of carbanions [2].

Behaviour similar to that seen for bicarbonate salts was observed for  $(\text{COONa})_2$ , see Fig. 1g, which decomposes according to the scheme



However, the temperature at which rapid weight loss commences decreased by 20°, while the char residue was only 1.5 times more than that of pure cellulose at 500°C.

The addition of  $\text{Ca}(\text{OH})_2$  has a minor effect on the pyrolysis of cellulose in terms of DSC, TG curve profiles, endotherm peak shift and char residue (see Figs. 1h, 2c). The decomposition of  $\text{Ca}(\text{OH})_2$  takes place according to the equation



Similar results were obtained with soda lime (see Figs. 1i, 2c). However, the DSC profile changed in the region of 100°C to 300°C and an endotherm peak at 266°C is attributed to the decomposition of soda lime which starts at 127°C.

Finally, it should be noted that the exotherm peaks appearing in the DSC curves of cellulose before and after treatment with the retardants are attributed to the recombination of smaller fragmentary molecules to form char.

### 3.2. Pyrolysis of pine needles

The DSC curve of pyrolysis of pure pine needles treated with  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaHCO}_3$ ,  $\text{KHCO}_3$ ,  $(\text{COONa})_2$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{O} \cdot \text{CaO}$  are presented in Fig. 3. The endotherms appearing in the region of 75°C to 90°C may be attributed to the softening and/or melting of the waxy constituents and to moisture, while the exotherms in the region of 315°C to 342°C could be correlated to lignin pyrolysis [6]. A comparison between the DSC curves of pine needles before and after treatment with the retardants has not shown any noticeable changes in terms of peak shift and profile pattern, the exception being the exotherm shift to lower temperatures in the cases of  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{NaHCO}_3$ ,  $\text{KHCO}_3$  and  $(\text{COONa})_2$ . Minor differences are the appearance of peaks correlated with the degradation of fire retardants.

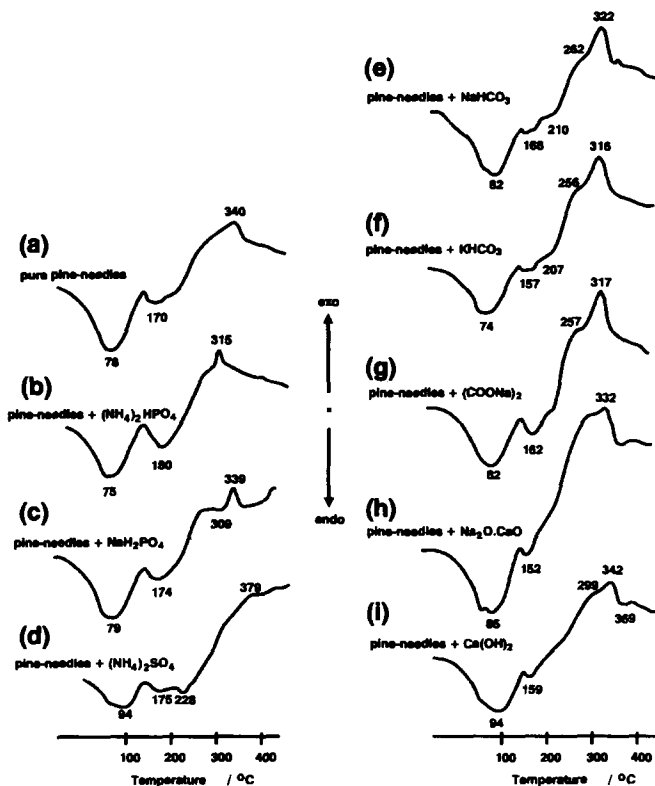


Fig. 3. DSC curves in nitrogen of (a) untreated pine needles and pine needles treated with 4% w/w: (b)  $(\text{NH}_4)_2\text{HPO}_4$ ; (c)  $\text{NaH}_2\text{PO}_4$ ; (d)  $(\text{NH}_4)_2\text{SO}_4$ ; (e)  $\text{NaHCO}_3$ ; (f)  $\text{KHCO}_3$ ; (g)  $(\text{COONa})_2$ ; (h)  $\text{Ca}(\text{OH})_2$ ; and (i)  $\text{Na}_2\text{O}\cdot\text{CaO}$ . Heating rate  $10^\circ\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere.

In contrast, the solid pyrolysis residue increased 21% and 32% at  $500^\circ\text{C}$ , when the pine needles were treated with  $(\text{NH}_4)_2\text{HPO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ , respectively. However, minor changes in the solid residue, i.e. less than 8%, were noticed when  $(\text{COONa})_2$ ,  $\text{NaHCO}_3$ ,  $\text{KHCO}_3$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{O}\cdot\text{CaO}$  were applied on pine needles (see Fig. 4).

#### 4. Conclusions

The pyrolysis of cellulose has been studied extensively by various analytical methods. In this work, it was shown that DSC and TGA can be used for a systematic study of the effects of various salt and oxide-hydroxide additives on the pyrolysis of cellulose. The criteria used, pyrolysis temperature shift, DSC and TG curve profile and the solid pyrolysis residue, appeared to be simple and effective.

In addition, it appeared that cellulose is not an ideal model compound for the study of the pyrolysis of pine needles under the experimental conditions and thermal methods



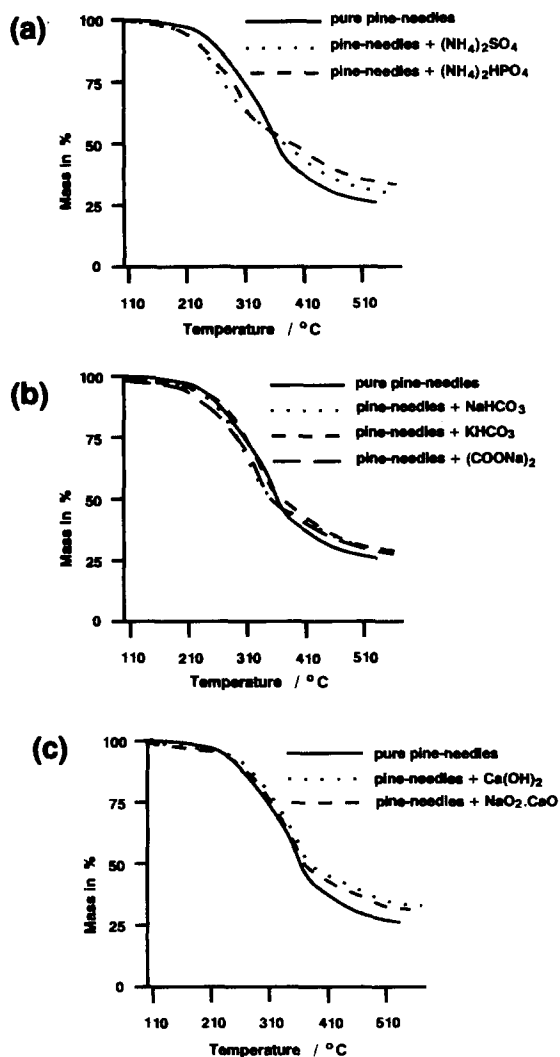


Fig. 4. TG curves of (a) untreated pine needles and pine needles treated with 4% w/w: (b)  $(\text{NH}_4)_2\text{HPO}_4$ ; (c)  $\text{NaH}_2\text{PO}_4$ ; (d)  $(\text{NH}_4)_2\text{SO}_4$ ; (e)  $\text{NaHCO}_3$ ; (f)  $\text{KHCO}_3$ ; (g)  $(\text{COONa})_2$ ; (h)  $\text{Ca}(\text{OH})_2$ ; and (i)  $\text{Na}_2\text{O}\cdot\text{CaO}$ . Heating rate  $10^\circ\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere.

used in this work. However, the cellulose used (microcrystalline form) could still be a model compound for other forest fuels or with different methods; this remains to be investigated.

It was also shown that DSC and TG curves of pine needles treated with various additives as fire retardants are quite complicated and can only provide indications of the effectiveness of the additives used.

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