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Low-temperature pyrolysis of CCA-treated wood: thermogravimetric analysis

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Abstract

A thermo-analytical study of untreated and chromated copper arsenate (CCA) treated wood samples is performed in order to obtain a better understanding of the low-temperature pyrolysis of CCA-treated wood waste in an inert atmosphere. The type of wood used in this study is *Pinus sylvestris* sapwood. The influence of the presence of CCA and the heating rate on the pyrolytic behaviour of wood samples is studied, as well as the release of volatile compounds and metals (Cr, Cu, As) during the pyrolysis process. This paper shows that CCA has a significant influence on the thermal behaviour of wood samples, which is more pronounced the higher the CCA concentration of the sample is. The temperature at the onset of pyrolysis, as well as the temperature where the maximum rate of decomposition occurs, are lowered by the CCA treatment. The final char yield (including the metals) is higher and the rate of weight loss is much more peaked for CCA-treated wood. It could be postulated that the CCA compounds act as promotors of the pyrolysis reactions favouring the formation of char. For higher heating rates, there is a shift of the DTG peak to higher temperatures for both untreated and CCA-treated wood samples. Within the accuracy of the evolved gas analysis (EGA) method applied, it is observed that the presence of CCA does not significantly influence the type and relative amount of measured volatiles. The volatilisation of metal compounds is shown to be strongly dependent on temperature and residence time of the wood sample at a given temperature. A critical point (10 min at 400°C) exists, below which the release of Cr and Cu is negligible and the release of As is below 10%. Above this critical point (longer times at 400°C), there is a dramatic increase in metal release for all three metals. The CCA concentration itself also has an influence in the sense that higher

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concentrations in the original sample give higher relative concentrations of metals in the resulting pyrolysis residue.

Keywords: Pyrolysis; Treated wood waste; CCA; Heavy metals; Biomass; TG analysis; TGA-MS; Metal analysis

1. Introduction

Waterborne salts have been used to preserve wood from insects, fungi and water damage for many years. One of the more common formulations contains copper, chromium, and arsenic salts and is known as chromated copper arsenate or CCA. For example, in 1990 the North American wood treating industry produced 437.7 million cubic feet of CCA-preserved wood. After impregnation of the wood with a CCA solution the metal compounds will be fixed to the cell walls of the wood matrix. Substantial amounts of CCA remain in the wood for many years, and the disposal of scrap wood is a growing problem in Europe. In Germany, for example, the total amount of wood waste is around 6–8 million tons per year. In France about 26 million poles treated with CCA (railway, electricity and telephone) are in service. Every year 500 000 poles (50 000 tons) are taken out of service, which means that the waste disposal problem will last for at least 50 years without putting new poles in service.

Telephone poles, railway sleepers, timber from landscape and cooling towers, wooden silos, hop-poles, cable drums and wooden play-ground equipment generate wood waste for which environmentally benign disposal technologies need to be developed. The number of waste disposal sites is decreasing and redundant poles, piling and lumber, which constitute a large volume of material, may not be accepted at the limited number of sites in the future. Numerous studies and experiments have been carried out on burning contaminated wood by various organisations and universities, in particular in the USA and Canada, but also in Europe, in Germany, the Netherlands, Denmark, Switzerland and the UK. Their conclusions reflect three common points. Burning this wood waste emits highly toxic smoke and fumes in the environment. The municipal waste incinerators, and most of the industrial waste incinerators, are not equipped to retain this type of toxic elements, especially at the concentrations involved. Each attempt to mix the polluted wood with other waste streams has caused the destabilisation of the combustion conditions in the incinerators resulting in the appearance of highly dangerous and uncontrollable chemical compounds. Conventional pyrolysis systems (fixed bed, batch or grate; fluidized bed; rotary kiln, etc.) operate at too high a temperature to prevent the release of metal vapours, and often require that the wood is chopped before processing. Percentages of arsenic (As(III)) volatilised have been reported [1–3] to range between 8 and 95%. Amounts of copper andchromium volatilised are not well documented, but are found to be much lower than for arsenic. Public concern has been raised over the possible formation of toxic smoke when CCA wood is burned in wood stoves, fireplaces, or boilers.

Pyrolysing the CCA-treated wood at low temperature is a promising solution to the growing disposal problem since low temperatures and no oxidising agents are used. In turn, this leads to a smaller loss of metals than in combustion or even a total recuperation of the metals. The recent consciousness of the need for abatement of air pollution leads to further interest and investigation of pyrolysis as a major process for the disposal of enormous quantities of cellulosic wastes and residual materials. A study has been set up to design a low-temperature pyrolysis facility for the CCA-treated wood waste such that at least 90% of the metals are contained in a concentrated solid product stream, and the pyrolysis gases and liquid are used to their maximum potential with respect to energy recuperation [4].

There has been very little study on the pyrolysis of CCA-treated wood samples. The thermal degradation of cellulose has attracted widespread interest due to its importance in the fields of fire research, fabric flammability, nuclear weapons effects, waste incineration and aerospace technology. Although the addition of chemicals to wood to modify its burning behaviour (fire retardants. char producers, etc.) dates back many centuries (the Romans attempted to flame proof their houses and war vessels by dipping the wood in a bath of vinegar and clay [5]), there has been comparatively little study of the action of inorganic additives on the pyrolysis product distribution [6]. Fire retardants are known to catalyse the formation of non-flammable char at the expense of flammable volatiles production. An acid catalyst promotes dehydration and favours the formation of levoglucosenone, furan derivatives, dextrins and tars. Alkaline catalysts enhance the fission and disproportionation reactions as evidenced in increased yields of glyoxal, acetaldehyde and other low-molecular weight carbonyl compounds, and char. The influence of catalysts on the pyrolysis process confirms the ionic nature of pyrolytic mechanisms [6]. Richards and coworkers [7–9] established the extraordinary influence of salts and metal ions on the productivity of the pyrolysis pathways. They showed that K, Li and Ca ions strongly promoted the formation of char from wood at the expense of tar (and levoglucosan) formation. Other metal ions (particularly Fe and Cu) enhanced the yield of levoglucosan and char from wood and newsprint [9]. A coordinated approach to the chemical utilization of lignocellulosic biomass was foreshadowed, whereby ions such as Fe and Cu are incorporated into the biomass to catalyze pyrolytic production of levoglucosan and/or levoglucosenone, while at the same time generating an increased charcoal yield. Simultaneously, a char is produced which is very active towards gasification due to the presence of an efficient gasification catalyst. Other researchers [10–15] investigated the influence of inorganic salts ($MgCl_2$, NaCl, $FeSO_4$, $ZnCl_2$, Na_2SO_4, CsCl and other alkali metal carbonates, phosphates, borates and chlorides) on pyrolysis products. A decreased amount of low molecular weight organic products and an increased char yield were reported, as well as an earlier onset of pyrolysis.

The mechanism by which trace quantities of salts and metal ions exercise a dramatic influence on the course of pyrolysis is not exactly known [16]. There seemsto be no agreement whether the effect of salts during pyrolysis of cellulose is catalytic in nature or otherwise. It has been proposed that the added chemicals may undergo definite chemical reactions, along stoichiometric lines, with equivalent quantities of the carbohydrate, and that the type of reaction thus initiated affects

the course of char forming reactions [14]. On the other hand, the action of inorganic additives is said to be catalytic in nature, for example potassium carbonate, iron(III) oxide and zinc(II) chromite are reported to have catalytic effects on solid-phase pyrolysis rates [15]. Richards and co-workers [9] postulated a stepwise mechanism for cellulose pyrolysis which also evidenced the extraordinary influence of inorganic compounds on the yield of levoglucosan. Since pyrolysis reactions are a complex set of heterogeneous reactions occurring at relatively high temperature, more than one type of chemical interaction between the inorganic salt and the organic molecules are likely to take place. Moreover, the very chemical and physical nature of the inorganic salt might determine its role during pyrolysis [14].

In this paper, a thermo-analytical study of CCA-treated wood samples is performed. The objective of this study is to determine the pyrolytic behaviour of *Pinus sylvestris* and CCA-treated *Pinus sylvestris* at low temperatures in an inert atmosphere. The results of studying the effect of the presence of CCA (copper, chromium and arsenic) in wood waste and heating rate on the pyrolysis characteristics are reported. The release of volatile compounds and metals (copper, chromium and arsenic) during the pyrolysis of the wood samples is also studied.

2. Methods and materials

2.1. Samples and sample preparation

The type of wood used in this study is untreated *Pinus sylvestris* sapwood and *Pinus sylvestris* sapwood which is impregnated with type C CCA oxide: 32.6% As_2O_5, 49.2% CrO_3, 18.2% CuO. The crushed wood chips were between 10 and 50 mm long, between 2 and 10 mm wide and between 0.5 and 3 mm thick. These chips were impregnated with a 3.30% solution of type C CCA oxide (batch CCA1) or with a 5.01% solution of type C CCA oxide (batch CCA2). A full-cell treatment (according to the procedure 'Breant-Bethell') was applied to the wood chips, which had a moisture content of less than 22%, in a lab-scale autoclave in five stages. After the wood was placed in the cylinder (volume of 10 l) and its door was hermetically sealed, a vacuum of -1 kPa was applied for 15 min (step 1). Subsequently and without introducing air, the cylinder was filled with preservative by opening the valve which is connected to the tank containing the diluted CCA solution (3.30 or 5.01%) (step 2). More solution was pumped until the reaction vessel was filled completely, after which the valve was closed and the content of the cylinder was pressurized by compressed air: 800 kPa for 40 min (step 3). Finally the pressure was released, while at the same time preservative was removed from the cylinder (step 4), and a low vacuum (-2.5 kPa for 5 min) was applied to prevent bleeding of preservative from the surface of the treated wood (step 5). The duration of this total cycle was approximately 70 min. Fixation of the metals in the wood started. The treated wood samples were placed in a conventional oven with air-

circulation at a preset temperature of 105°C for 60 min, after which the fixation was allowed to continue for about 3 months, while the samples were left to air dry. The exact retention of the CCA-treated samples is not known but is estimated as:

$$\text{CCAretention (kg/m}^3) = \frac{\Delta m_{\text{CCA solution}}}{m_{\text{untreated wood}}} \cdot \rho_{\text{wood}}$$

resulting in 753 kg/m^3 for the CCA1 samples and 770 kg/m^3 for the CCA2 samples. Hereby, a wood density (ρ_{wood}) of 400 kg/m^3 is assumed, $\Delta m_{\text{CCA solution}}$ is the mass of the CCA solution used during impregnation and $m_{\text{untreated wood}}$ is the original mass of the untreated wood. The metal content of the samples is also determined using ICP-MS (procedure is described elsewhere [17]), resulting in the average concentrations given in Table 1. These concentrations are calculated as the mean value of three independent measurements. The corresponding spread on the average values is also given. As can be seen in Table 1 the spread is low enough to consider the treated wood samples as being homogeneous. The CCA2 samples have higher metal concentrations than the CCA1 samples. As described above, both samples are impregnated using the same procedure but for the CCA2 samples a more concentrated CCA solution was used, resulting in higher metal retentions.

The untreated and CCA-treated wood samples are cut into smaller pieces to be used in the thermogravimetric analysis. In this study the samples used throughout are more or less cylindrically-shaped and have a diameter of less than 2 mm. Consequently heat transfer effects are minimised.

2.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) is carried out using a DuPont Instruments 951 Thermogravimetric Analyser, supported by a PC and software for control and data handling. To analyse the gas stream, resulting from the wood decomposition, the TGA apparatus is coupled to a VG gas analysis system (Fisons Instruments—Thermolab) which is able to measure components up to mass 300 a.m.u. In this study the sample, approximately 20 mg in weight, is introduced into a quartz sample pan and heated to a preset temperature following a preset temperature profile using nitrogen (50 ml/min) as purge gas. Only when gas analysis is carried out, helium is used as purge gas. In order to ensure inert working conditions, the TGA apparatus has been modified as described elsewhere [18]. The apparatus

Table 1
Metal (Cr, Cu and As) concentrations (mg metal/g of dried wood) of the CCA1 and CCA2 samples

Sample	Cr (mg/g)	Cu (mg/g)	As (mg/g)
CCA1	14.2 ± 3.4	5.93 ± 1.6	11.5 ± 2.0
CCA2	19.1 ± 1.4	7.10 ± 1.2	16.3 ± 1.3

provides for the continuous measurement of sample weight as a function of temperature and provision is made for an electronic differentiation of the weight signal to give the rate of weight loss.

Some experiments are carried out with a condenser placed between the outlet of the TGA apparatus and the inlet of the gas analysis system (mass spectrometer). The type of condenser used is a cold-finger condenser placed in a Dewar flask filled with liquid nitrogen. The aim was to condense the heavier tar compounds and determine the tar yield through measured differences in mass of the condenser and connecting tubes before and after the experiment. Unfortunately the differences in mass were to small (starting from a 20-mg sample) to obtain reliable results. However, a comparison of gas composition between experiments with and without condenser can be made. From this comparison it can be seen which compounds can be captured in the condenser and which compounds are more difficult to capture simply by condensation. This observation is important in the study of the development of pyrolysis reactors aiming at recovering some chemical compounds.

2.3. Experimental procedure

2.3.1. Temperature profiles

Thermogravimetric analyses of untreated and CCA-treated (CCA1 and CCA2) wood samples were carried out using heating rates between 10 and 50°C/min. When the sample is heated from room temperature (25°C) to 500°C using a heating rate of 10°C/min, the experiments are referred to as slow heating. A repeatability check was carried out for these conditions. When a stepwise temperature profile, using higher heating rates is applied, the experiments are referred to as fast heating. In these experiments the temperature is raised to 100°C using a heating rate of 20°C/min and maintained for 20 min to ensure that no moisture is left in the sample. The sample was then heated to 380°C at a heating rate of 50°C/min and maintained for 30 min after which the experiment was terminated. Slow and fast heating conditions were compared for the different samples.

To study the release of metals when a CCA-treated wood sample is heated in an inert atmosphere, TGA is carried out following a preset temperature evolution. The treated wood sample was heated to 100°C at a rate of 20°C/min. From previous experiments it was seen that the drying time of the samples was less than 10 min (no changes in weight loss after 10 min at 100°C). The sample was maintained at 100°C for 10 min after which the temperature was slowly (10°C/min) raised to 400°C and further maintained at 400°C. This experiment was repeated five times, but each experiment was terminated after different residence times, represented in Table 2.

The different temperature profiles (slow heating, fast heating and preset temperature profile) applied in the TGA experiments are represented in Fig. 1. These are the temperatures, measured by a thermocouple that was placed very close to the sample. As can be seen in Fig. 1 an overshoot of 30°C (410°C was recorded instead of the preset temperature of 380°C) takes place when the sample was heated from 100 to 380°C at 50°C/min (fast-heating experiment).

Table 2
Different residence times considered in the experiments to study the metal release

Point	Termination point	Corresponding duration (min)
1	300°C	32.8
2	400°C	42.9
3	After 5 min at 400°C	47.9
4	After 10 min at 400°C	52.9
5	After 20 min at 400°C	62.9

2.3.2. Gas analysis

Some experiments were carried out with a coupling between the TGA apparatus and the mass spectrometer (MS) for gas analysis. Compounds with masses up to 300 a.m.u. can be measured with the MS. The only volatile metal (Cr, Cu, As) compounds with mass less than 300 are As_2O_3 with mass 198 and CrO_2Cl_2 with mass 155. None of these are detected by the MS since they condense in the transfer line between the TGA apparatus and the MS, which is held at 300°C, due to their high sublimation point. With this equipment it is thus impossible to measure the metal release directly on-line; it has to be calculated from the amount of metals that is retained in the residue, after the experiment. Other (non-metal) volatile compounds, however, can be measured. The chemical composition of pyrolysis gases and liquids resulting from different pyrolysis systems, has been reported by several other researchers [6,19–24]. More than 400 compounds have been identified. In this study, the evolution of some expected volatile compounds is followed in time and the influence of presence of CCA and presence of condenser between the outlet of the TGA and the inlet of MS is examined. The volatile compounds, whose evolution is followed, are chosen such that compounds

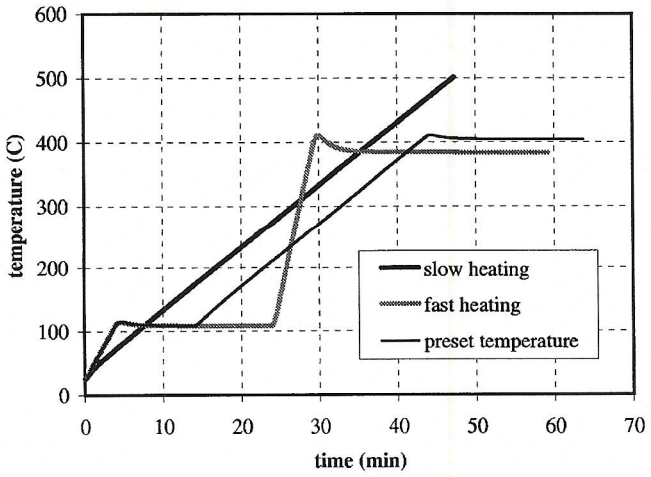

Fig. 1. Temperature profiles used in the TGA experiments.

from different chemical groups are considered. The analysis is limited to lower-weight compounds whichwill probably not condense in the transfer line between TG and MS. The measured compounds are given in Table 3. Ethane and propene are identified by Evans and Milne [23] as prominent intermediate ion peaks in the secondary cracking regime of wood, while benzene and toluene are identified as prominent growth ion peaks in the tertiary cracking regime of wood. All other compounds mentioned in Table 3 are said to be major ions in primary oils and gases.

2.3.3. Metal analysis

The metal (Cr, Cu and As) content of the five pyrolysis residues, resulting from the experiments following the preset temperature profile with CCA1-treated wood samples, is determined. Furthermore, a comparison is made between the metal contents of the residues resulting from CCA1 and CCA2 samples after applying the slow-heating process.

The metal contents, expressed as percentage of the metal found in the residue, are calculated as:

$$\text{metal content (wt\%)} = \frac{[\text{metal}]_{\text{residue}} \cdot m_{\text{residue}}}{[\text{metal}]_{\text{dried wood}} \cdot m_{\text{dried wood}}}$$

$[\text{metal}]_{\text{residue}}$ and $[\text{metal}]_{\text{dried wood}}$ are the metal concentrations (in wt%) in residue and dried wood, respectively, and m_{residue} and $m_{\text{dried wood}}$ are the masses of residue and dried wood, respectively. The concentrations were determined using a dissolution procedure (BSI for dried CCA-treated wood and Reflux for pyrolysis residue) followed by ICP-MS analysis [17,25]. The masses of dried wood and residue were measured at the beginning and the end of the TG experiments with a very precise balance.

Table 3
Volatile compounds expected to be released during wood pyrolysis

Chemical group	Compound	m/z	Formula
	Water	18	H_2O
Linear hydrocarbons	Ethane	30	C_2H_6
	Propene	42	C_3H_6
Aldehydes	Acetaldehyde	44	C_2H_4O
Ketones	Acetone	58	C_3H_6O
Organic acids	Acetic acid	60	$C_2H_4O_2$
Furans	Furan	68	C_4H_4O
	2-Methylfuran	82	C_5H_6O
	Furfural	96	$C_5H_4O_2$
Aromatics	Benzene	78	C_6H_6
	Toluene	92	C_7H_8

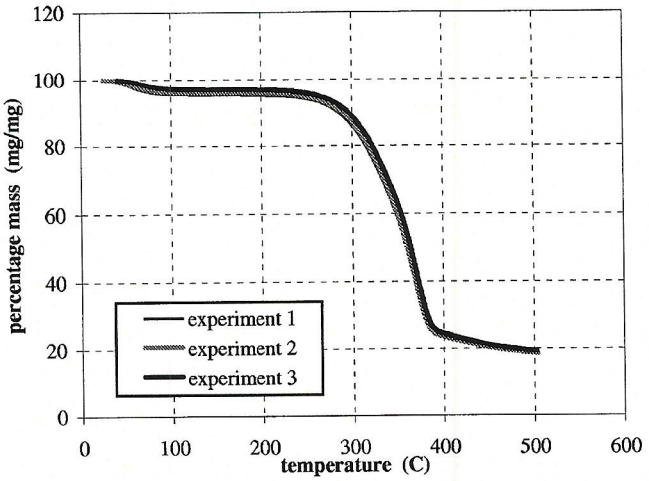

Fig. 2. Weight loss versus temperature for three identical runs: repeatability check.

3. Results and discussion

3.1. Repeatability check

In order to check the repeatability of the experiments, one experiment is repeated three times and the corresponding temperature and weight loss evolutions are compared. The temperature profile corresponds to the profile used in the slow heating experiments (heated at 10°C/min to 500°C) and the samples used for the repeatability check are the untreated wood samples (20 mg). The weight loss curves for the three experiments, represented as percent of original weight versus temperature, are shown in Fig. 2. The results are very reproducible, as can be seen in this figure. Based on this finding, it was decided to carry out one experiment for each condition.

3.2. Weight loss

In the following discussion, the integral as well as the differential TG curves will be presented since both curves contain information which is relevant for the understanding of the thermal behaviour. In the case of non-isothermal TGA, the mass and derivative of mass vs temperature curves are presented, while the mass and derivative of mass vs time curves are considered in the case of isothermal or stepwise TGA.

A comparison of the thermal behaviour of the different samples (untreated, CCA1-treated and CCA2-treated wood) in the slow-heating regime is presented in Fig. 3. At temperatures below 100°C drying takes place with a corresponding peak in the DTG curve, representing the release of water vapour. The peaks observed at higher temperatures can be attributed to the pyrolysis process.

The temperature threshold for which the pyrolysis of untreated wood starts is around 200°C at a heating rate of 10°C/min. The temperature where the maximum rate of decomposition occurs (T_{peak}) is around 365°C and the final char yield (at 500°C) is around 19%. For the untreated wood, there are two areas of weight loss producing a single DTG peak with a shoulder located at the lower temperature region. There is a flat tailing section at higher temperature corresponding to the slow charring process of the solid residue. It has been debated in the literature that the two different regions of weight loss observed for wood pyrolysis may be represented as a combination of the individual decomposition of hemicellulose and cellulose, i.e. the lower temperature shoulder representing the decomposition of hemicellulose and the higher temperature peak representing the decomposition of cellulose [26]. Lignin decomposes slowly over a very broad range of temperatures, providing a gently sloping baseline to the DTG curve [16]. The main area of lignin

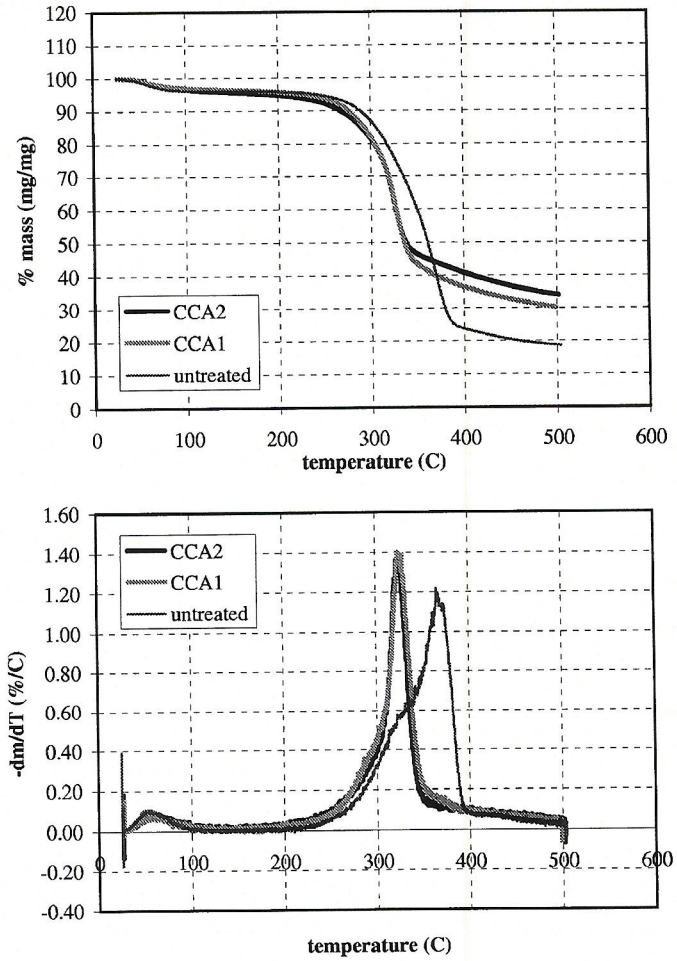

Fig. 3. Thermal behaviour of untreated, CCA1- and CCA2-treated wood (slow-heating).

weight loss occurs at higher temperatures which means that lignin is mainly responsible for the flat tailing section which can be observed at higher temperatures. Softwood, like pine wood, contains less hemicellulose than hardwood, causing the hemicellulose-shoulder to be less visible. The cause of merged DTG peaks is mineral matter naturally present in the biomass, which catalyzes the pyrolytic decomposition in an unpredictable variety of ways [16]. An attempt has been made to single out or separate the partially overlapping peaks of hemicellulose and cellulose by using high-resolution TGA (TGA 2950 HI-resolution module), but with no result. In high-resolution TGA, the temperature is raised slowly and from the moment weight loss is observed the temperature is maintained constant as long as compounds are released. Grønli [26] reported that the separation of the hemicellulose shoulder from the cellulose peak was not possible for pine by applying a washing procedure which aims at minimizing the catalytic effects of minerals.

As can be seen in Fig. 3, the CCA treatment has a significant influence on the thermal behaviour of wood samples. The temperature threshold for which the pyrolysis of CCA1- and CCA2-treated wood starts is around 175°C at a heating rate of 10°C/min which is lower than the value obtained for untreated wood. The temperature at the onset of pyrolysis is thus lowered by the CCA treatment. The temperature where the maximum rate of decomposition occurs (T_{peak}) is around 325°C for the CCA1 sample as well as for the CCA2 sample, which is again lower than the value for the untreated wood. The final char yield (at 500°C) is around 30% for the CCA1 sample and 34% for the CCA2 sample. Since these values are not corrected for the metal content, values higher than those for the untreated wood were expected, as well as higher values for the CCA2 sample compared to the CCA1 sample. All the changes in thermal behaviour of wood due to impregnation with a CCA oxide solution, mentioned above, are more pronounced for the CCA2 sample than for the CCA1 sample due to the higher CCA retention of the CCA2 sample. In particular, a higher char yield as well as a narrower DTG peak are clearly observed for the CCA2 sample.

The lower temperature side of the DTG peak is still less steep than the higher temperature side, but the shoulder located at the low temperature region of the DTG peak for untreated wood has disappeared when CCA-treated wood is used. The decomposition of hemicellulose and cellulose occurs in a narrower range of temperatures and the ranges for both overlap, resulting in a more peaked DTG curve due to the presence of CCA. The flat tailing section at higher temperatures, corresponding to lignin decomposition is still present. The decomposition of CCA-treated wood seems to occur in two steps, a fast decrease in weight loss followed by a slow decrease in weight loss.

The experimental TGA curves of this investigation correspond qualitatively with the TGA curves obtained in other studies with fire retardants and inorganic salts. The resulting change in the nature of the pyrolysis reactions was reported there to be apparent in the higher rate of volatilisation at the lower temperatures and the increased yield of the residual char [5]. The two-stage decomposition has also been observed by Zaror [14] who studied the low-temperature pyrolysis of wood sam-

ples treated with sodium and potassium carbonates and chlorides. He defined a first stage characterized by a rapid evolution of volatiles, which is controlled by chemical reactions. Since the apparent rate was extremely sensitive to the amount of salt present in the sample, catalytic action of salt upon the pyrolysis reactions was postulated. The second stage was characterized by a much slower rate of weight loss for which the mass transfer from the interior of the sample to the surroundings is likely to be the rate-controlling step. The mass transfer process becomes more important with an increase in salt content. Richards and Zheng [9], who reported results with ion exchanged and sorbed salts wood samples, also observed effects similar to the observations in this study. In their study, the most dramatic effect was shown by ferrous wood, which exhibited the lowest breakthrough temperature and DTG maximum of the samples examined. Furthermore, the highest char yield (27% at 390°C) was produced. This char was very susceptible to further slow pyrolysis at higher temperatures, the yield falling to 4% at 700°C. All of the transition metal wood samples showed similar effects to a smaller extent. Richards and Zheng attributed the very low DTG maximum with ferrous sulfate to acid-catalyzed pyrolysis associated with the sulfate ion.

A comparison is made between the slow-heating regime and the fast-heating regime for the untreated and CCA1 samples. Since the fast-heating regime (stepwise heating) contains isothermal parts, the TGA results are normally presented as percentage mass or derivative of mass vs time instead of temperature curve. The derivative of the percentage mass is then calculated with respect to time. Because it is difficult to compare the results of two TGA experiments with different temperature–time histories by comparing the time-curves, temperature–DTG curves are presented for the non-isothermal parts (120–380°C) in the fast-heating regime when comparing slow and fast heating experiments. A comparison between untreated and CCA1 samples for the fast-heating regime is made in Fig. 4.

The temperature threshold for which the pyrolysis starts is around 225°C for the CCA1 sample and 250°C for the untreated sample when stepwise heating is applied. The temperature where the maximum rate of decomposition occurs (T_{peak}) is around 353°C (reached after 28.5 min) for the CCA1 sample and around 399°C (reached after 29.4 min) for the untreated sample. The final char yield (at 383°C, after 60 min) is around 20.3% for the untreated sample and 30.9% for the CCA1 sample. From the values given above and from Fig. 4 some conclusions drawn for the slow-heating regime can also be drawn for the fast-heating regime. The temperature at the onset of pyrolysis is lowered by the CCA treatment in the fast-heating regime too. The temperature where the maximum rate of decomposition occurs (T_{peak}) is again lower for the CCA-treated sample and the final char yield is higher for the CCA-treated sample. CCA can thus be seen as a promotor in the pyrolysis reactions of wood, favouring the formation of char for both slow- and fast-heating regimes.

A comparison between the slow-heating and fast-heating regime is given in Fig. 5 for the untreated sample and in Fig. 6 for the CCA1 sample. The shoulder on

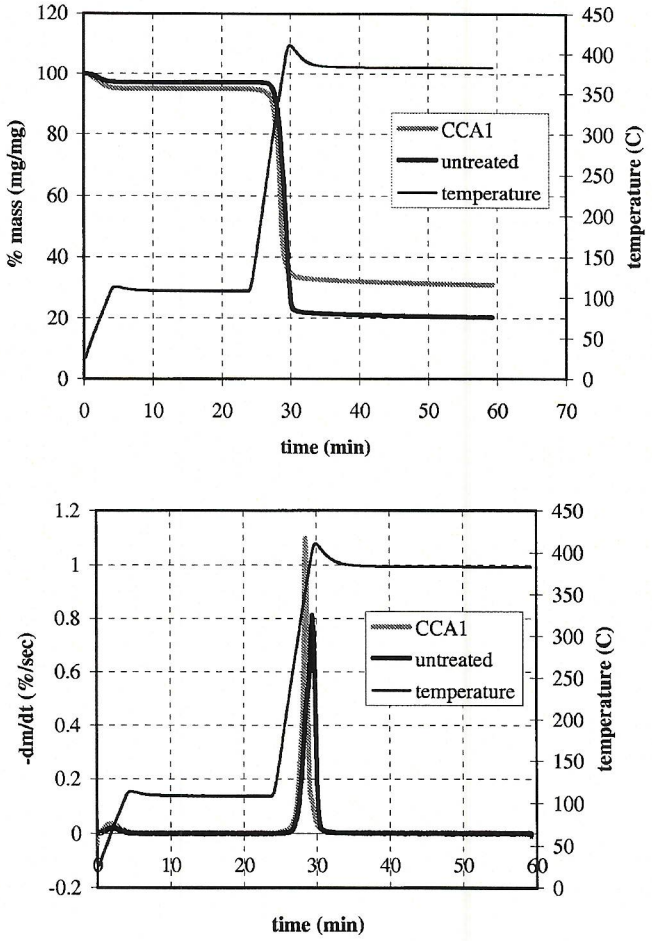

Fig. 4. Thermal behaviour of untreated and CCA1-treated wood (fast-heating).

the low-temperature side of the DTG peak from the untreated wood, observed in the slow-heating regime, is also visible in the fast-heating regime. For the untreated sample as well as for the CCA1 sample, the DTG peak is shifted to higher temperatures when fast heating is applied. The temperature used in the TGA analysis is the temperature measured by a thermocouple that is placed very close to the sample. The particle temperature lags the reactor temperature if heating rate is increased, because external heat transfer resistances become more important when higher heating rates are applied. As a result, the decomposition process of cellulose and hemicellulose starts at higher (measured) temperatures. As soon as the decomposition reactions start, some of the added heat is used for reaction (endothermic reaction), representing a supplemental heat transfer resistance. The final charcoal yields cannot be compared in a valid way since higher temperatures are preset in the slow-heating regime, resulting in lower charcoal yields after the same duration.

3.3. Gas analysis

MS is used to follow the release of volatile compounds during the thermal degradation of the different samples. The volatile compounds, measured in this study are given in Table 3 together with their m/z ratio, formula and chemical group. The evolution in time of the components water, ethane, propene, acetaldehyde, acetone, acetic acid, furan, benzene, 2-methylfuran, toluene and furfural during the slow-heating experiment is presented in Fig. 7 for the untreated sample and the CCA1 sample. The evolution obtained for the CCA2 sample is comparable to that of the CCA1 sample and is not shown here.

The ordinate scale is logarithmic and represents the intensity measured by the MS. The aim of this evolved gas analysis (EGA) is only to study the evolution of some volatile compounds qualitatively without giving absolute gas concentrations. The drying and pyrolysis stage can be clearly identified as respectively the stage of

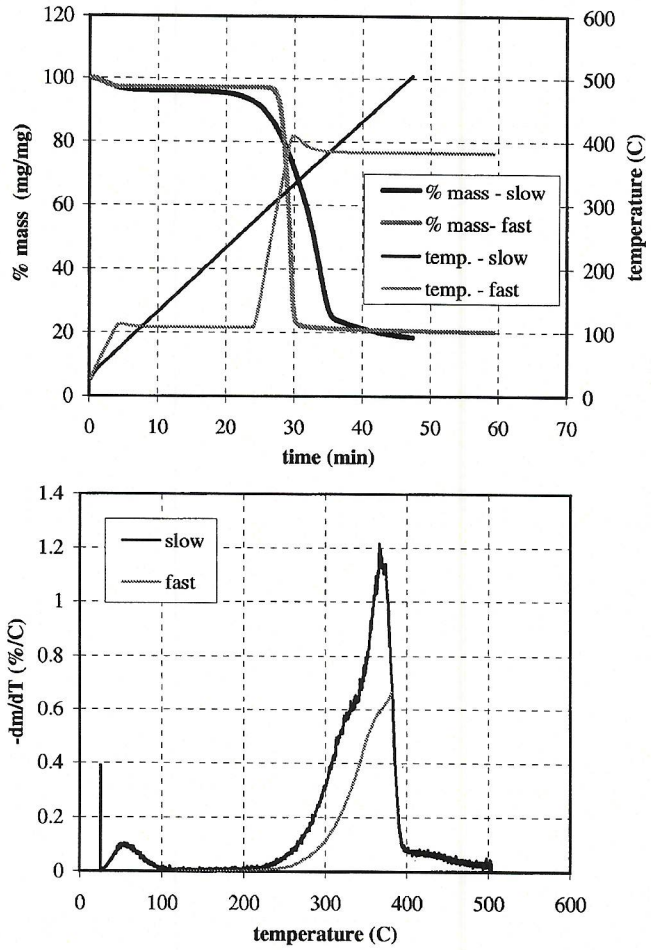

Fig. 5. Thermal behaviour of untreated wood: comparison between slow- and fast-heating.

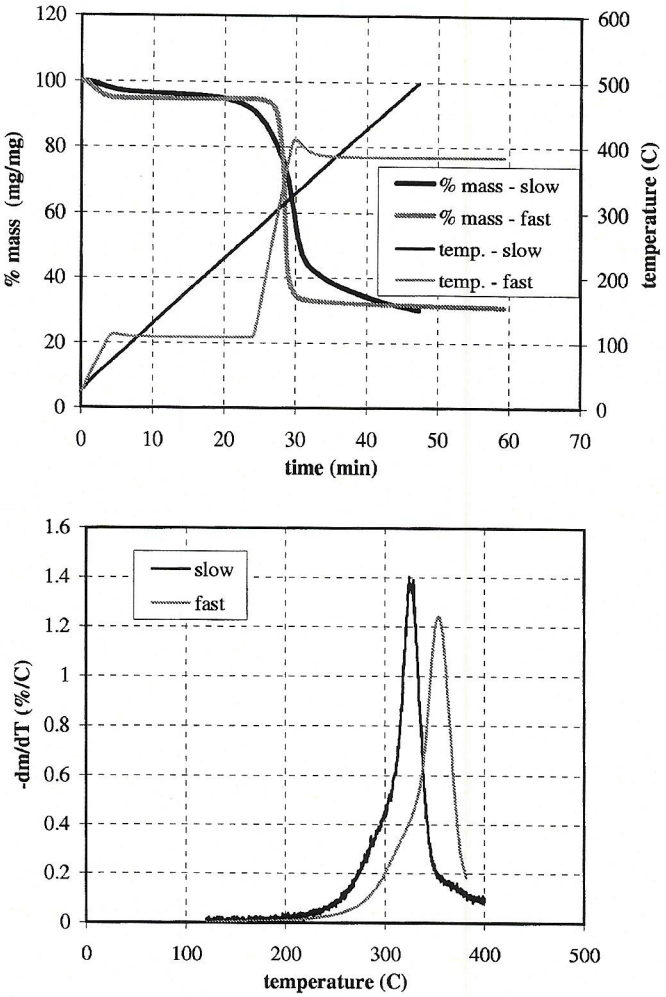

Fig. 6. Thermal behaviour of CCA1-treated wood: comparison between slow- and fast-heating.

water evolution and the stage of water and other volatiles evolution. All the compounds that were expected to be released (Table 3) are found in the gas stream originating from the pyrolyzing sample for the untreated wood as well as for the CCA-treated wood. All volatile compounds considered attain their point of maximum evolution at approximately the same time, only benzene and toluene have a broader peak. Evans and Milne [23] identified these compounds as prominent growth ion peaks in the tertiary cracking regime of wood, confirming the later evolution of benzene and toluene, observed in this study. It can be concluded that within the accuracy of the EGA analysis method applied, the presence of CCA does not significantly influence the type and relative amount of volatiles released. The same compounds are detected in approximately the same ratios. However, the absolute amount of volatiles released should decrease in the presence of CCA, because of the higher char yield and the observed TGA curves (see Section 3.2).

This conclusion cannot be drawn from this EGA study, which is not capable of detecting these changes due to the limited amount of compounds analysed and the qualitative character of this study. Some other conclusions drawn when studying the TG and DTG curves, can be confirmed by observations made in this EGA

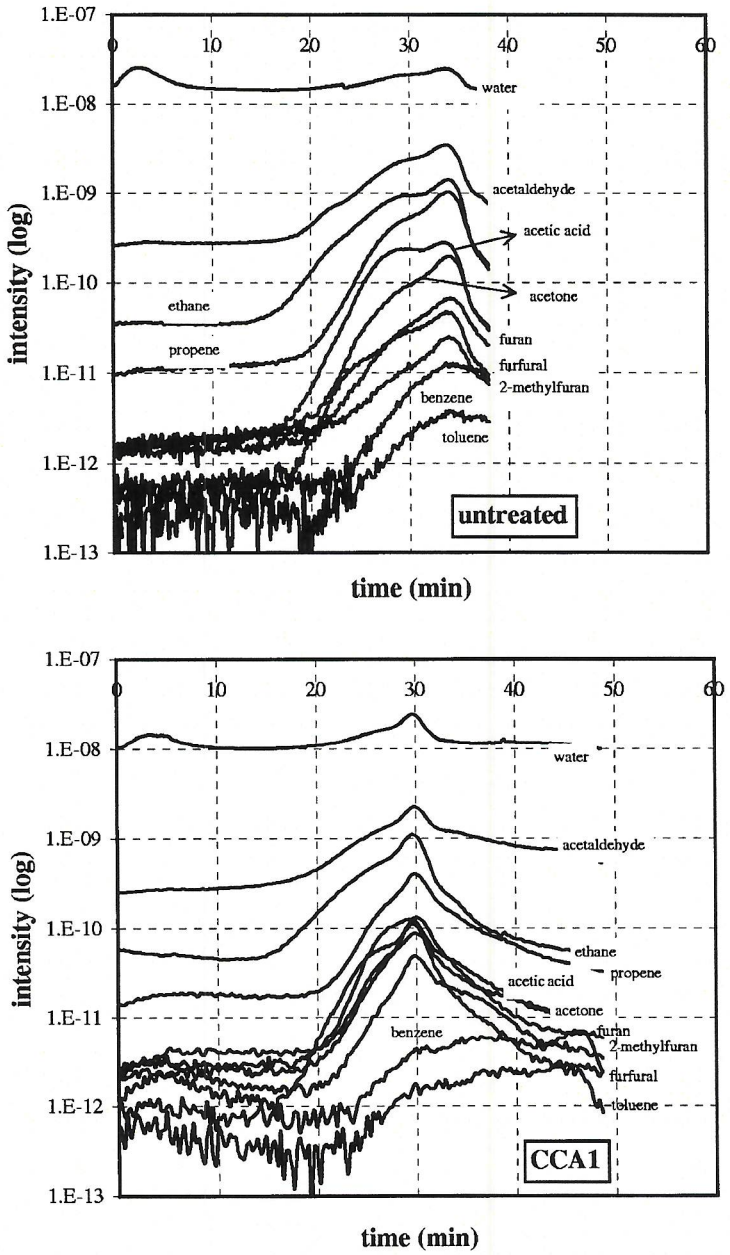

Fig. 7. Evolution of some volatile compounds at the outlet of the thermogravimetric analyser: slow-heating regime, untreated and CCA1 sample.

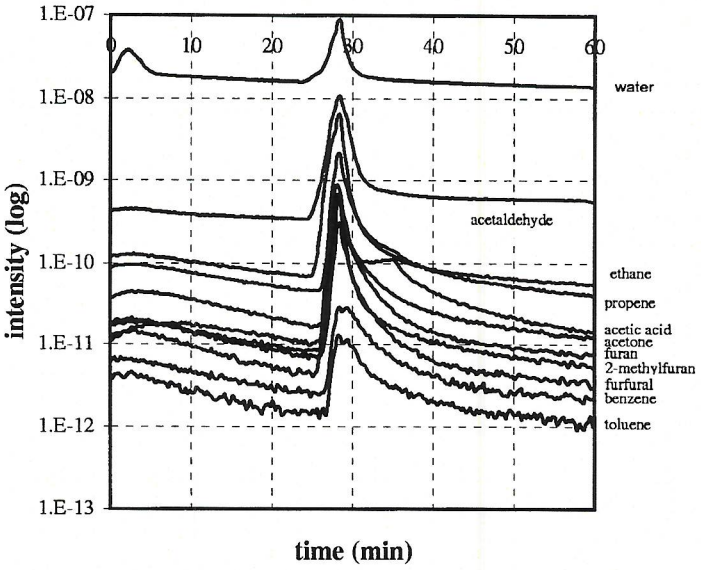

Fig. 8. Evolution of some volatile compounds at the outlet of the thermogravimetric analyser: fast-heating regime, CCA1 sample.

study. The time at which the peak (maximum) of volatiles intensity is measured is smaller for the CCA1 sample compared to the untreated sample. The release of volatiles is spread over a larger period, i.e. the peak is broader in the case of untreated wood compared to CCA-treated wood.

To examine the influence of heating rate on the release of volatiles during pyrolysis, the evolution of the same compounds in the fast-heating regime is presented in Fig. 8 for the CCA1 sample. As can be seen in Fig. 8, the same compounds are released in approximately the same ratios as in the slow-heating experiment but the release is much more peaked in time. These peaks occur at lower times, but the corresponding temperatures are higher in the fast-heating experiment. Again the same conclusions can be drawn as in the study of the DTG peaks (see Section 3.2). The lower-temperature side of the peak is much steeper than the higher-temperature side, which means that the volatilisation starts relatively abruptly if high heating rates are applied. The evolution of one compound, acetic acid, is different in fast- and slow-heating regimes, reaching a flat part on the higher-temperature side of the peak in the fast-heating experiment.

Some experiments were carried out with a condenser placed between the outlet of the TGA apparatus and the inlet of the MS. The evolution of the above-mentioned compounds, measured at the outlet of the condenser in the preset-temperature regime (see Section 2.3.1) is presented in Fig. 9 for the CCA1 sample. As can be seen in Fig. 9, some of the compounds considered are condensed completely, while others are condensed partly. Among the completely condensed compounds are water, propene, acetaldehyde, acetone, furan, benzene, 2-methylfuran and toluene. The partly condensed compounds are ethane, acetic acid and furfural. The con-

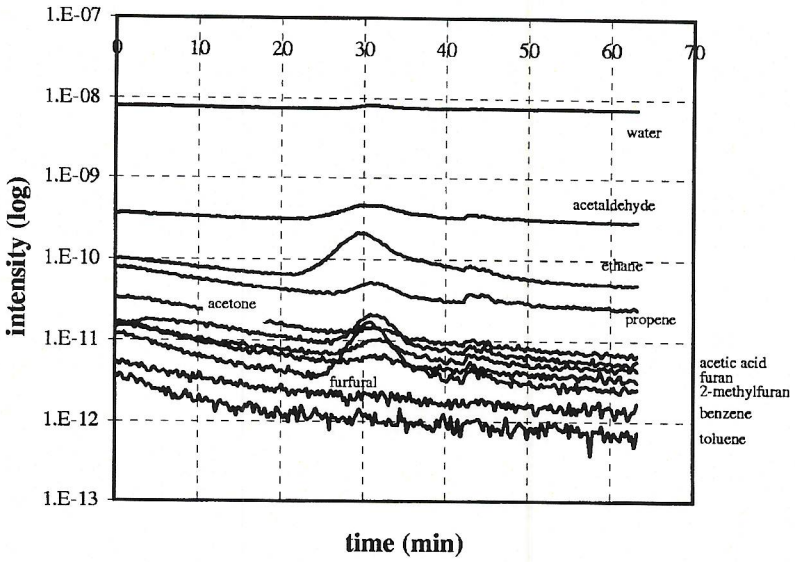

Fig. 9. Evolution of some volatile compounds at the outlet of the condenser placed after the thermogravimetric analyser: preset-temperature regime, CCA1 sample.

denser which is a type that is often used in the laboratory, is thus effective in condensing volatile compounds, but does not succeed in condensing all of them. Some compounds escape from the condenser and are detected by the MS. This observation can be very useful in the study of pyrolysis processes aiming at collecting the pyrolysis liquid as much as possible and identifying the constituting compounds.

3.4. Metal analysis

3.4.1. Metal release as a function of temperature and time

The metal contents of the residues resulting from the pyrolysis of CCA1 wood samples following the preset temperature profile (the five points are given in Table 2) are given in Table 4.

Table 4
Metal content (%) of the five residues resulting from the pyrolysis of CCA1 wood samples following the preset temperature profile

Point	Cr (% in residue)	Cu (% in residue)	As (% in residue)
1	110	114	105
2	100	112	95
3	103	105	93
4	108	105	92
5	92	89	79

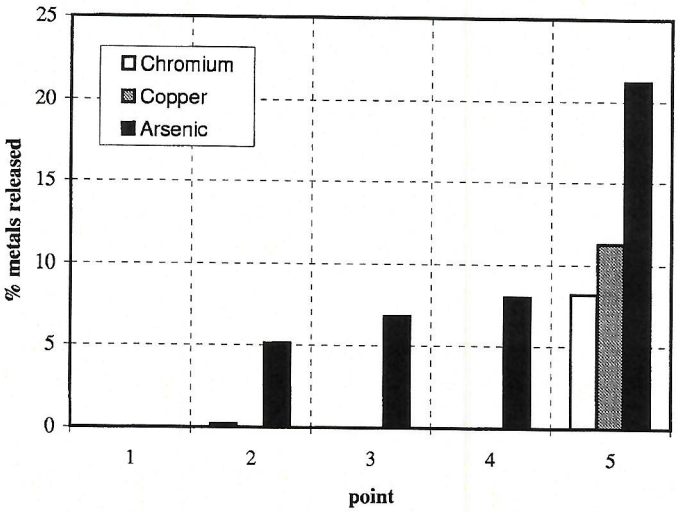

Fig. 10. Metal (Cr, Cu, As) release during the pyrolysis of CCA1 samples following a preset temperature profile.

An error estimation is made for these results. Errors originate from the determination of concentrations and masses. The relative errors for mass determination (by the TGA apparatus) are estimated to be 1% for residues and 1.5% for dried wood. The relative errors for concentration determination are dominated by the ICP-MS measurements and can be found using standard solutions. This results in relative errors of 5% for Cr, 7% for Cu and 9% for As, which can be reduced to 3.5% for Cr, 5.0% for Cu and 6.5% for As when an average value of two independent measurements is used. The errors made by weighing the samples before dissolution, filtration, making some dilutions, etc. are negligible compared to the error caused by ICP-MS analysis. Using the general rules of error estimation, the resulting spreads on the calculated metal contents (%) are 7% for Cr, 10% for Cu and 13% for As. As can be seen in Table 4 these errors are still underestimated since recoveries as high as 114% are found.

Using the values from Table 4, which represent the retention of metals in the pyrolysis residues when a preset temperature profile is followed, the release of metals during pyrolysis can be studied. This is represented in Fig. 10, where negative values of release are set to zero. As can be seen in Fig. 10, the release of Cr, Cu and As during pyrolysis is strongly dependent on temperature and time at a given temperature. Points 1 and 2 represent temperature increase, while points 2, 3, 4 and 5 are all points at the same temperature but for different residence times. The release of Cr and Cu is negligible up to point 4 (10 min maintained at 400°C) and sharply increases after point 4. This increase is sharper for Cu than for Cr, indicating that the copper compound is more volatile than the chromium compound. Arsenic is a more problematic compound, being released already before reaching 400°C. The release of As is below 10% up to point 4, but sharply increases when the sample is held at

400°C for more than 10 min, reaching 21% when the sample is maintained at 400°C for 20 min.

If only Cr and Cu are considered the treated wood may be heated up to 400°C and maintained at 400°C for 10 min without any problem, but not longer than 10 min. Point 4 is the critical point for Cr and Cu. Point 4 can also be identified as the critical point for As, in the sense that As release increases drastically from the moment the sample is held at 400°C for more than 10 min. Before this critical point the release of As is not negligible, but is lower than 10%. There is a non-negligible release of As from the moment the sample is heated to 400°C. When pyrolyzing CCA-treated wood As starts to volatilise at a temperature somewhere between 300 and 400°C. The sublimation temperature and boiling point of pure arsenic trioxide are tabulated as respectively 315 and 457.2°C [27]. The presence of other components can alter these points significantly. It can be concluded that not only temperature, but also the residence time of the wood sample are very important parameters in the study of the release of metals during pyrolysis.

3.4.2. Comparison CCA1–CCA2

A comparison between the metal content in the pyrolysis residue resulting from CCA1 and CCA2 samples after applying the slow-heating process, is given in Fig. 11. As can be seen, the metal content of the residue (expressed as percentage of metal found in the pyrolysis residue) resulting from the CCA2 sample is significantly higher than the metal content of the residue resulting from the CCA1 sample. From this experiment the following conclusion can be drawn: the higher the CCA concentration of the original sample, the higher the relative concentration (%) of metals (Cr, Cu, As) in the pyrolysis residue.

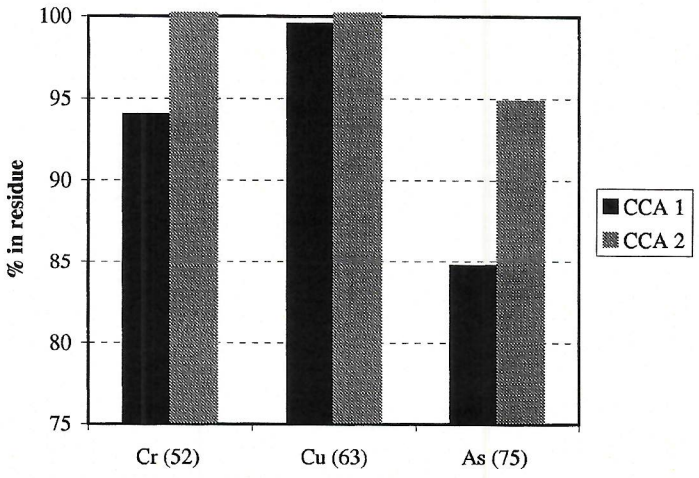

Fig. 11. Metal (Cr, Cu, As) content in the pyrolysis residues resulting from CCA1 and CCA2 samples after applying the slow-heating process.

4. Conclusions

It can be concluded that TG curves as well as DTG curves provide a useful tool to compare the thermal behaviour of different samples. Supplemental information can be obtained by coupling the TGA apparatus with a gas analysis system, such as MS. Due to condensation of some compounds in the transfer-line (300°C) between the TGA apparatus and the MS, the study of metal release cannot be done on-line and has to be carried out off-line.

CCA treatment has a significant influence on the thermal behaviour of wood, which is more pronounced the higher the initial CCA concentration is. The temperature at the onset of pyrolysis, as well as the temperature where the maximum rate of decomposition occurs, are lowered by the CCA treatment. The final char yield (including the metals) is higher for CCA-treated samples. The rate of weight loss is much more peaked for CCA-treated wood, resulting even in the disappearance of the shoulder observed at the low-temperature region of the DTG peak for untreated wood. A promoting action of the CCA compounds upon the pyrolysis reactions which favours the formation of char, could be postulated. The higher the heating rate, the more important the external heat transfer processes become as rate-controlling mechanisms. As a result, for higher heating rates there is a shift of the DTG peak to higher temperatures for both untreated and CCA-treated wood samples. During the pyrolysis process, the endothermic heat of reaction represents a supplemental heat transfer resistance.

The compounds water, ethane, propene, acetaldehyde, acetone, acetic acid, furan, benzene, 2-methylfuran, toluene and furfural, which were expected to be released, are all found in the gas stream originating from the pyrolyzing sample for the untreated as well as for the CCA-treated wood. Within the accuracy of the EGA method applied, the presence of CCA does not influence the type and relative amount of volatiles released significantly. As observed in the study of the TG and DTG curves, the absolute amounts of volatiles released decrease in the presence of CCA, but this trend cannot be seen in this qualitative EGA study. The remaining above-mentioned influences of CCA and heating rate on the DTG peak are also visible in the curves of volatiles evolution. A cold-finger condenser, placed between the TGA apparatus and the MS, is capable of condensing volatile compounds, but does not succeed in condensing all of them.

From the study of the release of metals (Cr, Cu, As) during pyrolysis, it can be concluded that the volatilisation of these metal compounds is strongly dependent on temperature and residence time of the wood sample at a given temperature. A critical point (10 min at 400°C) exists, below which the release of Cr and Cu is negligible and the release of As is below 10%. Above this critical point (longer times at 400°C), there is a dramatic increase of metal release for all three metals. Since the time at a preset temperature is an important parameter in the study of the release of metals, a valid comparison between slow- and fast-heating cannot be made due to the difference in duration of these experiments. The influence of the CCA concentration can be formulated as: the higher the CCA concentration of the original sample, the higher the relative concentration of metals (Cr, Cu, As) in the pyrolysis residue.

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