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Estimation of the Thermal Decomposition and Analysis of Evolved Species and Char of Wood Preservatives Using Thermogravimetric Analysis Combined with Spectrometric Techniques

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Three types of wood preservatives, creosote oil (Creosote), chromated copper arsenate (CCA–3) and ammoniacal copper quats (ACQ–1) were studied, first by using thermogravimetric analysis (TGA) under different heating rates (5 or 40 °C/min), and then by using thermogravimetric analysis with infrared spectrometry (TGA–IR) and energy dispersive X-ray spectrometry (EDX). The results obtained from the TGA tests found that the decomposition temperature of each of the preservatives for the heating rate at 5 °C/min was lower than that at 40 °C/min. Regardless of different heating rate, the char (wt %) of the CCA–3 was more than that of the ACQ–1, and the amount of char for the Creosote was lower than that for either of the water-based preservatives. The IR response of all preservatives in the TGA–IR tests showed that at a heating rate of 5 °C/min, the absorbance of Creosote and ACQ–1 was higher than that of CCA–3. This indicated that the concentration of evolved species of CCA–3 was less than that of Creosote and ACQ–1. However, at a heating rate of 40 °C/min, the absorbance of CCA–3 and ACQ–1 was higher than that of Creosote. Considering the decomposition step (thermal time or temperature) at different heating rates in the TGA tests and the IR response from the TGA–IR analysis, the results obtained showed that at the slow-heating regime, the concentrations of CO₂ produced by Creosote and ACQ–1 were higher than that of CCA–3, but at the fast-heating regime, the concentration of CO₂ for ACQ–1 was higher than that of Creosote and CCA–3. The EDX analysis of all preservatives showed that the main element of the char for Creosote was C (82.75%) after combustion. The char of CCA–3 had an amount of Cr (34.99%) that was obviously more than that of As (11.89%) and Cu (16.69%) due to Cr being a stable element during combustion. The char of ACQ–1 left a high amount of inorganic metal elements, such as Cu (50.14%). These results, when compared to the chemical ingredients of all preservatives, enabled us to point out the kinds of evolved species for referencing the thermo-decomposition processes of the preservatives. The use of TGA for analyzing the thermal properties of three types of preservatives, in combination with TGA–IR and EDX analysis, has led to useful results, regarding the identification of thermal decomposition products (evolved species and char).

INTRODUCTION

Extra protection is needed when wood is exposed to adverse environments. This is because wood becomes subject to degradation by a variety of natural causes when left untreated in many outdoor applications. For the past few decades, wood can be protected from the attack of decay fungi, harmful insects, or marine borers by applying chemical wood preservatives with long-lasting results (Connell, 1991). Wood preservatives can be divided into two general classes: (1) oilborne (oil-based) preservatives, such as coal-tar creosote (creosote oil) and petroleum solutions of pentachlorophenol and (2) waterborne (water-based) preservatives that are applied as water solutions, such as chromated copper arsenate (CCA) and ammoniacal copper Quats (ACQ) (Ibach, 1999). However, environmen-

tal concerns have drastically changed the active ingredients of wood preservatives, resulting in restricted use (Sanders and Windom, 1980; Sanders and Riedel, 1987; Weis and Weis, 1992a, b, 1996, 1999; Cooper, 2001), especially since substantial amounts of CCA or creosote oil remain in the wood for many years and the disposal of scrap wood has become an ever increasing problem (Cox, 1991; Cooper *et al.*, 2003; Solo-Gabriele *et al.*, 2003). Some years ago, alternative copper-based preservatives, ACQ, comprised of a combination of copper and organic biocides were developed relatively, and are being used increasingly for wood preservation in many countries.

At the same time, there is an increasing concern worldwide about the disposal of preservative-treated wood products after use (Cooper, 1994). Discarded wood treated with any of these above mentioned wood preservatives will need to be reused, recycled, or disposed of in an environmentally acceptable manner (Ibach, 1999; Cooper, 2001; Lin *et al.*, 2006). The waste stage of preservative treated woods also has a very significant impact on its life cycle assessment results (Esser *et al.*, 2000). Preservative-treated woods, however, are not included in the wood recycling industry, basically because of technical problems and regulatory concerns, and the same applies to waste wood manage-

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ment (Falk, 1997). The common waste disposal options for spent preserved wood are combustion and landfilling (Kuwahara, 1996; Jang, 1997; Kobayashi *et al.*, 2000). Even though wood is considered an ecological material (Takahashi *et al.*, 1995), it is necessary to determine the thermal composition of these preservatives during combustion, including such things as, decomposition temperature, compounds emitted, total amount of volatiles evolved (Kercher and Nagle, 2001) and the amount of char formed (residual elements) (Lin *et al.*, 2007). This is due to the fact that both CCA and ACQ are not organic compounds, and their precise molecular composition may vary. In addition, the thermal decomposition of all combustible materials produces a toxic smoke. Combustion toxicology indicates adverse effects produced from exposure to fire-generated toxic species (Hartzell, 1996).

In order to provide an understanding of the fundamental thermal decomposition and to analyze the evolved species and the char of wood preservatives, the examinations were divided into two categories. The first category involves the study of thermal decomposition, and examines the effectiveness of the thermal properties of 3 types of wood preservatives, creosote oil, CCA and ACQ, using thermogravimetric analysis (TGA). In the second category two kinds of spectrometric techniques are applied. One applies thermogravimetric analysis with infrared spectrometry (TGA-IR), to monitor the effectiveness, on an analytical scale, of the three preservatives and also to examine the emissions of certain compounds in each particular analysis. The other applies energy dispersive X-ray spectrometry (EDX) to examine certain residual elements of the char from each preservatives used in this study, before/after thermal decomposition. The goal of this research was to acquire fundamental knowledge of the thermal decomposition of the preservatives, while at the same time obtaining an air pollution reference for gas emissions and a disposal-end practice (of the residual elements) reference for the char.

MATERIALS AND METHODS

Wood preservatives

The commercial wood preservatives used were provided by Kunnyih Co. Ltd., Taiwan. The basic details of these preservatives are as follows:

- a. Coal-tar creosote (creosote oil): type CRO33 of creosote oil (Creosote) was used, and is a black or brownish oil made by distilling coal tar that is obtained after high temperature (315 to 355°C) carbonization of coal, and is produced by China steel chemical Corp., Taiwan. Its solid content is about 23.72%, specific gravity was 1.085 (28.0°C).
- b. Chromated copper arsenate (CCA): type 3 of CCA (CCA-3) was used, and is produced by Tanalith C Corp., England. CCA-3 oxide is light yellow in color and its concentration in an oxide-base was 2.5% containing a mixture of 28.90 wt % of chromium trioxide (CrO_3), 10.60 wt % of cupric oxide (CuO), and 16.70 wt % of arsenic pentoxide (As_2O_5). The concentration of CCA-3 was 3.0%, and its solid content was about 2.32%, specific gravity was 1.065 (28.0°C), with a pH of 3.6.
- c. Ammoniacal copper quats (ACQ): type 1 of ACQ (ACQ-1) was used, and was obtained from Koshi Corp., Japan. ACQ-1 oxide is deep green in color, and includes CuO with 9.00 wt %, as well as 7.20 wt % of N-alkyl benzyl dimethyl ammonium chloride (BKC). The concentration of ACQ-1 was 6.0%, and its solid content was about 0.95%, specific gravity was 1.008 (27.8°C), pH value was 10.3.

Thermogravimetric analysis (TGA)

TGA is an established technique, used in the quantification of weight changes within a material, as a function of temperature or time (Hsu *et al.*, 2000). Throughout this, TGA was carried out using a Perkin-Elmer TGA 1, fully supported by computer-controlled software options from Perkin-Elmer Thermal Analysis Systems for control and data handling. The samples, 3 types of wood preservatives after being oven dried at a temperature of 105°C for over 24 h, each weighing approximately 5.0–10.0 mg, were placed into an open experimental sample pan and suspended from a sensitive microbalance. A furnace surrounded the sample to provide accurate heating ranging from 50 to 850°C, while the measurements were taken. In order to isolate the decomposition step, all runs were purged in an air atmosphere, at a flow rate of 50 mL/min, with 2 kinds of heating rate, at 5°C/min (slow-heating regime) or at 40°C/min (fast-heating regime). That is to say, the slow-heating and fast-heating regimes were applied to compare the differences in their thermal properties and their char. The thermal decomposition for the three types of preservatives was then carried out.

Thermogravimetric analysis with infrared spectrometry (TGA-IR)

TGA, as described in previous section, is a quantitative technique that does not identify evolved compounds. To understand the evolved species produced by the thermal decomposition of the three types of wood preservatives, an analysis was carried out using a TGA (Perkin-Elmer Pyris 7 TGA model), linked to a secondary method of analysis, the Fourier-Transform Infrared Spectroscopy (using a Perkin-Elmer FTIR), which was able to identify the evolved species during the TGA measurements (Statheropoulos and Kyriakou, 2000). The TGA and FTIR (TGA-IR) were connected using a transfer line with a continuous scanner in a gaseous cell. The infrared spectrometric (IR) response data was recorded by a personal computer. The spectrum time based version 2.0 software (2000, Perkin-Elmer, Inc.) obtained and analyzed the evolved species as they occurred. The samples, weighing about 5.0 mg each, were placed in an open pan and suspended from a sensitive microbalance in the Pyris 7 TGA model.

The conditions were set the same as for the Perkin-Elmer TGA 1, described above, regarding heating and air flow rates. The evolved species analysis was performed on the TGA-IR, and their IR spectra was then investigated by spectrum version 5.3 (2005, Perkin-Elmer, Inc.). However, the IR response obtained for various evolved species using the TGA-IR appeared about 10 sec later, when compared to the traces of the TGA tests. To discuss the criteria and limitations of both TGA-IR and TGA for each particular analysis, and to ensure accurate results, it was necessary to carefully calculate and compare the results obtained between the decomposition temperature (obtained from the TGA) and the decomposition time of the evolved species from the IR response (obtained from the TGA-IR).

Energy Dispersive X-ray Spectrometer (EDX)

TGA-IR, described in the previous section, is a technique to investigate the evolved species by thermal decomposition, but it does not identify the char after combustion. To understand the char of the preservatives, the scanning electron microscope combined with the energy dispersive X-ray spectrometer (SEM-EDX) was employed. It can be applied directly to a material, to determine the amount of all the elements in a single image analysis. It is a powerful tool for studying the mineral distribution and more precisely the effect of the elements on this distribution (Kotz *et al.*, 1990). In these experiments, to simulate the char obtained from the end of the TGA tests, all preservative samples were each placed into an individual crucible and then burned using a burner (DF-303, Deng Yng Co. Ltd.). The temperature was managed the same as for the TGA test, from room temperature to 850 °C, but with a heating rate of 20 °C/min (Lin *et al.*, 2006). The residual char was analyzed using a SEM-EDX (E HONG Instrument Co. Ltd., a Hitachi general agent in Taiwan, from Hitachi High-Technologies Corporation, Japan). SEM pictures were taken using a Hitachi S-3400N scanning electron microscope. For all investigations in this study the beam energy was 10 nm at 15.0 kV with a distance of 10.0 mm to the preservatives samples, in order to obtain the excitation of all the elements. Analysis of the elements was carried out by EDX analysis using a Horiba EDX 7021 H system. To determine their distribution, a smart Map acquisition was used, which is capable of the simultaneous acquisition of the X-ray data from each pixel on the image area with 2.00 kSE of magnification. The results of the residual elements in the char were analyzed for all samples.

RESULTS AND DISCUSSION

Thermal decomposition of wood preservatives

Thermogravimetric analysis (TGA) is a common technique for measuring the weight change of a material as a function of temperature. To comprehend the thermal properties (thermal decomposition, decomposition step, and char) of the three types of preservatives, the preservatives samples were measured by TGA, after

having been oven-dried. Decomposition profiles were obtained while the samples were being heated at a rate of 5 or 40 °C/min in air, between 50 °C (initial temperature) and 850 °C (end temperature). The relationships of the TGA and the DTG curves between temperature and weight loss, and the derivative weight for each preservatives sample, Creosote, CCA-3 and ACQ-1, are shown in Fig. 1.

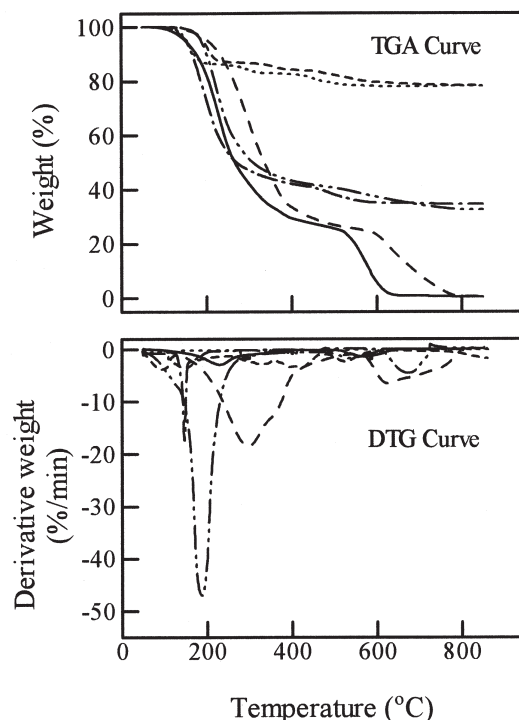


Fig. 1. TGA and DTG curves for 3 types of wood preservatives (Creosote, CCA-3, and ACQ-1) in air at 5 or 40 °C/min.

Symbols: — : Creosote (5 °C); --- : Creosote (40 °C);
 : CCA-3 (5 °C); - · - · : CCA-3 (40 °C);
 - - - : ACQ-1 (5 °C); - - - : ACQ-1 (40 °C).

Notes: CCA-3: The type 3 of chromated copper arsenate;
 ACQ-1: The type 1 of ammoniacal copper quats;
 Creosote: the type CRO33 of creosote oil (creosote oil-CRO33).
 5 °C: 5 °C/min of heating rate; 40 °C: 40 °C/min of heating rate.

Regardless of the heating rate, the three types of wood preservatives typically showed gradual weight loss. The thermogram, resulting from the analysis of Creosote at 5 °C/min (solid line) or 40 °C/min (dash line) heating rate, showed that at temperatures of 50 to about 600 °C there were three subtle changes (shoulders) for the solid line and two shoulders for the dash line, suggesting that the thermal decomposition of Creosote was influenced by the slow-heating regime and by the fast-heating regime in an air atmosphere. The onset of weight loss under air was observed at temperatures of 179.20, 400.42 and 547.63 °C for heating at a rate of 5 °C/min, as well as at temperatures of 228.54 and 599.77 °C for a heating rate of 40 °C/min. This is supported by the derivative (DTG) curve, which shows three peaks at temperatures of 230.78, 371.48 and 586.77 °C for a heating rate of 5 °C/min, and at tempera-

tures of 295.26 and 622.89 °C for a heating rate of 40 °C/min, (the bottom of Fig. 1). The amount of char for both heating rates, at a temperature of 850 °C, 5 °C/min was 0.50 wt % and for 40 °C/min it was 0.63 wt %. Regardless of the heating rate, these decomposition temperatures of Creosote were all lower than for CCA-3 and ACQ-1.

To elucidate the comprehension of the thermal properties of CCA-3 and ACQ-1 because they both are water-based preservatives, a comparison is made between the slow-heating regime and the fast-heating regime in air atmosphere for both preservatives. The results are also shown in Fig. 1. Regardless of the heating rate, the CCA-3 weight loss at a heating rate of either 5 °C/min (dot line) or 40 °C/min (short dash line) is significantly less than that of ACQ-1 at a heating rate of 5 °C/min (dash dot dash line) or 40 °C/min (dash dot dot dash line). The results of CCA-3 show that the weight loss gradually decreases. The onset of weight loss for the 40 °C/min heating rate was observed at temperatures of 176.27, 330.96, 460.39 and 512.26 °C. For the heating rate of 5 °C/min the weight loss was evident at temperatures of 138.84, 273.08, 420.36 and 431.08 °C. These findings are supported by the derivative (DTG) curve, and agree with those in the literature (Helsen and Bulck, 1998; Kercher and Nagle, 2001; Lee *et al.*, 2005; Lin *et al.*, 2006). For the amount of char, at a tempera-

ture of 850 °C, for CCA-3 it was 78.06 wt % at a heating rate of 5 °C/min and 78.73 wt % at a heating rate of 40 °C/min. These numbers are higher than the ACQ-1 at heating rates of either 5 or 40 °C/min. Hirata *et al.* (1993) reported that Cr (chromium) and Cu (copper) from the CCA preservatives were largely present in the char and that As (arsenic) was easily volatilized with the increase in temperature during combustion. Some researches (Kercher and Nagle, 2001; Cooper *et al.*, 2003; Helsen and Bulck, 2005) stated that in the TGA tests, when CCA preservatives were analyzed with air, As_2O_5 was formed in a gaseous state and that it disappeared at a temperature of over 600 °C. In addition, CuO produced Cu_2O when the temperature reached about 800 °C both in air atmosphere, CO was then further volatilized and only Cu remained. Also, Cr (III) is a stable element with an unproductive thermal decomposition (Lin *et al.*, 2006). In other words, it is evident that after combustion the Cr and Cu from the preservatives (CCA-3) are remained.

The results of ACQ-1 show that the weight loss drastically decreases in air at either heating rate. The composition temperature for the heating rate of 5 °C/min was lower than that of 40 °C/min. The onset of weight loss for the 5 °C/min heating rate under air was observed at temperatures of 156.49, and 464.40 °C. At a 40 °C/min heating rate under air, the onset of weight loss was

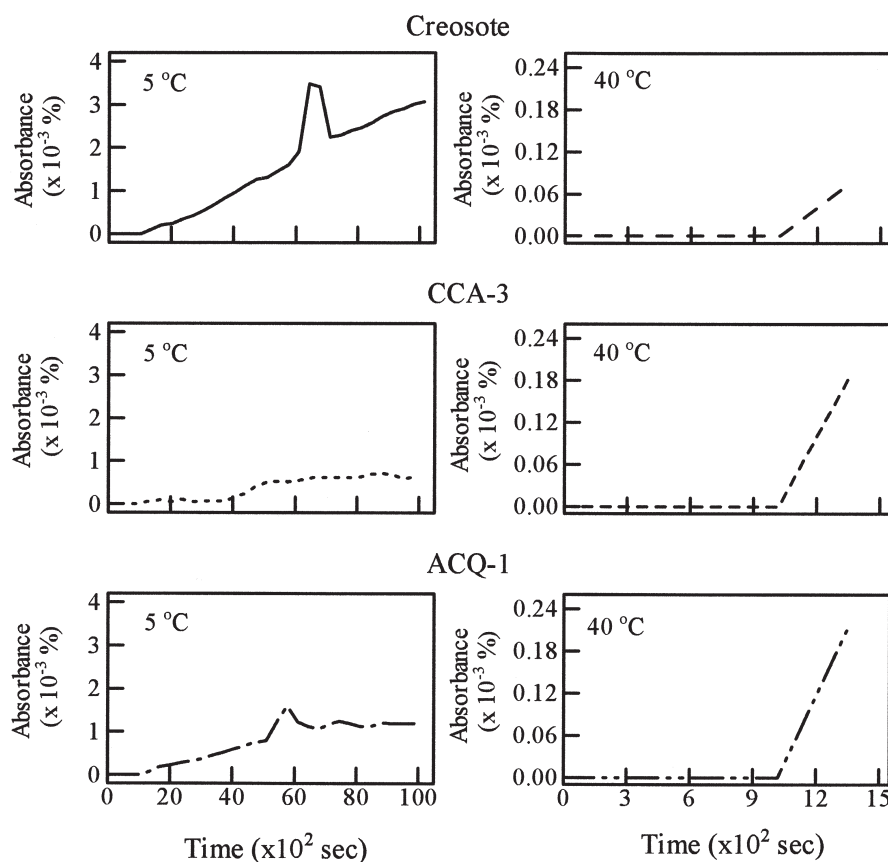


Fig. 2. IR response of 3 types of wood preservatives (Creosote, CCA-3, and ACQ-1) in air at 5 or 40 °C/min from TGA-IR analysis.

Symbols: The symbols are the same as Figure 1.

Note: Abbreviations of Creosote, CCA-3, ACQ-1 and 5 °C, 40 °C are the same as Figure 1.

obtained at temperatures of 187.00 and 515.95°C. These findings are also supported by the derivative (DTG) curve. For the amount of char in this portion of the TGA tests, ACQ-1 was 34.59 wt % at 5°C/min heating rate and 32.62 wt % at 40°C/min heating rate. These results were the same as reported previously (Lin *et al.*, 2006). ACQ preservatives, a combination of copper and organic biocides, indicated that the main residual element was Cu (Lin *et al.*, 2007), that is, the other elements were volatilized with the increase in temperature during combustion, such as BKC, one of the main compounds used in this study for ACQ-1. Therefore, the char of CCA-3 was higher than that of ACQ-1 (the top of Fig. 1), based on the different heating rates (5 or 40°C/min) set in this study.

Infrared spectrometric response of wood preservatives

Figure 2 shows the infrared spectrometric (IR) response of the three types of preservatives for both heating rates, at 5°C/min (the left side of Fig. 2) and 40°C/min (the right side of Fig. 2) in the TGA-IR measurements. The change in absorbance (concentration of evolved species, %) corresponds to the increase in decomposition time for the three preservatives. The concentration of evolved species for the IR response of Creosote with a slow-heating regime, 5°C/min, increased slowly to about 1019.75 sec (134.15°C) from the start of decomposition. Subsequently, this increasing tendency rose linearly to about 6095.85 sec (557.15°C). The high point of absorbance was 6433.37 sec (585.28°C). After that, the change in concentrations of evolved species decreased to about 7108.85 sec (641.57°C) and then tended to increase until the end of decomposition. Furthermore, the IR response of Creosote at a 5°C/min heating rate, between 6433.37 and 6771.06 sec (613.42°C), showed a greater mountain peak.

The concentration of evolved species from the IR response of CCA-3 at a 5°C/min heating rate took the shape of a plateau. The high point of absorbance occurred at 8791.23 (781.77°C). For ACQ-1 the concentration of evolved species in the IR response increased slowly to about 5088.32 sec (473.19°C) from the beginning of decomposition. Subsequently, the time change in the concentration of evolved species became like the ridge of a house in which the increasing tendency rose linearly to a sharp peak of about 5763.73 (529.48°C). After that, the change in concentrations of evolved species decreased to about 6782.00 sec (614.33°C) and then increased slowly until the end of decomposition. This suggests that at a heating rate of 5°C/min, the concentration of evolved species for ACQ-1 is higher than that for CCA-3.

Comparing the IR response of all preservatives at a heating rate of 5°C/min, the absorbance levels for Creosote were higher than for CCA-3 and ACQ-1. This indicated that the concentration of evolved species of water-based preservatives was less than those of oil-based ones. Of them all, CCA-3 was inferred to be

the best preservatives with the least environmental impact in this study, if the disposal process of the preservatives was combustion and considering the results of air pollution only. A similar conclusion was reached in a previous research (Lin *et al.*, 2007), which indicated that CCA-3 was the better environmentally friendly preservatives for wood protection, because the emission contents (such as carbon monoxide, nitrogen monoxide and sulfur dioxide) of CCA-3 were less than those of ACQ-1, considering their environmental impact only during combustion.

The right side of Fig. 2 also shows the IR response of the three types of wood preservatives with a heating rate of 40°C/min in the TGA-IR measurements. The change in concentration of evolved species corresponds to the increase in decomposition time for the three preservatives. The concentration increased slowly, about 1018.54 to 1024.46 sec (722.36 to 726.31°C), from the start of decomposition. Subsequently, the increasing tendency rose linearly to the end of decomposition. The IR response of ACQ-1 showed a greater peak at the end than that of Creosote and CCA-3. This suggests that at 40°C/min of the heating rate, the concentration of evolved species for ACQ-1 is higher than that for either Creosote or CCA-1. Comparing the IR response of all preservatives at both heating rates, the absorbance levels at 5°C/min for oil-based preservatives were higher than for water-based one, but at 40°C/min the results were reversed. This indicates that for wood preservatives the concentration of evolved species is related to the heating rate, because of the variation in decomposition steps.

TGA-IR spectra and typical structure of wood preservatives

At present much attention is being given to the use of wood preservatives, because of the fact that during combustion they emit toxic gases and produce a corrosive smoke. Exposure to these toxic emissions is harmful to humans and in addition can cause damage to expensive equipment (Ladomersky, 2000; Lin *et al.*, 2007). With the use of TGA-IR, it is possible to simultaneously monitor evolved species, decomposition temperature and the concentrations formed (absorbance), as well as the evolution profile of certain compounds. Moreover, IR spectrometry is a common means of evaluating a functional base when a material undergoes degradation. Lin *et al.* (2004) reported that the use of TGA-IR in combination with TGA analysis for analyzing the thermal behavior of 4 types of adhesives led to useful results, involving the identification of pyrolysis products.

The evolution of decomposition time (or temperature) on absorbance and wavenumbers (basically, IR spectra) for three types of preservatives samples (Creosote, CCA-3 and ACQ-1 after oven-dried) is shown in Fig. 3. The distribution of wavenumbers at the end of each 600 sec for the heating rate of 5°C/min (the left side of Fig. 3) and at the end of each 100 sec for a heating rate of 40°C/min (the right side of Fig. 3), during

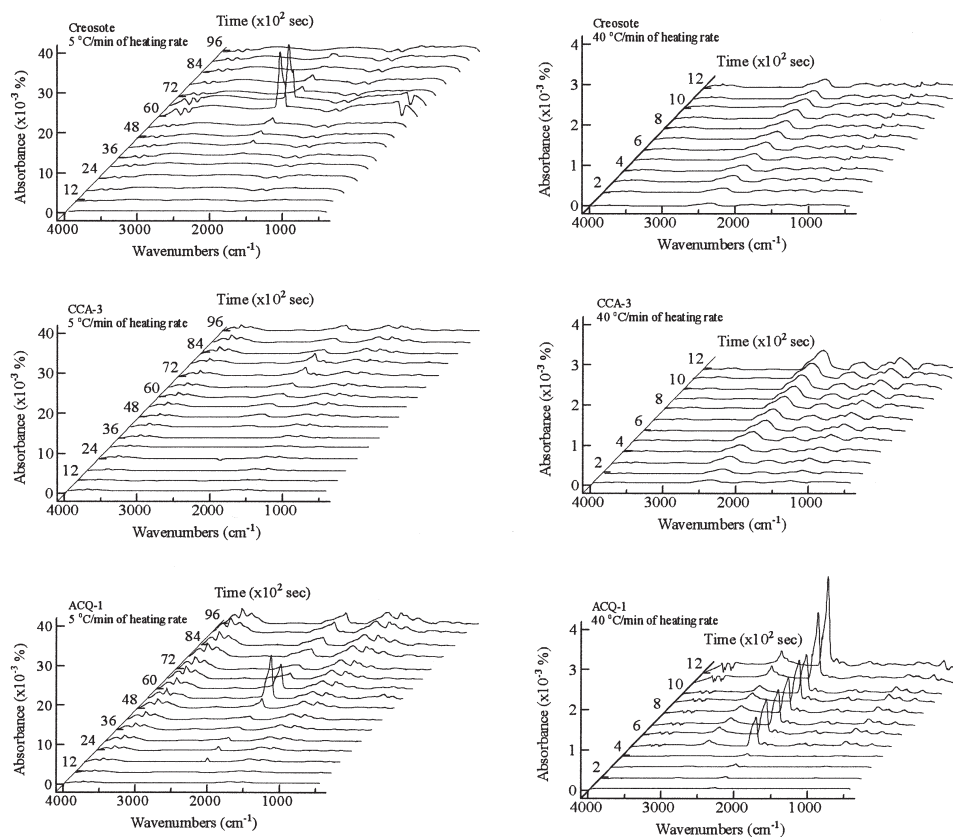


Fig. 3. TGA-IR spectra of 3 types of wood preservatives in air with 5 or 40 °C/min (Creosote, CCA-3, and ACQ-1).

Note: Abbreviations of Creosote, CCA-3 and ACQ-1 are the same as Figure 1.

decomposition, was analyzed. The results are summarized below, it analyzes the data between the TGA curve (decomposition temperature) in the TGA tests and the TGA-IR response (decomposition time along with wavenumbers and absorbance) in the TGA-IR measurement.

For the TGA-IR spectra of Creosote at a heating rate of 5 °C/min (top left in Fig. 3) and at a heating rate of 40 °C/min (top right in Fig. 3), the carbon dioxide (CO₂) peak, located at 2296 and 2356 cm⁻¹, started showing from about 3600 sec (at a temperature of about 349 °C in the TGA tests) to the end for a heating rate of 5 °C/min and was steady from beginning to the end for a heating rate of 40 °C/min. The CO₂ increased linearly to maximum absorbance at about 6000 sec (549 °C), then decreased at about 6780 sec (614 °C) and decreased linearly the concentration of CO₂ till the end of the tests for the heating rate of 5 °C/min. The other CO₂ peak was located at 617 cm⁻¹ for the heating rate of 5 °C/min, and was from about 2400 sec (249 °C) to the end, but at 666 cm⁻¹ for a heating rate of 40 °C/min the other CO₂ peak was from about 400 sec (82.5 °C) to the end. In addition, the peaks at 1585 and 3780 cm⁻¹ were due to the N-H stretching of NH₂ moieties (Zhu and Shi, 2001) from about 1200 sec (149 °C) to the end for the heating rate of 5 °C/min. A higher concentration of N-H stretching was seen between 6000 and 6600 sec (549 to 599 °C). For the heating rate of 5 °C/min the range from 5400 to

9000 sec (499 to 799 °C) showed a slight peak at 718 cm⁻¹, which was attributed to the groups of -CH₂-rocking and another slight peak, at 3670 cm⁻¹, was attributed to the OH group, from about 1800 sec (199 °C) to the end. However, for the heating rate of 40 °C/min, some of the weak peaks, at 3741, 1794, 1316 and 814 cm⁻¹, were due to the OH group, C=O (carbonyl group) stretching, the group of C-NO₂ stretching and N-H deformation vibration of NH₂ moieties, all ranging from the beginning of the combustion to the end. These results indicate that from the TGA-IR response the evolved species for the slow-heating regime (5 °C/min) were less than those for the fast-heating regime (40 °C/min).

The TGA-IR spectra of CCA-3 are shown in Fig. 3. The spectra on the centre left in Fig. 3 is for the heating rate of 5 °C/min and the one on the centre right is for the heating rate of 40 °C/min. These results indicate that the fast-heating regime presented many more evolved species. The absorbance peaks and the time location (including the decomposition temperature) of CO₂ at 2296 and 2356 cm⁻¹ were from about 2400 sec (249 °C) to the end for the heating rate of 5 °C/min, but from the beginning to the end for the heating rate of 40 °C/min. C=O stretching at 1725 cm⁻¹ was from about 1200 sec (149 °C) to the end for the heating rate at 5 °C/min and from the beginning to the end for the heating rate of 40 °C/min. One of the lower peaks was from the begin-

ning to the end for the heating rate of 5 °C/min and from about 200 sec (176 °C) to the end for the heating rate of 40 °C/min. This is attributed to N–H stretching at 3780 cm⁻¹. Other low peaks for the groups of –CH₂–rocking at 710 to 718 cm⁻¹ from the beginning to the end showed up in the slow and faster-heating regimes. Except those evolved species, several weak peaks, for the heating at a rate of 40 °C/min only, at 1805, 1437, 1300, 932 and 817 cm⁻¹ emerged due to =CH₂, OH groups, C–NO₂ stretching, –OH out-of plane wagging, –NH₂ moieties etc., during the period of the TGA-IR tests. These results of CCA-3 indicated that there were more evolved species for the heating rate of 40 °C/min than those for the heating rate of 5 °C/min.

For the TGA-IR spectra of ACQ-1 at the heating

rate of 5 °C/min (bottom left in Fig. 3), the peaks of CO₂ were located at 2296 and 2356 cm⁻¹ and began from about 1800 sec (199 °C) to the end of the tests, and the highest absorbance showed at 5400 sec (499 °C). The other CO₂ weak peak, located at 666 cm⁻¹, was from about 2400 sec (249 °C) to the end and a higher concentration of CO₂ was also seen at that point (5400 sec.). Another wavenumber at 3747 cm⁻¹ was assigned to the N–H stretching of NH₂ moieties (Zhu and Shi, 2001) from about the beginning to the end and the highest point was located at the end. For the heating rate of 40 °C/min (bottom right in Fig. 3), the CO₂ peak was located at 2296 and 2356 cm⁻¹ from the beginning to about 1210 sec (850 °C). The concentration of CO₂ increased linearly from about 400 sec (310 °C) till the

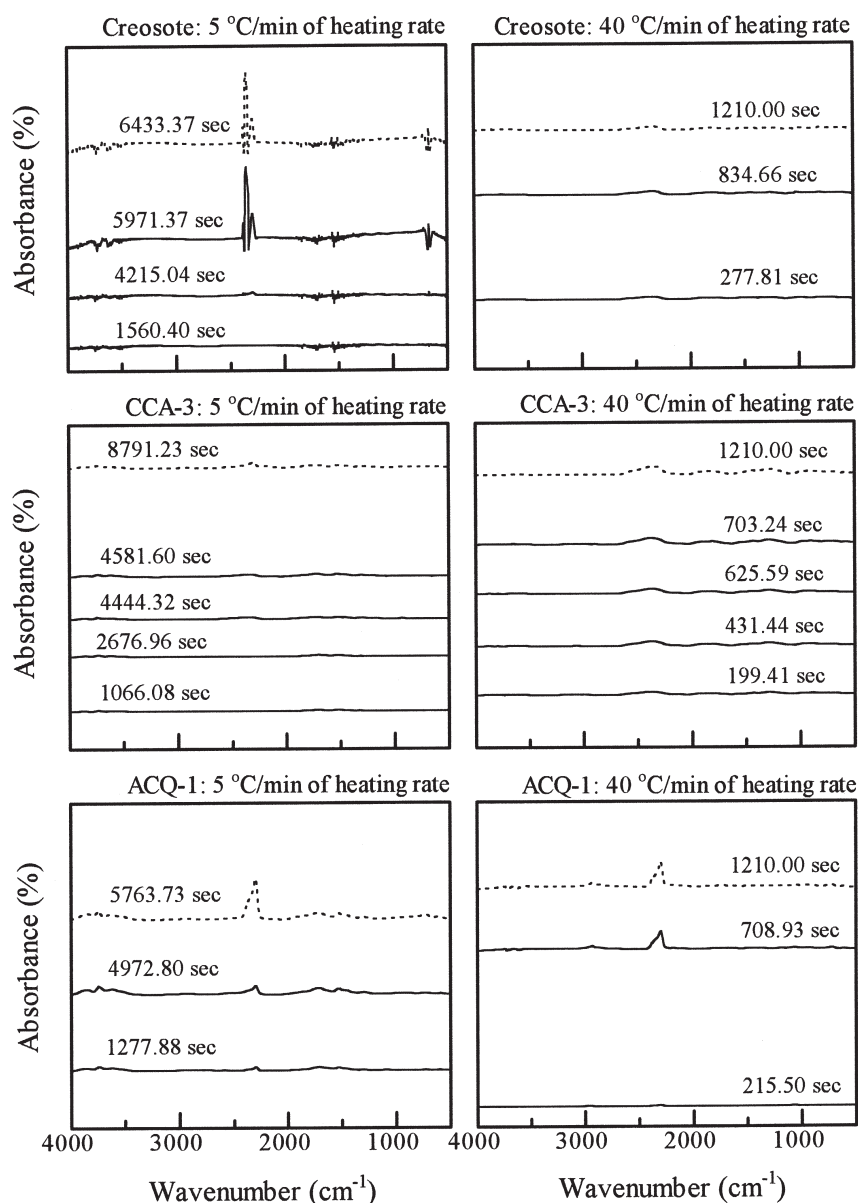


Fig. 4. IR spectra of 3 types of wood preservatives (Creosote, CCA-3 and ACQ-1) at the maximum value of absorbance from IR response and at the decomposition steps of each specimen.

Symbols: - - - : Maximum value, — : decomposition step.

Note: Abbreviations of Creosote, CCA-3 and ACQ-1 are the same as Figure 1.

Table 1. EDX analysis for 3 types of wood preservatives before and after the combustion

| Element | Orbital | Unit: weight (%) | | | | | |
|---------|---------|------------------|-------|---------------------|-------|---------------------|-------|
| | | Creosote | | CCA-3 ¹⁾ | | ACQ-1 ¹⁾ | |
| | | before | after | before | after | before | after |
| C | K | 88.58 | 82.75 | 4.30 | 2.70 | 3.74 | 22.13 |
| O | | 7.77 | 14.64 | 59.78 | 33.50 | 29.94 | 26.38 |
| Al | | — | — | — | — | — | — |
| Mg | | — | — | — | — | — | 0.36 |
| Na | | — | 0.55 | — | — | — | — |
| S | | 3.65 | 2.06 | 1.39 | 0.86 | — | 0.66 |
| P | | — | — | — | — | — | — |
| K | | — | — | — | — | — | 0.33 |
| Cl | | — | — | — | — | 0.55 | — |
| Ca | | — | — | — | — | — | — |
| Cr | | — | — | 7.41 | 34.99 | — | — |
| Cu | L | — | — | 16.29 | 16.69 | 65.76 | 50.14 |
| As | | — | — | 10.21 | 11.89 | — | — |

¹⁾ Abbreviations of CCA-3 and ACQ-1 are the same as Figure 1.

end of the tests and the highest level of absorbance was at the end of the tests. The range from about 400 sec (310°C) to the end showed two weak peaks of absorbance at 3609 cm⁻¹ and 3747 cm⁻¹, which were attributed to the N–H stretching of NH₂ moieties and the OH groups. In addition, several weak peaks, for the heating at a rate of 40°C/min only, at 1731, 1385, 1273, 1075, 930, and 716 cm⁻¹ were due to C=O stretching, –CH₃, N–NO₂, C–O and –OH out-of plane wagging, and groups of –CH₂–rocking etc. from about 400 sec (310°C) to the end, during the period of the TGA–IR tests. These results were also the same as CCA-3, indicating evolved species for the heating rate of 5°C/min were less than those for the heating rate of 40°C/min.

Relationship of thermal decomposition and IR response of wood preservatives

Considering the sharp increase (decomposition step) of weight loss in the TGA tests and the IR response from the TGA–IR analysis, the relationships for all preservatives used in this study are shown in Fig. 4.

The maximum value (dot line) of the three types of preservatives from the IR response in the TGA–IR tests, and the decomposition step (solid line) in accordance with the decomposition time in the TGA tests, found that all preservatives did not show a lot of evolved species during the initial decomposition step: Creosote at 1560.40 sec (179.20°C), CCA-3 at 1066.08 sec (138.84°C) and ACQ-1 at 1277.88 sec (156.49°C) for a heating rate of 5°C/min and Creosote at 277.81 sec (228.54°C), CCA-3 at 199.41 sec (176.27°C) and ACQ-1 at 215.50 sec (187.00°C) for a heating rate of 40°C/min. Nevertheless, they all showed a significantly higher amount (concentration) of CO₂ emitted at the top point (dot line) during absorbance between 2296 and 2356 cm⁻¹, particularly for Creosote with a heating rate of 5°C/min at either 5971.37 (547.63°C; the third decomposition step) or at 6433.37 (585.28°C; the top point of absorbance) and CCA-3 with a heating rate of 5°C/min at 5763.73 (479.01°C; the top point of absorbance), as

well as ACQ-1 with a heating rate of 40°C/min at either 708.93 (515.95°C; the second decomposition step) or at 1210 (850.00°C; the end of the tests). In combustion toxicology, CO₂ is normally considered to be a significant toxicant and is also the best-known greenhouse gas, capable of increasing the average global temperature (Allaby, 2000; Aplin *et al.*, 2000). The results (Fig. 5) also showed that at either the slow or the fast-heating regime both Creosote and ACQ-1 produced more types and higher concentrations of evolved species than CCA-3.

EDX analysis of wood preservatives

Because the chemical ingredients of both CCA-3 and ACQ-1 are composed of salts, and Creosote is obtained from coal tar at a higher temperature through distillation, the residual elements will remain in the char after thermal decomposition (Lin *et al.*, 2006). In general the residual char is processed by landfilling it. (Jang, 1997). The residual elements in char, therefore, need to be investigated to determine what the char contents of these three types of preservative are. In this portion of the experiment, in order to analyze the char of these three preservatives in the end of the TGA tests, all samples were individually burned using a burner to simulate the char obtained from the end of the TGA tests, and then were carried out by using EDX. The results are shown in Table 1.

The main element of the oil-based preservatives used in this study, was C (carbon), 88.58% before combustion and 82.75% after combustion. For the water-based preservatives, CCA-3 was 4.30%, and ACQ-1 was 3.74%. After combustion, the relative proportion of C was 2.70% for CCA-3 and 22.13% for the ACQ-1. The results for element O (oxygen) showed that Creosote had a relative twofold increase, 7.77% before being burned, 14.64% after being burned. For water-based preservatives this was relatively decreased, 59.78 to 33.50% for CCA-3 and 29.94 to 26.38% for ACQ-1. The results also showed that the amount of S

(sulfur) for Creosote was 3.65% before combustion, and 2.06% after being burned. For two water-based preservatives, the results showed that the amount of Cr (chromium) for the CCA-3 was 7.41% and after being burned it was 34.99%, but the amount of Cu (copper) and As (arsenic) were almost unchanged (Cu from 16.29 to 16.69; As from 10.21 to 11.89%). In a previous work (Lin *et al.*, 2007) reported that due to the fact that CCA-3 was composed of a mixture of chromium trioxide (CrO_3), cupric oxide (CuO), and arsenic pentoxide (As_2O_5), the EDX results for these oxides after being burned were that the residual Cr from the CrO_3 was 64.15%, Cu from the CuO was 58.39% and As from the As_2O_5 was 36.92%. This indicates that Cr and Cu from the char of the CCA preservatives was a stable element, but that As_2O_5 was formed in a gaseous state and that it disappeared at a temperature of over 600 °C. With other words, As is easily volatilized with the increase in temperature during combustion. The above results agree with the literature (Hirata *et al.*, 1993; Kercher and Nagle, 2001; Cooper *et al.*, 2003; Helsen and Bulck, 2005; Lee *et al.*, 2005). For the ACQ-1, the char contained a great amount of inorganic metal elements, such as Cu (50.14%). This indicates that the main char of the ACQ-1 was Cu, which was almost unable to be combusted toward the end of the TGA tests. The above results of the EDX analysis indicate that the char of CCA-3 includes Cr, Cu and As amounting to about 63.57% of the residual elements. Therefore, if the disposal method of landfilling is adopted, the amounts and types of residual elements of CCA-3 need to be known.

From the results, it is concluded that the ignition point, the % of chemical ingredients and/or the heat decomposition of the preservatives may influence their thermal properties in relation to the extent and chemical nature of the smoke released during the burning process. The authors of this research, therefore, suggest that further identification of decomposition products may lead to useful results concerning the discarding process of chemical compounds by conducting principal component analysis, using combined methods, such as TGA-IR for investigating the evolved species and using EDX to analyze the char, as well as the preservatives themselves.

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