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Combustion Emissions Analysis of Wood-Based Waste Processing-Materials

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1. Introduction

The pursuit of economic development by the human has come at a great cost to the animals and plants of this planet, and has damaged the quality of our air and water. In the last 100 years more problems have come to threaten the environment, such as vanishing forests, acid rain, the burning of fossil-fuels and global warming. Currently, researchers are focusing on so-called “eco-materials” that make effective and environmentally friendly use of natural resources, such as the recycling of industrial wastes, the development of new environmentally friendly materials, etc. The evaluated items are included the frontier, amenity and adjustment of materials (Okuma, 1998). Besides, Life Cycle Analysis (LCA), started in the early 1970s, is a method that considers energy and raw material consumption, different types of emissions and other important factors related to a specific product’s entire life cycle. The Society of Environmental Toxicology and Chemistry (SETAC) published the widely accepted series of guidelines and definitions of LCA, and the ISO 14040-14043 is considered the LCA standard (Bras & Román, 2006). Recycling of wood products, as one item of the LCAs, generally includes two kinds of methods. The first type is recycling of discarded forest products or resource-recovered (renewable) materials, which means to develop new wood-based materials in accordance with the principle of cascade utilization (Akiyama, 1998). The second type is the waste disposal options for spent various wood materials, including demolition, combustion and/or landfilling (Jang, 1997; Kobayashi et al., 2000). However, discarded the wood-based waste processing-materials, especially wood or/and wood-based materials that have been processed with different types of adhesives, coatings and preservatives, are extremely difficult to be recycled as a raw material, because these materials for wood products used cannot presently be used as a raw material again (Lin et al., 2001), and the waste stage has a very significant impact on the life cycle assessment results (Esser et al., 2000).

As we know, carbon dioxide (CO_2) is one of elemental compounds in the atmosphere (air) and a factor in photosynthesis and absorption. CO_2 is also the best-known greenhouse gas because it is capable of increasing the average global temperature depending on the sensitivity of the atmosphere (such as the concentration of CO_2) to greenhouse forcing (Allaby, 2000; Aplin et al., 2000). Carbon monoxide (CO), one of tasteless, colorless and non-odorous gases, is produced primarily by car exhaust and incomplete combustion of organic materials. Hence, CO can easily be inhaled and combined with the hemoglobin in blood,

which prevents oxygen (O_2) transportation in the blood and causes intoxication effects such as headache, giddiness, tiredness and buzzing in the ears etc (Lin, 1992). Sulfur dioxide (SO_2) is one of the precursors for acid rain because not only a sulfurous acid (H_2SO_3) reaction is formed when SO_2 is compounded as mist in the atmosphere, but also SO_2 has a chemical reaction with O_2 and forms sulfur trioxide (SO_3). SO_3 then becomes liquid SO_3 because its' dew point is $22\text{ }^\circ\text{C}$. At the dew point a sulfuric acid (H_2SO_4) reaction is formed. When inhaling SO_2 at about 30 to 40 ppm, the body will feel giddy and experience breathing difficulty (Lin, 1992; Aplin et al., 2000). Nitrogen oxide (NO_x) is so-called "thermal induced compound" because it has two reactions during combustion. The first reaction is from oxidization in which a nitric (N) substance after combustion is formed with the numerator of O_2 . The second reaction involves the reaction of O_2 and N_2 from the air during the combustion process (Li et al., 1993; Jang, 2000; Takabashi et al., 1995).

On the other hand, the thermal behavior (pyrolysis, thermal decomposition or combustion) of every combustible material or product produces a toxic smoke atmosphere. This toxic smoke atmosphere, in sufficiently high concentrations, presents a hazard to exposed animals and humans. Discarded woods treated with any of these above mentioned wood-based waste processing-materials from the combustion are therefore need to be disposed of in an environmentally acceptable manner (Ibach, 1999; Lin et al., 2001; Cooper, 2001; Lin et al., 2006). The thermal composition of these wood-based waste processing-materials during combustion, including such things as, decomposition temperature, compounds emitted, total amount of volatiles evolved (Kercher & Nagle, 2001) and the amount of char formed (residual elements) (Lin et al., 2007) is need to be investigated. This is due to the fact that some of the materials 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), but they are not included in the wood recycling industry, basically because of technical problems and regulatory concerns, and the same applies to waste wood management (Falk, 1997). In many cases the final treatment for used wood products is destruction by the combustion (Jang, 1997). The emitted gases from burning the wood-based waste processing-materials, such as CO_2 , CO , SO_2 and NO_x , and so on are discharged and contribute to environmental pollution.

To provide an understanding of the emitted gases and the fundamental thermal decomposition, as well as to analyze the evolved species and the char of wood-based waste processing-materials, including wood adhesives, wood coatings and wood preservatives, the focus for this chapter is divided into three categories. The first category involves using a Flue-gas Analyzer from the exit of a 45° flammability testing cabinet as specified in the Continuous Emission Monitoring (CEM) technique; the emission gas concentrations during the combustion are analyzed. The second category involves the study of thermal decomposition, and examines the effectiveness of the thermal properties of these materials, using Thermogravimetric Analysis (TGA). In the third 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 these processing-materials and also to examine the emissions of certain compounds (evolved species) in each particular analysis. The others apply, Fourier Transform Infrared Spectroscopy (FTIR), Energy Dispersive X-ray Spectrometry (EDX), and Elemental Analysis (EA) etc, to examine certain residual elements (organic and inorganic materials) of the char, before/after thermal decomposition. The main goal of this chapter is to realize fundamental

knowledge of the thermal decomposition of the wood-based waste processing-materials, while at the same time understanding an air pollution reference for gas emissions, evolved species and a disposal-end practice (of the residual elements) reference for the char.

2. Analysis methods of emission gas, thermal decomposition and evolved species

2.1 Continuous emission monitoring

Detecting flue-gas emissions is required by strict environmental legislation. Combustion better detects the flue-gas emission value for analyzing waste products (Jang, 2000). Continuous Emission Monitoring (CEM) techniques are utilized widely for detecting gaseous emissions such as CO, NO_x, SO₂ and O₂ and CO₂ concentration at the chimney exit of furnaces to determine the concentrations of various pollutants (Jang, 2000). This portion is to introduce the emission gas concentrations during the combustion of wood-based waste processing-materials by using the CEM technique. A Flue-gas Analyzer (MSI, 2000 W. Germany) was used to examine the gas emitted of wood adhesives, wood coatings and wood preservatives from the exit of a 45° flammability testing cabinet (with reference to CNS 7614 A3125, NCYU handmade). The fuel used was liquid propane. The gas flow direction during the combustion was determined using a gas-measuring probe (MSI 2000 type B). The design and methods are shown in Fig. 1.

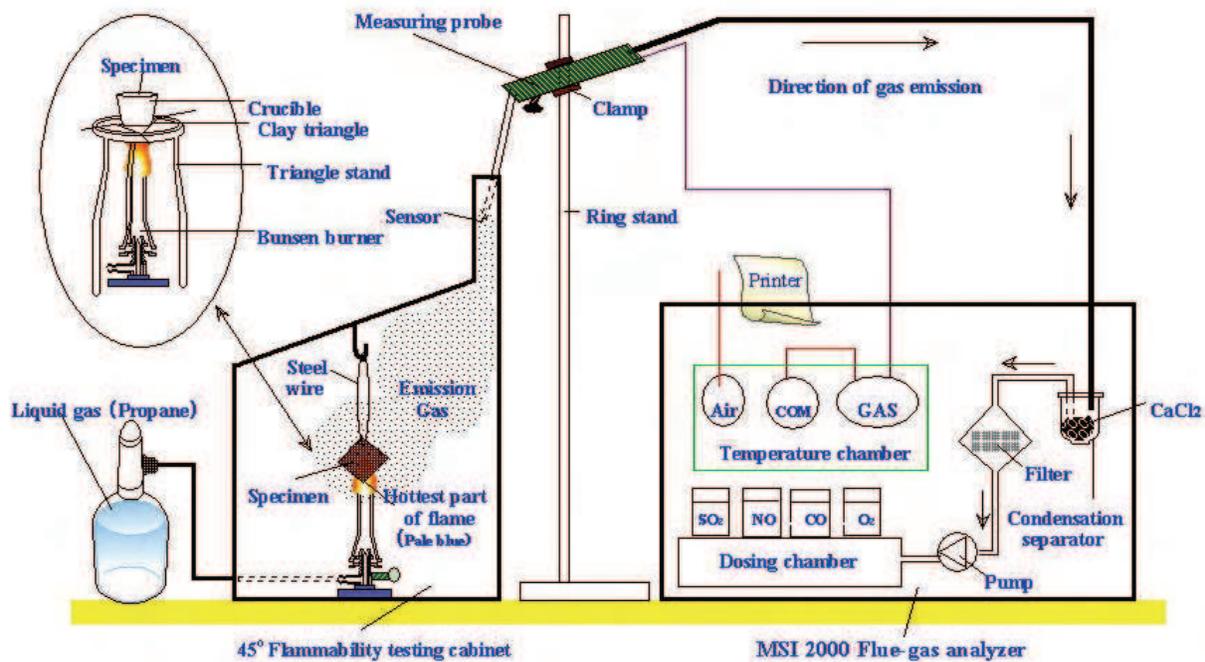


Fig. 1. Diagrams of emissions gas measuring apparatus.

The method involved two combustion treatments in accordance with each type of material. The first used for particleboards (PBs) with 4 types of wood adhesives, coatedwoods with three types of wood coatings and the coatings on a stainless steel, as well as preservative-treated woods with 2 types of wood preservatives. The specimen is hung inside the test cabinet with a steel wire and burned with a Bunsen burner adjusted to (pale blue flame)

about 850 to 980 °C. For the second treatment, the adhesives, the preservatives or wood particles was placed into a crucible on a clay triangle with a triangle stand, respectively. This method is displayed in the oval figure at the upper left in Fig. 1. The flame temperature was verified using a temperature-element apparatus (SUNTEX, ST-54) for both methods.

The combustion measured method is described as follow. The first cycle run in the Flue-gas Analyzer involved no combustion with a specimen in the test cabinet to be certain that the measured value of the emission gas was zero and the gas temperature was room temperature. The material was ignited and then examined for 10 cycles continuously. A measured cycle for the emission gas concentrations and the emission gas temperature during specimen combustion was about 40 sec. The maximum experimental value was obtained and compared with the value from each cycle. The CO, SO₂ and NO_x gases were determined according to parts per million (ppm). The O₂ and CO₂ concentrations were defined as the volume percent (VOL %) of the air in the emission exit. The gas temperature was measured simultaneously.

2.2 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a common technique for measuring the weight change of a material as a function of temperature. Throughout this chapter, 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 wood-based waste processing-materials, including wood adhesives and wood preservatives, approximately 5.0-10.0 mg in weight, were placed into an open experimental sample pan, and suspended from a sensitive microbalance. A furnace surrounded each material sample to provide accurate heating from 50 to 850 °C, while the measurement was taking place. In order to isolate the pyrolysis step, considered the most important step in the burning process for materials or products, a nitrogen atmosphere was selected for TGA analysis (Hsu et al., 2000). All runs were purged in nitrogen atmosphere, at a flow rate of 50 mL/min, with several heating rates of 5, 20 and 40 °C/min. The thermal behavior for the wood-based waste processing-materials was then analyzed.

2.3 Thermogravimetric analysis with infrared spectrometry

TGA, described in the previous section, is a quantitative technique, which does not identify evolved compounds. To understand the evolved species produced by the pyrolysis of the wood-based waste processing-materials, analysis was carried out using a TGA (Perkin-Elmer Pyris 7 TGA model), linked to a secondary method of analysis, Fourier-Transform Infrared Spectroscopy (using a Perkin-Elmer FTIR), which was able to identify the evolved species during the TGA measurements (Statheropoulos & 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 time-based software obtained and analyzed the evolved species as they occurred. The samples, weighing about 5.0 mg, 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, for heating and nitrogen flow rates. The evolved species analysis was performed on the TGA-IR. However, the IR response obtained for various evolved species using the TGA-IR appeared about 10 sec later, when compared to the TGA traces. In order 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 study

and compare the results obtained between the pyrolysis temperature (obtained from TGA) and the decomposition time of the evolved species from the IR response (obtained from TGA-IR).

3. Emission gas, thermal decomposition and evolved species

3.1 Wood adhesives

3.1.1 Emission gas of various adhesive types of particleboard

For particleboard (PB) with various adhesives, the particles used were shaving-type wood particles (involved import mixer wood particles 85 % and dismantling material 15 %) from a PB plant in Japan, the Dantani Corporation. Urea formaldehyde resin (UF, Oshika Resin-180), melamine-urea formaldehyde copolymer resin (MUF, PB-1230), phenol formaldehyde resin (PF, PB-1310) and diphenylmethane diisocyanate adhesives (MDI, PB-1605), from the Oshika Shinko CO. LTD, Japan, were used to project as the manufacture the PBs. The preparation and manufacture of PB please see the reference (Lin et al., 2001).

The results of the relationships between emission gas temperatures, the concentration of O_2 and CO_2 and the combustion time for PB manufactured with 4 types of adhesives are shown in Fig. 2.

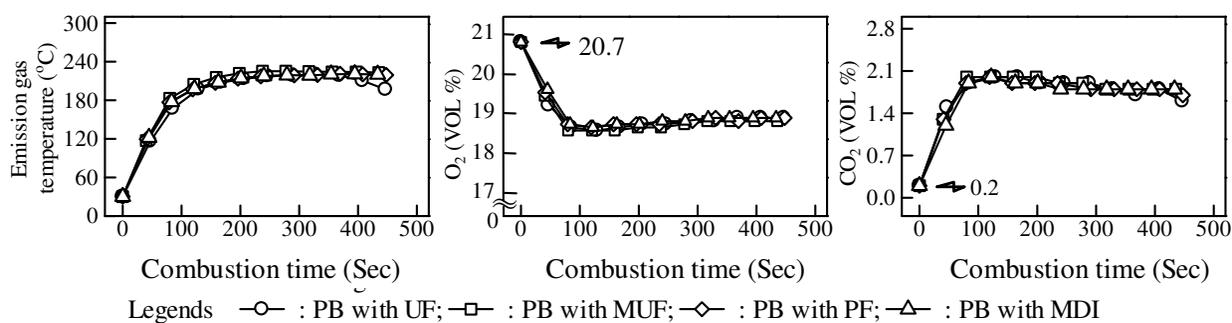


Fig. 2. Relationship between combustion time and emission gas temperature, O_2 , CO_2 concentration in particleboard manufacturing with various adhesives.

The increase in emission gas temperature corresponded to the increase in combustion time for each PB. The emission gas temperature increased rapidly up to about 175 °C, then slowed down in the temperature range of 180 to 240 °C, shown as a plateau curve. From the Flue-gas Analyzer used, the standard value of the O_2 and CO_2 concentrations (VOL %) is 20.7 % and 0.2 %. The concentration of O_2 decreased from 20.7 % to about 18 % linearly, and on the contrary the concentration of CO_2 increased from 0.2 % to about 2.0 %. Both O_2 and CO_2 approached the shape of a plateau curve and had a close relationship during combustion. It was indicated that the influence of adhesive types for manufacturing the PB on the gas temperature and either of the concentration of O_2 or CO_2 during the combustion was insignificantly.

It is well known that PB is basically manufactured from particles and adhesives. In order to understand the above-mentioned PB which produced serious pollution gases, the combined results for emission gases for these PB, 4 types of adhesives, and wood particles are shown in Fig. 3. The peak for CO gas was found at about 100 sec during combustion and then the decreasing tendency slowed down to the end of combustion treatment for all of the materials. The CO had the highest point at about 100 sec for about 20 ppm and the decreasing tendency was reached quickly after 100 sec. In other words, the influence of

different type adhesives on CO was insignificantly during the combustion. For the adhesives, MDI was more significant on the emission of CO for about 70 ppm (at about 100 sec) during the combustion than the others because it was considered that the reason of incomplete combustion in which MDI had the higher resin solids, 96.3 % (Lin et al., 2001). The result showed that CO was also produced from the wood particles during the combustion at about 100 sec for about 16 ppm. This is attributed to the particles from the wood and a carbon-hydrogen chemical compound.

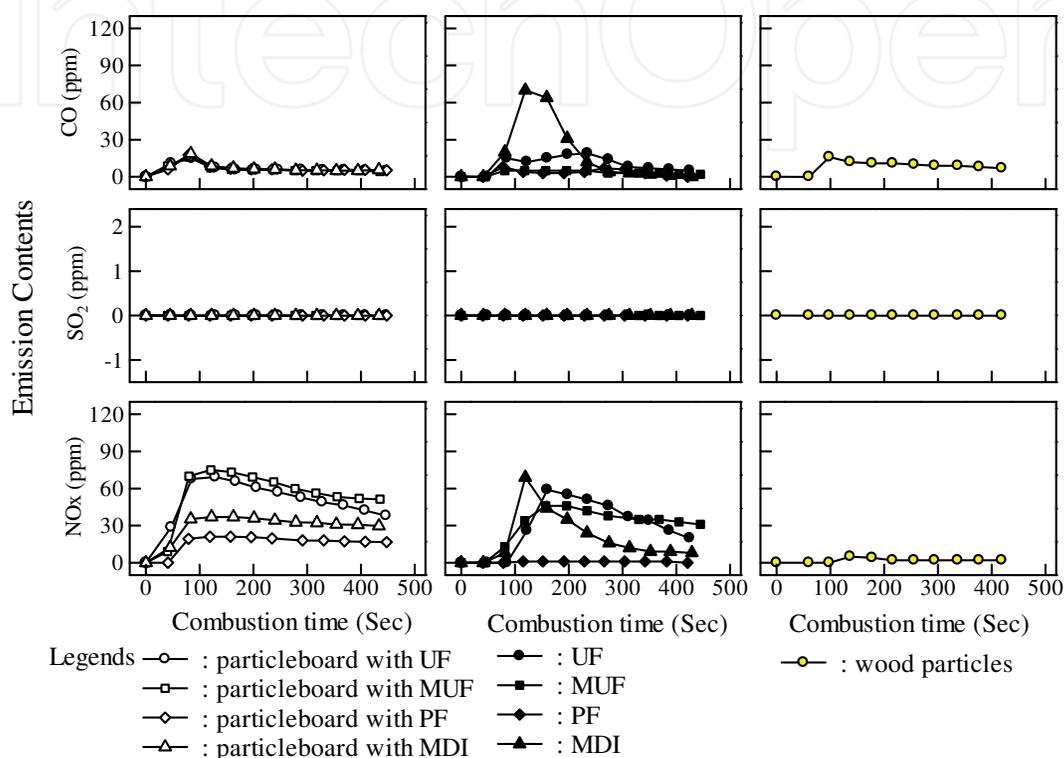


Fig. 3. Relationship between combustion time and emission contents (CO, SO₂, NO_x) in particleboard manufacturing with various adhesives, various adhesives and wood particles.

The emission SO₂ did not produce in the emission gas during the combustion for the PB with various adhesives and the adhesives because the sulphur (S) content was not included in 4 types of adhesive from the typical molecular structure (Chen, 1996; Lin et al., 2004). It is suggested that PB and wood adhesives was not the origin of the SO₂ in environment when it was concerned with final disposal (combustion).

The results showed that the PB and the adhesives were all produced the emission gas, NO_x, but it for the wood particles was insignificantly during the combustion. It is considered that NO_x is a main pollution origin. The reason for NO_x occurring is because N is included in both wood particles and adhesives. Either the O₂ and N₂ reaction from the air and particles or the fuel, propane, produced the N residues. The typical molecular structure UF, MUF and MDI, in addition to PF, was involved a nitric-base that was easily to produce the oxidization with the numerator of O₂ during the combustion (Lin et al., 2004). Moreover, the NO_x emissions for PB had the same tendency in which the peak point was about 100 sec from the start of combustion with a decreasing tendency with the combustion time from 100 sec to the end of the experiment. The quantities of emission gases, NO_x, for the PB after about 100 sec were followed by MUF (70 ppm), UF (67 ppm), MDI (35 ppm), and PF (20 ppm) in that

order. MDI produced the highest quantities of NO_x at about 100 sec. It is inferred that the ignition point or/and heat decomposition of the adhesive might influence the combustion time and the quantity of emission gas (Lin et al., 2001).

As the results, the emission contents of CO, SO₂ and NO_x from the combustion of PB and adhesives were found that the PB manufactured with PF adhesive had the least pollution gas during the combustion than the others. It is suggested that PF is the best adhesives with the least environmental impact to use for manufacturing PB, when considering the final treatment by the combustion.

3.1.2 Thermal decomposition of various adhesives

To comprehend the thermal behavior (pyrolysis, thermal decomposition) of the four types of adhesives, the specimens were measured by TGA, after being air-dried at ambient temperatures. Decomposition profiles were obtained while heating at a rate of 20 °C/min in nitrogen, between 50 °C (initial temperature) and 850 °C (end temperature). The relationships of TGA and DTG curves between temperature and weight loss, and the derivative weight for each adhesive specimen, UF, MUF, PF and MDI, are shown in Fig. 4.

As expected, the four types of adhesives typically showed gradual weight loss. The thermogram, resulting from the analysis of UF (solid line) and MUF (dotted line), showed that there were two subtle changes (shoulders) at temperatures of 50 to 390 °C, suggesting that both had almost identical initial (the first sharp step) and secondary decomposition temperatures, because UF and MUF are copolymers. The adhesive specimen weight for PF (dash line) was significantly less at temperatures between 50 °C and 500 °C in the TGA tests; the weight loss for MDI (dash-dot-dash line) was significant at temperatures from

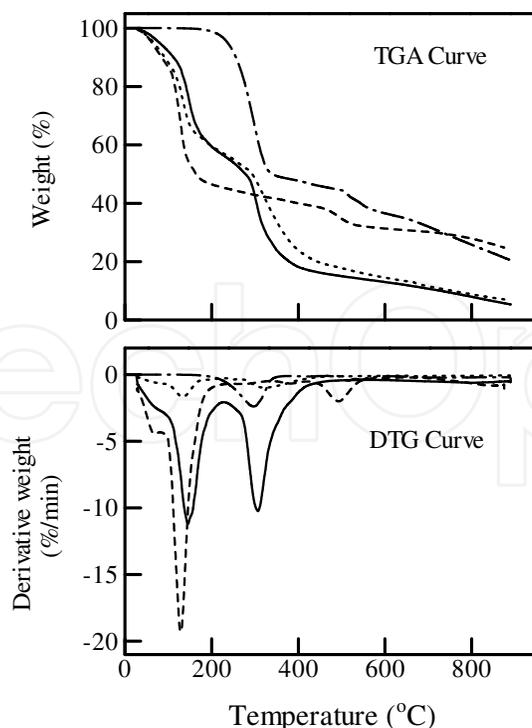


Fig. 4. TGA and DTG curves for 4 types of adhesives (UF, MUF and PF and MDI) in nitrogen at 20°C/min.

200 to 400°C. This indicates that the chemical structure, in the molecular chain, or chemical composition, of PF and MDI is different (Chen, 1996; Lin et al., 2004). The results also found that MDI exhibited the highest initial decomposition at a temperature of 297°C and better overall thermo-stability than the other types of adhesives. PF and MDI provided a better yield of char at about 24.88 and 20.61 wt%, respectively, at 850°C. This showed that their thermal behavior was better than that of UF (5.40 wt%) or MUF (6.99 wt%), as the proposed action mechanism is based on the charred layer acting as a physical barrier, which slows down heat, and results in mass transfers between the gas and condensation phases (Camino et al., 1993, Hornsby, 1996 and Zhu & Shi, 2001).

3.1.3 Evolved species of various adhesives

Figure 5 shows the Infrared spectrometric (IR) response of the four types of adhesives in the TGA-IR measurements. The change in absorbance (concentration of evolved species %) corresponded to the increase in decomposition time for the four adhesives. The IR response of all adhesives in the TGA-IR tests showed that the absorbance of UF, MUF and MDI was higher than that of PF. This indicated that the concentration of evolved species of PF was less than that of MDI, and less than that of the urea copolymer series adhesives, UF and MUF. Of them all, PF was considered to be the best adhesive with the least environmental impact. A similar conclusion was reached in Fig. 3 and the previous research (Lin et al., 2001), which indicated that PF was the most environmentally friendly adhesive for manufacturing particleboard, because the emission contents (such as CO, SO₂ and NO_x gases) of PF were less than those of UF, MUF and MDI, when the used PB was destroyed by combustion. Therefore, it has been suggested that PF is the most environmentally friendly adhesive, because it has the least environmental impact when used in many industrial and domestic applications, such as for structural members in furniture or architecture.

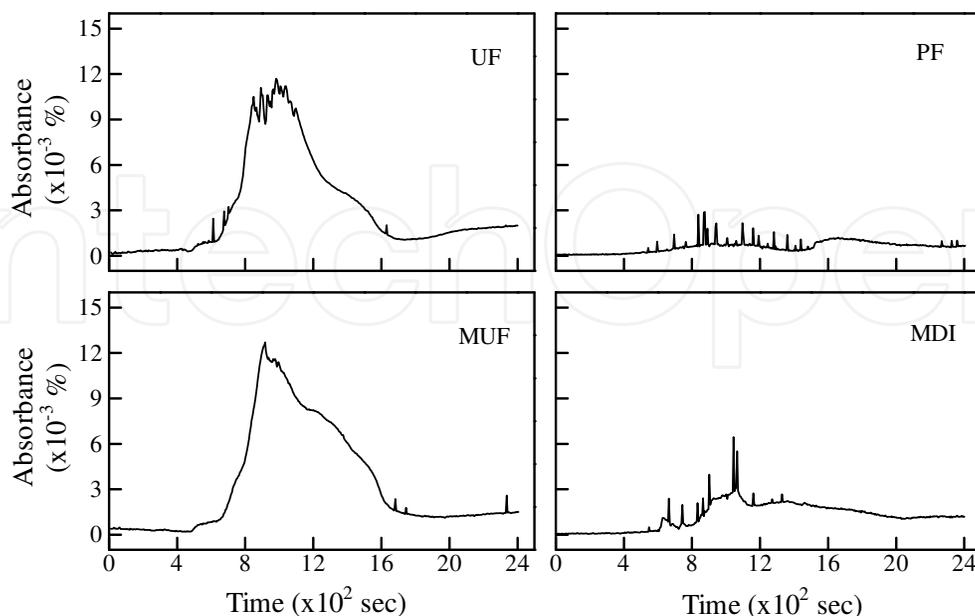


Fig. 5. IR response of 4 types of adhesives (UF, MUF and PF and MDI) from TGA - IR analysis.

In recent years, there has been much attention paid to the use of adhesives (formaldehyde copolymer compounds), because, during combustion, they emit toxic gases and corrosive smoke; exposure to these toxic and acidic fumes can cause great harm to people and can also damage costly equipment (Ladomersky, 2000). With the use of TGA-IR, it is possible to simultaneously monitor evolved species, pyrolysis temperature and 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. The evolution of decomposition time (or pyrolysis temperature) on absorbance and wavenumbers (basically, IR spectra) for the various types of adhesive specimens (UF, MUF, PF and MDI) is shown in Fig. 6.

For TGA-IR spectra of UF, the CO₂ peak, located at 2300 and 2400 cm⁻¹ was shown beginning from about 240 sec (at a temperature of about 127 °C in Fig. 4) to the end. CO₂ increased linearly to the top point of absorbance at about 960 sec (367 °C), then decreased at about 1680 sec (607 °C) and kept the same concentration of CO₂ till the end of the tests. 3545 and 3509 cm⁻¹ was assigned to the N-H stretching of NH₂ moieties (Zhu & Shi, 2001) from about 360 sec (167 °C) to the end. A higher concentration of N-H stretching was seen between 840 and 1440 sec (327 to 527 °C). The range from 480 to 1180 sec (207 to 440 °C) showed a weak peak at 2921 and 2851 cm⁻¹, respectively, which was attributed to the C-H stretching of CH₂ moieties. Another weak peak, at 1447 cm⁻¹, was attributed to C-H stretching of CH₂ moieties, from 480 sec. The weak peaks at 1701 and 1625 cm⁻¹ were assigned to the C=O (carbonyl group), stretching from 480 sec to the end. Moreover, several weak peaks at 972 or 962 cm⁻¹ also emerged due to C=O stretching, during the period from 480 sec to the end. The top point of absorbance for C=O stretching at 972 or 962 cm⁻¹ was found at 960 sec, which was the same as the top point of absorbance for CO₂. The results of MUF indicated that UF and MUF present the same tendency in the left side of Fig. 6, as both belong to the same copolymer urea formaldehyde series. The results for the absorbance peak and the time location (decomposition temperature) of CO₂, N-H stretching, C-H stretching and C=O stretching for MUF were the same as for the TGA-IR spectra of UF; the N-H deformation vibration of NH₂ moieties was found at 1605 and 1649 cm⁻¹, from about 360 sec (167 °C) to the end. The weak peak at 1449 cm⁻¹ was attributed to C-H deformation vibration of CH₂ moieties, while at 1414 cm⁻¹, it was assigned to C-N stretching. Both of these began close to 480 sec (207 °C) to the end. A weak peak of C=O stretching, located at 1736 cm⁻¹, was also found from 600 sec to the end (247 to 850 °C). In addition, two weak peaks of triazine, located at 1365 and 1565 cm⁻¹, began from about 480 sec to the end.

For the TGA-IR spectra of PF, the weak peaks of CO₂ were also located at 2300 and 2400 cm⁻¹ and began from about 600 to 1440 sec (247 to 527 °C), almost disappearing towards the end of the tests. Some weak board absorbance at 3300 to 3600 cm⁻¹ was assigned to OH groups from about 720 sec (287 °C) to 2160 sec (767 °C). A weak peak at 2980 cm⁻¹ was assigned to out-of-plane bending of C-H on the benzene (aromatic) ring, from 1440 sec (527 °C) to the end. The spectrum results in this study are similar to those reported by Reghunadhan Nair et al (2001). Another weak peak at 1100 cm⁻¹ was attributed to the stretching vibration of benzene C-C, from 1560 sec (567 °C) to the end. Besides, the results of MDI indicated that the two weak peaks of CO₂ were the same for UF, MUF and MDI, located at 2300 and 2400 cm⁻¹ and which began from about 480 to 1560 sec (207 to 567 °C), almost disappearing towards the end of the tests. Some weak board absorbance located at 3700 cm⁻¹, was assigned to N-H stretching from about 600 sec (247 °C) to 1440 sec (527 °C). In addition, some weak board absorbance, found at 3100 cm⁻¹, was assigned to OH group,

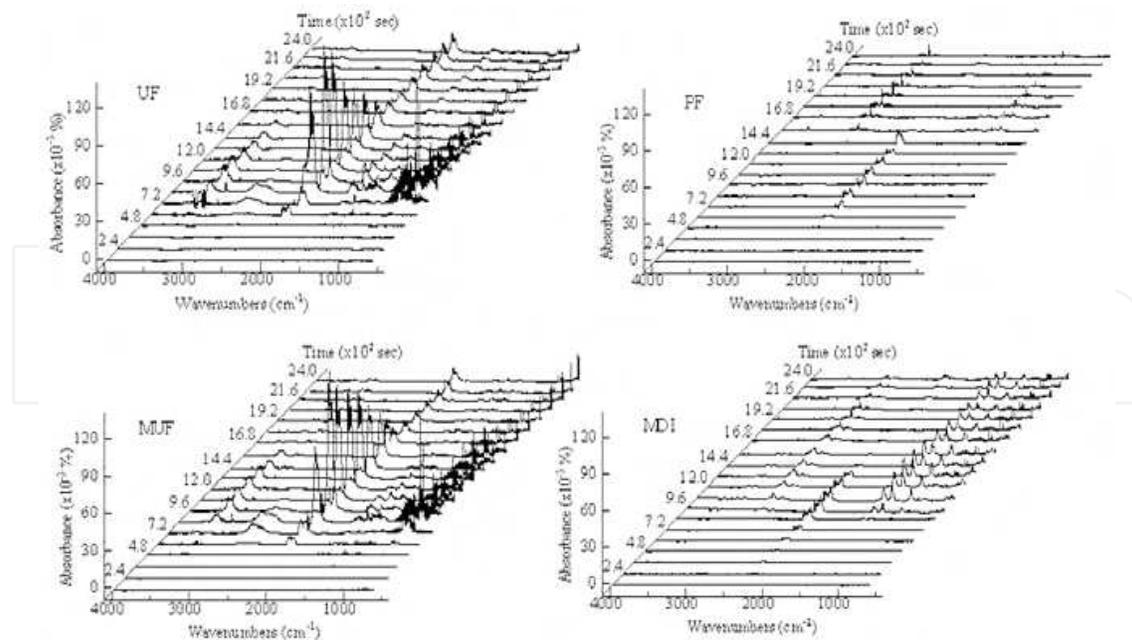


Fig. 6. TGA - IR spectra of 4 types of adhesives.

from about 960 sec (367 °C) to the end. Other weak peaks at 1624 cm^{-1} were assigned to C=O (carbonyl group) stretching from 840 sec (327 °C) to the end. Two weak peaks at 972 or 927 cm^{-1} also emerged as C=O stretching, from 1200 sec (447 °C). Results obtained also showed several weak peaks at 1114 and 1206 cm^{-1} , which were assigned to the C-NH group and N=C group (Levchik et al., 1995) from 840 sec (327 °C) to the end, respectively.

To clarify the effectiveness of the analytical scale towards the four adhesives, and to identify the evolved compounds of each particular analysis, the most probable structures for the different polymers found in these adhesives (Chen, 1996; Lin et al., 2004). UF analysis of the TGA-IR response showed that the thermal decomposition of the NH groups at a temperature of about 167 °C was initially determined as a possible degradation species. The same results were previously reported in literature (Zhu & Shi, 2001). The CH_2 and C=O groups were then degraded at about 207 °C; the final contents of the char, therefore, were practically negligible (5.40 wt%). Some of the MUF evolved species are the same as the UF evolved species, because they belong to the same series of copolymers. The TGA-IR results showed that the N-H groups were degraded at a temperature of 167 °C, while the CH_2 and triazine groups were degraded at 207 °C. In the case of PF, the thermal decomposition of the OH groups was found to be significant at 287 °C, although it could be degraded earlier, at temperatures of 65 and 129 °C; this information was obtained from the results of the TGA tests. In addition, the CH_2 groups were degraded at 527 °C and the benzene C-C at 567 °C. For MDI, the C=O and N=C groups were degraded at about 327 °C, which was analogous to the thermal decomposition of the OCN group during MDI pyrolysis, because of the resultant chemical reactions. Also, the char left at 850 °C in the TGA tests for PF and MDI was 24.88 and 20.61 wt%, respectively. The benzene (aromatic groups) structures are for PF and MDI; that is, the thermal performance was enabled when the chemical compounds included aromatic groups.

As the results, when compared to the molecular structures of the adhesives, enabled us to point out the kinds of evolved species (functional bases or the change in molecular structures) for referencing the thermo-degradation processes of the adhesives.

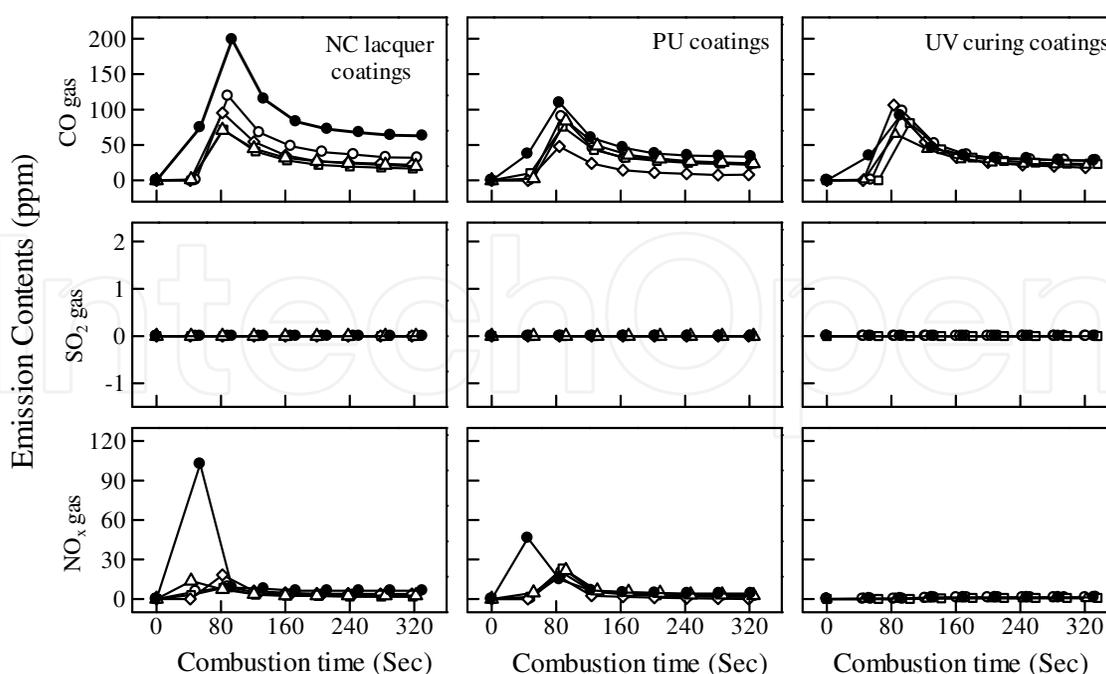
3.2 Wood coatings

3.2.1 Emission gas of wood coatings specimens

In the style-conscious wooden furniture industry, good finishing is perhaps the most critical factor. The sale of furniture is highly influenced by its decorative value and attractive appearance. However, the expectation of life for wooden furniture is about 17 years (Akiyama, 1998). Discarded wooden furniture are extremely difficult to recycle because the coatings on the furniture surface cannot presently be used as a raw material (particles or chips) again when it is considered with the bond quality of reuse materials, such as various PBs. In many cases the final treatment for used wooden furniture is destruction and then treated with combustion. Moreover, wood coatings are generally produced with various chemical compounds. The follow portion is to introduce the combustion emissions from wood coatings, and also to explore the modification of chemical structure using a potential application of Fourier Transform Infrared Spectroscopy (FTIR) from wood coated with various wood coatings before/after an accelerated weathering test, which is the QUV artificial accelerated-degradation (QUV degradation). Three types of commercial coatings, nitrocellulose lacquer coatings (NC lacquer, Kuo Rong Corporation in Taiwan), polyurethane coatings (PU coatings, Kuo Rong Corporation in Taiwan), and ultraviolet curing coatings (UV curing coatings, Chia Tai Corporation in Taiwan) were coated on the tangential sections of *Cryptomeria japonica* D. DON., and on a stainless steel, respectively. Before combustion, the nondegraded and degraded coating woods were analyzed using the FTIR. The data produced are to comprehend and compare the environmental pollutions from the coated materials with wood coatings before/after QUV degradation when they are discarded by combustion, and to as a basic reference to develop the environmentally friendly wood coatings hopefully. The basic properties of coatings, the finishing process and the accelerated weathering tests please see the references (Lin & Huang, 2004; Lin, 2005).

The emission gas temperature of all coated materials was rapidly up to about 160-170 °C, increased slowly up to 180-200 °C and then kept in the temperature range of 200-210 °C, shown as a plateau curve. The concentration of O₂ decreased from 20.7 % to about 18-19 % linearly, and on the contrary the concentration of CO₂ increased from 0.2 % to about 1.2-2.0 %. Both O₂ and CO₂ then approached the shape of a plateau curve as well as had a close relationship during combustion.

It is well known that wood coatings are generally combined with various chemical compounds. To understand the coated specimen produced serious pollution gases after QUV degradation, the combined results of emission contents are shown in Fig. 7. The highest emission quantity of CO and NO_x for the coated specimens of NC lacquer coatings was about 198 and 102 ppm, 110 and 47 ppm for PU coatings and 90 and 9 ppm for UV curing coatings. The emission SO₂ in this experiment as expected did not produce in the emission gas during the combustion for the coated specimens before/after QUV degradation because the sulphur content was not included in 3 types of wood coatings from the typical molecular structure (Lay, 1985). It is suggested that the coatings are not the origin of the SO₂ in environment when it was concerned with final disposal (combustion). Three types of coatings still produced those pollutants (CO, SO₂ and NO_x) after QUV degradation, especially for NO_x gas. This is because the chemical structure of these coatings produced a series of photochemical chain reaction and the coating film separated (peeled) from the coated substrate (Chang & Chou, 1999). However, the pollutants were relatively a decreasing tendency for the coatings after QUV degradation. The above-mentioned results



Legends Various coated specimens were processed with QUV degradation.

—●— :0 h (Stainless steel only), —○— :100 h, —□— :200 h, —◇— :400 h and —△— :800 h.

Fig. 7. Relationship between combustion time and emission contents (CO₂, SO₂, NO_x) for stainless steel and various coated specimens.

suggested that UV curing coatings is the most environmentally friendly coatings while the coatings are considered to discard process with combustion.

3.2.2 FTIR analysis of wood coatings

Chang (1990) reported that FTIR, possessing many unique advantages, is a powerful and potential technique for the analysis and characterization of micro-specimens of various wooden materials, coatings and coatedwood, especially with particular attention to the chemical modifications of materials after weathering and photodegradation. Moreover, It is well known that wood coatings are generally composed with various resin and chemical compounds. Basically, the manufactured principle of NC lacquer is to substitute NO₂+ for OH of CH₂OH or vascular cellulose and then became NC lacquer. In other wards, NC composed with alkyd resin and then added some of additives to become NC lacquer. To comprehend and compare the production of combustion emissions from three types of wood coatings, the coatedwoods before/after degraded at 0, 100, 200, 400 and 800 h with the QUV accelerated weathermeter were analyzed using the FTIR, shown in Fig. 8. The FTIR spectra of NC lacquer for QUV 0 h showed that the peaks at 1643 and 1273 cm⁻¹ were assigned to the asymmetric NO₂ stretching vibration and symmetric NO₂ vibration of CH₂ONO₂ or vascular cellulose, and another peak at 830 cm⁻¹ was assigned to N-O (nitrogen-oxygen) stretching vibration (Pouchert, 1981). Results showed that these peaks disappeared on the FTIR spectra when the NC lacquer coatedwoods after QUV degradation of 100, 200, 400 and 800h. This is because CH₂ONO₂ of NC lacquer is easily degraded by photodegradation (Chang, 1994). Therefore, the results in Fig. 7 obtained that the emission of NO_x for the NC lacquer after QUV degradation decreased significantly more than control ones.

In general, the main compound of commercial NC lacquer is alkyd resin. To improve the properties of NC lacquer, it added some of additives, such as plasticizer etc. This indicated that from the FTIR spectra of NC lacquer (Fig. 8), the control coatedwood was showed a location of peak at 1720 cm^{-1} , assigned to C=O (carboxylic group) stretching vibration that was probably from alkyd resin and plasticizer, or NC degradation to become -COOH base. After QUV degradation, this peak frequency was changed its intensity and location. This is because the change in the chemical structure of NC lacquer occurred, as well as C=O produced some degraded derivatives (Chang, 1990). The results in Fig. 7 indicated that the emission of CO for the NC lacquer coatedwoods after QUV degradation decreased significantly more than control ones. The results in Fig. 8 also showed that the FTIR spectra of NC lacquer coatedwoods after QUV degradation at 100 h appeared a peak at 1015 cm^{-1} , assigned to -COOH stretching. It is indicated that this commercial NC lacquer due to QUV degradation produced a degraded derivative, -COOH base, but this degraded derivative disappeared at QUV degradation of 200, 400 and 800 h. Hence, the results in Fig. 7 showed that for the NC lacquer coatedwoods after QUV degradation at 100 h, the emission of CO decreased after 120 sec during combustion and the decreasing tendency then slowed down to the end of combustion. It is inferred that because -COOH base decomposed easily during the combustion.

FTIR spectra in the middle of Fig. 8 showed that PU coatings degraded by QUV degradation at 0, 100, 200, 400 and 800 h. The FTIR spectrum for the coatings control ones showed that the location of peak at 1716 cm^{-1} was assigned to C=O (carboxylic group) stretching vibration of urethane and peak at 1217 cm^{-1} was assigned to -N-C-O-R (Pouchert, 1981). After QUV degradation, FTIR spectra showed that both C=O produced the change in the intensity and the shift of peak frequency, and then increased its width. Chang (1990) reported that PU coatings due to photodegradation occurred yellowing, generated quinone-imides structure, on the coating film and then produced the degraded derivatives of ester or/and carboxyl. Hence, the results in Fig. 7 showed that for the PU coated specimens after various QUV degradations the emission of CO decreased significantly. Moreover, the peak at 1531 cm^{-1} was assigned to -C-NH of R-N-C-O-R' for QUV degradation at 0 h. Results also showed that this peak disappeared on the FTIR spectra when the PU coatings coatedwoods after QUV degradation at 100, 200, 400 and 800 h. Therefore, the results in Fig. 7 obtained that the emissions of CO and NO_x for the PU coatings coatedwoods decreased more than control ones.

FTIR spectra in the bottom of Fig. 8 showed that UV curing coatings coatedwoods degraded by various time of QUV degradations. Because the main compounds of UV curing coatings used are epoxy oligomer and acrylate monomer, the FTIR spectrum of the UV curing coatings coatedwoods after QUV degradation at 100 h showed that the location of peak at 1724 cm^{-1} was assigned to C=O stretching vibration and at 1604, 1505, 824 cm^{-1} was assigned to benzene ring. Moreover, the peaks at 1178 and 1175 cm^{-1} were assigned to C-H stretching vibration (Chang & Chou 1999). From the results of FTIR spectra, the UV curing coatings coatedwoods after QUV degradation at 100, 200, 400 and 800 h showed that the above-mention functional bases (group) do not change significantly, but from the emission of CO decreased (Fig. 7) the study is inferred that the benzene rings in UV curing coatings are extremely stable during the heat decomposition (combustion), but the UV curing coatings coatedwoods after QUV degradation are possible to produce the oxidation. It is inferred that the emission of CO, therefore, might decrease relatively during the combustion.

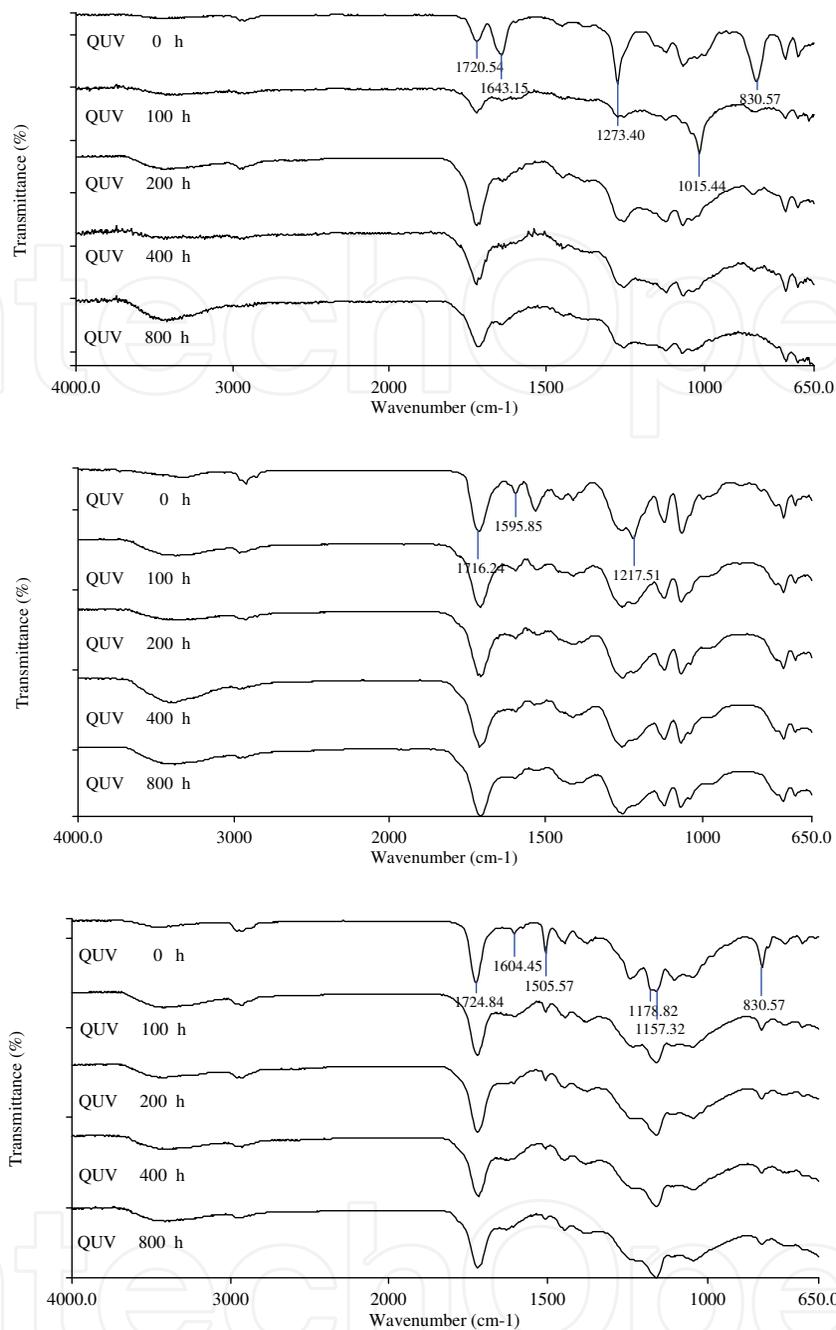


Fig. 8. FTIR spectra of NC lacquer (top of Fig), PU coatings (middle of Fig) and UV curing coatings (bottom of Fig) coated woods degraded by various time of QUV degradations.

To analyze the QUV degradation of coated woods, using FTIR showing the change in the functional bases or the molecular structures in combination with CEM analysis has led to useful results, involving the identification of emission products. Three types of coatings still produced those pollutants (CO and NO_x) after QUV degradation, but the pollutants are relatively a decreasing tendency while comparing to the control ones. When analyzed to the QUV degradation of the coatings, the results enabled us to point out the kinds of functional base or the change in molecular structures for referencing the emissions of the wood coatings.

3.3 Wood preservatives

3.3.1 Emission gas of preservative-treated woods

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, environmental concerns have drastically changed the active ingredients of wood preservatives, resulting in restricted use (Sanders & Windom, 1980; Sanders & Riedel, 1987; Weis & Weis, 1992a, 1992b, 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.

Because wood preservatives are generally produced with various chemical compounds, it is necessary to understand the composition of the gases that are emitted when burning these preservative-treated woods, and the amount of char formed (residual metal) during combustion (Jang, 1997; Kercher & Nagle, 2001; Humphrey, 2002). The recognition of the need for abatement of air pollution has led to further interest in, and investigation of combustion as a major issue when disposing of cellulose wastes and cellulose residual materials (Helsen & Bulck, 1998). Regardless of waste minimization efforts, improved disposal-end management practices will play a key role in minimizing the impacts of disposed of CCA-treated wood in the next 25 to 40 years (Cooper et al., 2003), and of the ACQ-treated woods as well (Lin et al. 2006). To provide an understanding of the disposal of CCA- and ACQ-treated woods and the basic emitted gases generated by burning these materials, our goal in this portion is to acquire fundamental knowledge of the disposal-end practice (residual elements) reference for the char. The emissions from the discharge gas during the preservative-treated specimen combustion and the residual elements of the char after combustion are interpreted, respectively.

One of the studies used *Taiwania cryptomerioides* Hay (Taiwania) as a specimen to be treated with chromated copper arsenate (CCA) or ammoniacal copper quats (ACQ) preservatives. CCA and ACQ-treated woods, the preservatives themselves as well as their individual ingredients during combustion were investigated (Lin et al. 2007). Basically, both woods treated with CCA or ACQ are considered to be a type of cellulose material (Humphrey, 2002). The recognition of the need to reduce air pollution has led to further interest in, and the investigation of the feasibility of combustion to dispose of cellulose wastes and residual materials (Helsen & Bulck, 1998). The results of the emission contents for *Taiwania* and the two types of treated woods are shown in Fig. 9.

The peak for CO gas for the samples of *Taiwania* (T) was found to be 40 sec with 116.0 ppm after the beginning of combustion, after which it showed a decreasing tendency until it became a plateau curve until the end of the combustion time,. However for the CCA specimens a maximum value of CO was obtained at about 115 sec with 108.0 ppm, and for

the ACQ specimens the measurement of the CO gas increased linearly to about 80 sec with 159.3 ppm from the start of the combustion. After that, both became a plateau curve and remained so until the end of the combustion time. This indicated that the emission of CO gas not only was concerned with the ignition time (Ladomersky, 2000; Lin et al., 2001), but also because it resulted in complete combustion at a different combustion time due to the different types of preservatives.

In middle of Fig. 9, The results also found no SO₂ being emitted gas by any of the specimens during combustion, but the specimens whether or not they were impregnated with preservatives all produced NO_x gas (the bottom of Fig. 9). Although it was insignificant for the amount of wood and CCA specimens during the combustion, the peak of NO_x gas for the ACQ specimens was about 26-26.5 ppm at about 75 to 115 sec of the combustion time. NO_x is considered the main source of pollution from burning wood treated with ACQ. The reason for NO_x occurring from the burning of preservative-treated wood is because N is included in both the wood (Shirokae & Samezima, 1996; Kercher & Nagal, 2001; Humphrey, 2002) and in the preservatives (Lin et al., 2006). Either the O₂ or the N₂ reaction from the air and the samples or the fuel, propane, produced the N residues (Lin, 1992; Takabashi et al., 1995). It is inferred that the ignition point and/or the heat decomposition of the preservatives may influence the combustion time and the quantity of emission gases, NO_x.

To understand which preservative-treated wood produced the more serious pollution, the combined results of the emission contents from CCA and ACQ preservatives and their main ingredients of chromium trioxide (CrO₃), cupric oxide (CuO), arsenic pentoxide (As₂O₅), and N-alkyl benzyl dimethyl ammonium chloride (BKC) are shown in Fig. 10.

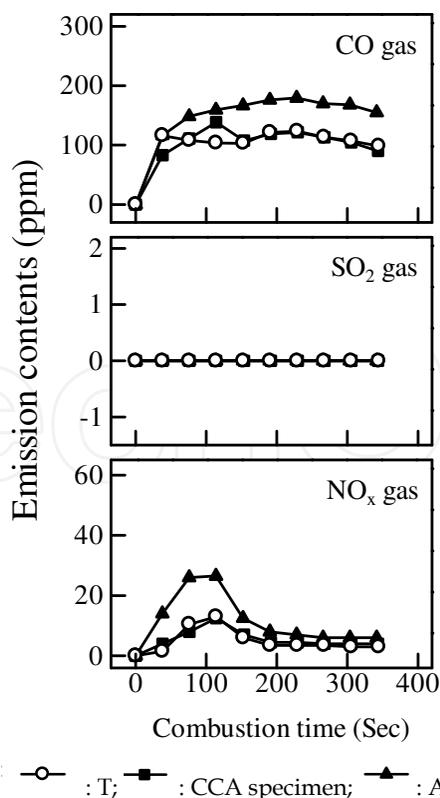


Fig. 9. Relationship between combustion time and emission contents for various experimental specimens.

The above-mentioned situation of incomplete combustion for wood particles (Taiwania) produced CO during combustion. This is attributed to the fact that the particles are wood and are a carbon-hydrogen compound. (Shirokai & Samezima, 1996; Helsén & Bulck, 1998). The same tendency was evident for the CCA and ACQ specimens (Fig. 10). In other words, the influence of different types of preservatives on the production of CO was insignificant during combustion. However, among the ingredients of the preservatives, As_2O_5 (157.0 ppm) and BKC (85.5 ppm) were more significant on the emission of CO during combustion than the others. As expected there was no SO_2 in the emission gases in this experiment during the combustion of the wood, the preservatives or their ingredients because there was no sulphur content in either of the 2 types of preservatives (Nicholas & Schultz, 1994). It is suggested that CCA and ACQ are not the source of the SO_2 in the environment. The results also showed that the ingredients of the preservatives all produced NO_x in the emission gases. However, during the combustion of the wood particles, CCA-3, As_2O_5 , CrO_3 , and CuO , produced less NO_x than the ACQ specimens and ACQ. Of these materials, ACQ and BKC were more significant for the emission of NO_x during combustion than the others chemicals (ingredients). The maximum NO_x of the ACQ and ACQ specimens was about 23.5-26.5 ppm, and was about 32.0 ppm for BKC. This is because the main combinations of ACQ are BKC, and in addition nitrogen (N) is also included in the BKC (Nicholas & Schultz, 1994). This indicates that NO_x is a main source of pollution in wood with ACQ preservatives. Moreover, wood is considered an ecological material (Takahashi et al., 1995), but it is necessary to determine the thermal composition of these preservatives during combustion,

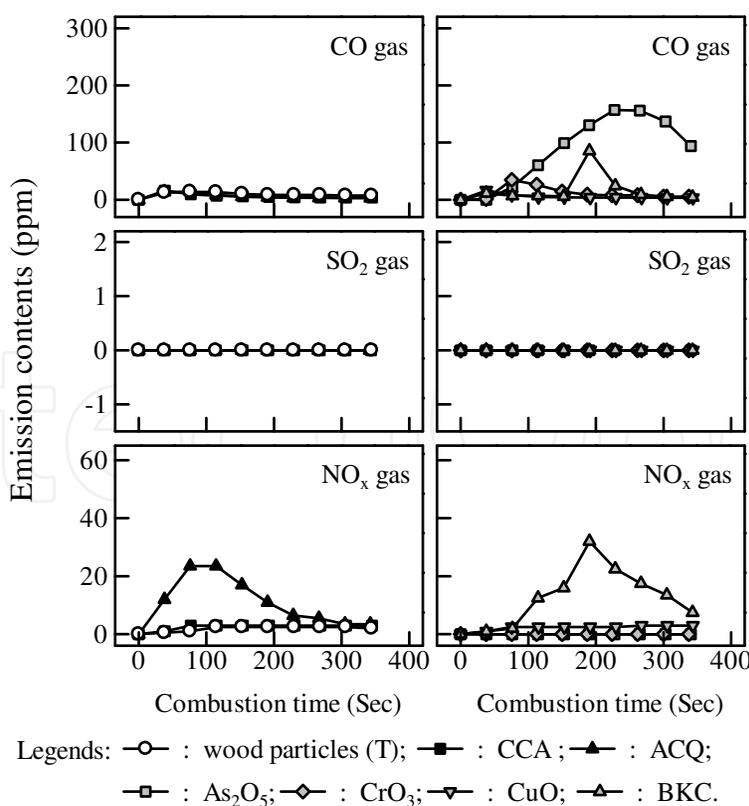


Fig. 10. Relationship between combustion time and emission contents for various wood preservatives and the main components of CCA and ACQ.

including such things as, decomposition temperature, compounds emitted, total amount of volatiles evolved (Kercher & 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. To clarify the residual elements (inorganic and organic materials) of discarded woods treated by either CCA or ACQ, the main ingredients, the wood preservatives, their make-up and the char before/after combustion are analyzed with an Energy Dispersive X-ray Spectrometer (EDX), and are analyzed after combustion using an Elemental Vario CHNS/O analyzer (EA, Germany). The result for the carbon (C), nitrogen (N), sulfur (S), and hydrogen (H) elements was then determined. The EDX results are shown in Table 1.

The main elements of *Taiwania cryptomeroides* (untreated specimens), both preservative woods and preservatives were C, 56.35 % for the untreated specimens, 47.96 % for the CCA specimens, and 50.24 % for the ACQ specimens. For the preservatives, CCA was 4.30 %, and ACQ was 3.74 %. For both of their ingredients, As_2O_5 was 3.25 %, CrO_3 was 1.50 %, CuO was 3.76 %, but BKC was 89.35 %. After combustion, the relative proportion of C was higher, 89.42 % for the untreated specimens, 60.42 % for the CCA specimens, 77.89 % for the ACQ specimens, and 2.70 % for CCA, and 22.13 % for ACQ. In addition As_2O_5 was 1.47 %, CrO_3 was 1.33 %, CuO was 14.02 %, and BKC was unmeasured (trace amount). The results of element O showed that it had relatively decreased for all samples after being burned and the amount of chromium (Cr) for the CCA specimens was 7.38 %, for CCA it was 34.99 %, and the CrO_3 was 64.15 % after being burned. Three of them were obviously more than the relative amount of As (Arsenic, 4.08 % for the CCA specimen, 11.89 % for CCA, and 36.92 % for As_2O_5), and Cu (copper, 5.18 % for the CCA specimen, 16.69 % for CCA-3, and 58.39 % for CuO). This is because the Cr from the char of the CCA preservatives is a stable element (Hirata et al., 1993; Kercher & Nagle, 2001; Cooper et al, 2003; Helsen & Bulck, 2005; Lee et al., 2005). The char of the ACQ specimens left an amount of inorganic metal elements, Cu (2.67 %). As the results (Table 1) indicated, the main char of the ACQ and CuO was Cu, 50.14 and 58.39 % which was almost unable to be combusted toward the end of the combustion (Kercher & Nagle, 2001; Lee et al., 2005; Lin et al., 2006).

Element	<i>Taiwania cryptomeroides</i> Hay (wt %)		CCA Specimen (wt %)		CCA (wt %)		As_2O_5 (wt %)		CrO_3 (wt %)		CuO (wt %)		ACQ Specimen (wt %)		ACQ (wt %)		BKC (wt %)	
	before	after	before	after	before	after	before	after	before	after	before	after	before	after	before	after	before	after
	C	56.35	89.42	47.96	60.42	4.30	2.70	3.25	1.47	1.50	1.33	3.76	14.02	50.24	77.89	3.74	22.13	89.35
O	43.45	8.09	49.43	20.55	59.78	33.50	28.59	49.23	28.14	34.52	24.69	21.89	49.30	7.17	29.94	26.38	—	—
Cr	—	—	0.08	7.38	7.41	34.99	—	—	70.36	64.15	—	—	—	—	—	—	—	—
Cu	—	—	1.75	5.18	16.29	16.69	—	—	—	—	71.55	58.39	0.45	2.67	65.76	50.14	—	—
As	—	—	0.72	4.08	10.21	11.89	68.16	36.92	—	—	—	—	—	—	—	—	—	—

^U Trace amount (can not be measured)

Table 1. EDX analysis of various experimental samples before and after the combustion

Furthermore, the results of EA are shown on Table 2. In addition to the high level of carbon (C), the amount of N (1.42 %) was higher for ACQ than that for the other specimens, and the BKC was almost burned out (could not be measured). This inferred that the ACQ specimen could greatly produce NO_x gases (Fig. 10) during combustion. The result of the EA analysis inferred that the ACQ specimen could produce NO_x gases during combustion, because the amount of N (1.42 %) was higher for ACQ than for the other specimens, and the BKC was

almost burned out. The above results suggest that by using EDX and EA to analyze the residual elements in char, the results can provide experimental data for referencing the char of preservative-treated woods in CEM tests.

Element	Taiwania <i>cryptomerioides</i> Hay	CCA specimen ¹	CCA	As ₂ O ₅	CrO ₂	CuO	ACQ specimen	ACQ	BKC
C	79.58 (0.03)	75.38 (0.54)	0.03 (0.01)	— ¹⁾	87.04 (0.17)	63.73 (0.08)	80.93 (0.20)	4.51 (0.11)	—
N	0.28 (0.04)	0.15 (0.01)	0.05 (0.01)	—	0.97 (0.05)	0.03 (0.02)	0.33 (0.01)	1.42 (0.01)	—
S	1.17 (0.62)	0.60 (0.04)	0.36 (0.02)	—	3.22 (0.02)	0.53 (0.17)	0.54 (0.08)	0.41 (0.07)	—
H	3.27 (0.03)	2.90 (0.04)	0.19 (0.01)	—	2.68 (0.20)	0.36 (0.59)	3.13 (0.03)	0.55 (0.03)	—

¹⁾ Trace amount (can not be measured).

Table 2. EA analysis of various experimental samples after the combustion

3.3.2 Thermal decomposition of wood preservatives

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. 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 (as a slow-heating regime) or at 40 °C/min (fast-heating regime), in order to isolate the decomposition step. 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 relationships of the TGA and the DTG curves between temperature and weight loss, and the derivative weight for each preservatives sample, creosote, CCA and ACQ, are shown in Fig.11.

The results obtained that regardless of the heating rate, the three types of wood preservatives typically showed gradual weight loss and 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 was more than that of the ACQ, and the amount of char for the creosote was lower than that for either of the water-based preservatives. Hirata et al. (1993) reported that Cr and Cu from the CCA preservatives were largely present in the char and that arsenic (As) was easily volatilized with the increase in temperature during combustion. Some researches (Kercher & Nagle, 2001; Cooper et al., 2003; Helsen & Bulck, 2005) stated that in the TGA tests, when CCA preservatives were analyzed with air, AS₂O₅ was formed in a gaseous state and that it disappeared at a temperature of over 600 °C. In addition, CuO produced Cu₂O 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 CCA are remained. The results of ACQ 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. These results are 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. Therefore, the char of CCA was higher than that of ACQ (the top of Fig. 11), based on the different heating rates (5 or 40 °C/min) set.

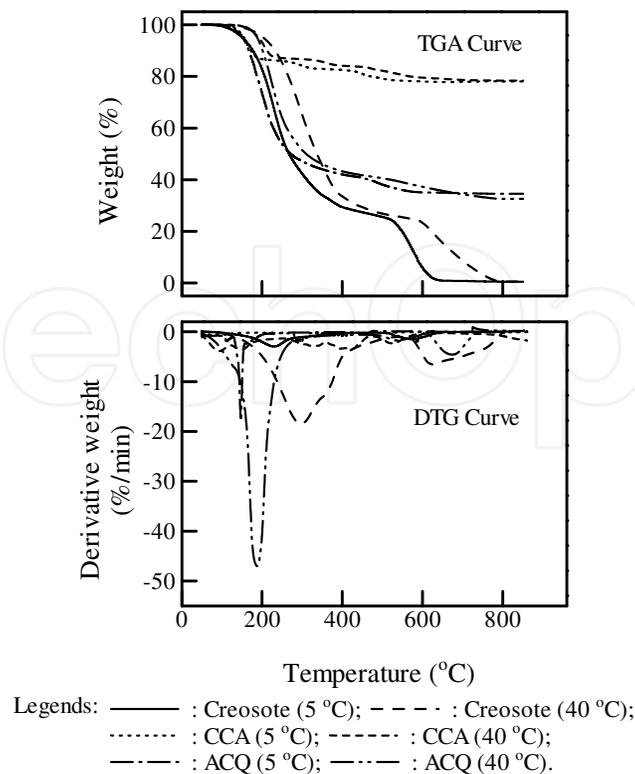


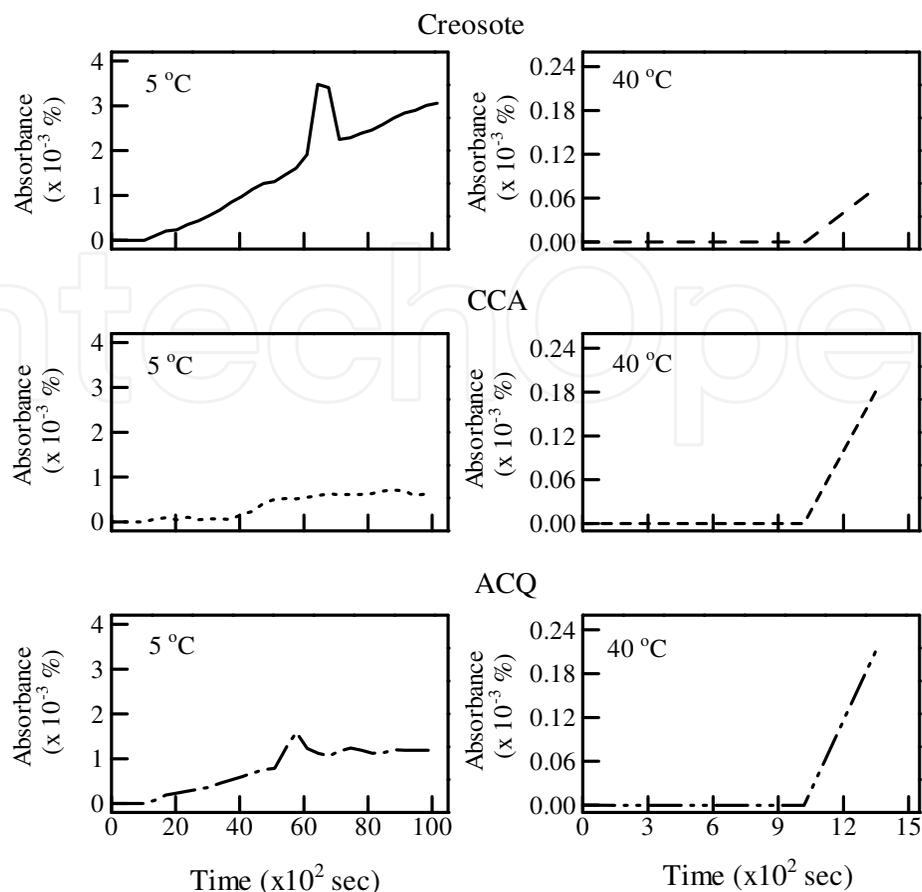
Fig. 11. TGA and DTG curves for 3 types of wood preservatives (Creosote, CCA and ACQ) in air at 5 or 40°C/min.

3.3.3 Evolved species and char of wood preservatives

Because the thermal decomposition of all combustible materials produces a toxic smoke, and combustion toxicology indicates adverse effects produced from exposure to fire-generated toxic species (Hartzell, 1996), the understanding of the evolved species and the char of wood preservatives is analyzed. Figure 12 shows the infrared spectrometric (IR) response of the three types of preservatives for both heating rates, at 5 °C/min and 40 °C/min in the TGA-IR measurements.

The change in absorbance (concentration of evolved species, %) corresponds to the increase in decomposition time for the three preservatives. 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 and ACQ. This indicated that the concentration of evolved species of water-based preservatives was less than those of oil-based ones. Of them all, CCA was inferred to be the best preservatives with the least environmental impact, if the disposal process of the preservatives was combustion and considering the results of air pollution only. It is indicated that CCA is the better environmentally friendly preservatives for wood protection, because the emission contents of CCA are less than those of ACQ, considering their environmental impact only during combustion.

Furthermore, the right side of Fig. 12 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 IR response of ACQ showed a greater peak at the end than that of creosote and CCA. This suggests that at 40 °C/min of the heating rate, the concentration of evolved species for ACQ is higher than that for either creosote or CCA. Comparing the IR



Legend: The legends are the same as Figure 11.

Fig. 12. IR response of 3 types of wood preservatives in air at 5 or 40 °C/min from TGA-IR analysis.

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.

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. The evolution of decomposition time (or temperature) on absorbance and wavenumbers (basically, IR spectra) for three types of preservatives is shown in Fig. 13. 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), even for the different preservatives.

For the creosote, the 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

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.

For CCA, 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 beginning 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.

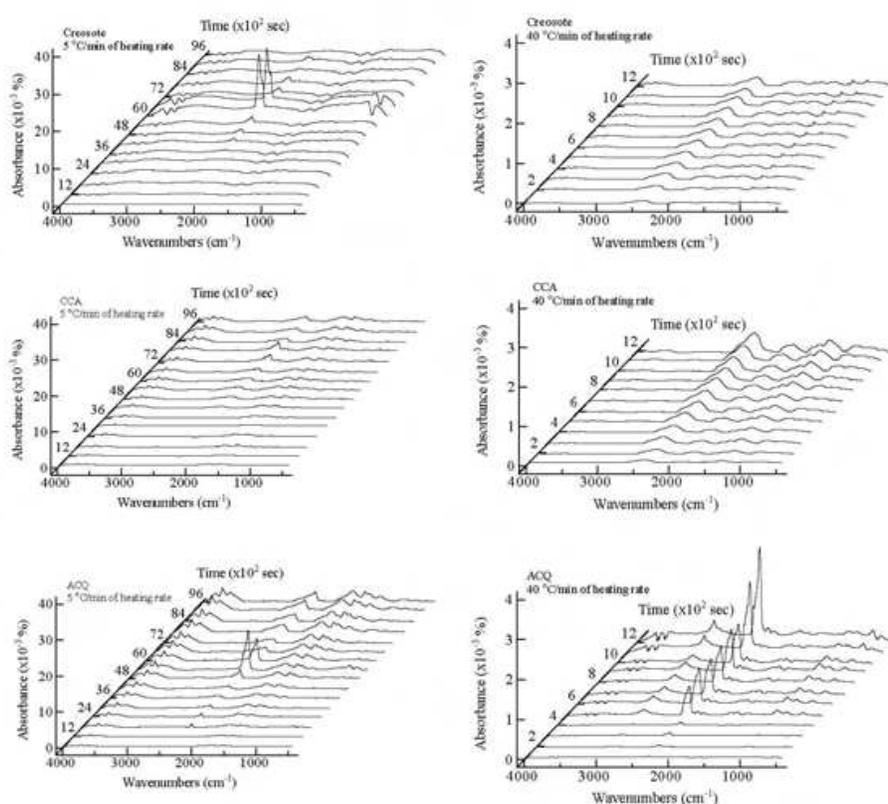


Fig. 13. TGA-IR spectra of 3 types of wood preservatives in air with 5 or 40°C/min.

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.

For ACQ at the heating rate of 5 °C/min (bottom left in Fig. 13), 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 , the CO₂ peak was located at 2296 and 2356 cm^{-1} from the beginning to about 1210 sec (850 °C). 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.

From the above results, it is suggested that using TGA-IR, to analyze the thermal behavior of wood preservatives, in combination with TGA analysis, has led to useful results, involving the identification of pyrolysis products.

4. Conclusion

To realize fundamental knowledge of the thermal decomposition of the wood-based waste processing-materials, including wood adhesives, wood coatings and wood preservatives, while at the same time understanding an air pollution reference for emission gases, evolved species and a disposal-end practice (of the residual elements) reference for the char. This chapter is mainly focused on examining the emission gas concentration and the fundamental thermal decomposition, as well as analyzing the evolved species and the char of wood-based waste processing-materials. The following results were obtained.

By using the CEM, the larger or greater these materials are, the greater the emission contents and the longer the combustion time. The concentration of O₂ was negatively and CO₂ was positively related to the emission gas temperature. Both O₂ and CO₂ had a close relationship during combustion. The main pollutants during combustion were from the ingredients of these materials, and the incomplete combustion was one of main variable factors related to the quantities of emission content (CO) and change O₂ and CO₂ concentration in the air. SO₂ was not produced during combustion for these materials because their ingredients did not have a sulfur-base. The emission contents of CO, SO₂ and NO_x were found that for the adhesive, the PB manufactured with PF adhesive had the least pollution gas during the combustion than the others. This suggested that PF is the best adhesive with the least environmental impact to use for manufacturing PB. For wood coatings and wood preservatives, the emission contents were still produced after having been accelerated weathering degradation, but they were relatively a decreasing tendency. Furthermore, the results of FTIR, when analyzed to the degradation of the coated woods for referencing the emissions of the coatings, indicated that the change of various functional bases or/and

molecular structures were occurred. The result of the EA indicated that prior to combustion, the amount of nitrogen (N) is higher for the ACQ-treated woods than that for the CCA ones; therefore, the NO_x gases during combustion were higher for the ACQ-treated woods.

By using the TGA, the results of wood adhesives found that MDI exhibited the highest initial decomposition and better overall thermo-stability than the other types of adhesives. PF and MDI provided a better yield of char and their thermal behavior was better than that of UF or MUF. The thermal properties of CCA- or ACQ-treated wood were similar to that of untreated wood in either nitrogen or air atmosphere, but the pyrolysis temperature for the slow-heating regime was lower than that of fast-ones. Regardless of different atmosphere or heating rate, the char of the CCA-treated wood and the CCA was more than that of the ACQ ones and the ACQ. The EDX analysis of both-treated woods indicated that the relative proportion of carbon was higher after thermal decomposition. Chromium (Cr) from the char of CCA is a stable element, and the amount of Cr is obviously more than that of Arsenic (As) and copper (Cu), and the char of ACQ left a high amount of Cu.

By using the TGA-IR, the IR response of the adhesives showed that the absorbance of UF, MUF and MDI was higher than that of PF; this indicated that the concentration of evolved species of PF was less than that of MDI, and less than that of UF and MUF. These results, when compared to the molecular structures of the adhesives, enabled us to point out the kinds of evolved species (functional bases or the change in molecular structures) for referencing the thermo-degradation processes of the adhesives. The preservatives showed that considering the decomposition step (thermal time or temperature) at different heating rates, the results obtained showed that at the slow-heating regime, the concentrations of CO₂ produced by creosote and ACQ were higher than that of CCA, but at the fast-heating regime, the concentration of CO₂ for ACQ was higher than that of creosote and CCA. Moreover, these results, when compared to the chemical ingredients of the preservatives and EDX analysis, enabled us to point out the kinds of evolved species for referencing the thermo-decomposition processes of the preservatives before/after time degradation.

The use of CEM for investigating the emission gases, TGA for analyzing the thermal properties of the wood-based waste processing-materials, in combination with TGA-IR, FTIR, EDX and EA analysis, has led to useful results, regarding the identification of thermal decomposition products (evolved species and char).

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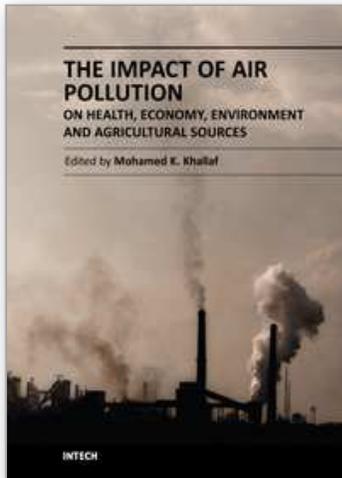
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This book aims to strengthen the knowledge base dealing with Air Pollution. The book consists of 21 chapters dealing with Air Pollution and its effects in the fields of Health, Environment, Economy and Agricultural Sources. It is divided into four sections. The first one deals with effect of air pollution on health and human body organs. The second section includes the Impact of air pollution on plants and agricultural sources and methods of resistance. The third section includes environmental changes, geographic and climatic conditions due to air pollution. The fourth section includes case studies concerning of the impact of air pollution in the economy and development goals, such as, indoor air pollution in México, indoor air pollution and millennium development goals in Bangladesh, epidemiologic and economic impact of natural gas on indoor air pollution in Colombia and economic growth and air pollution in Iran during development programs. In this book the authors explain the definition of air pollution, the most important pollutants and their different sources and effects on humans and various fields of life. The authors offer different solutions to the problems resulting from air pollution.

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