Faculty of Resource Science and Technology

ANALYSIS OF ORGANIC COMPOUNDS IN EFFLUENT FROM WOOD INDUSTRY

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DECLARATION

I hereby declare that no portion of the work referred to in this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

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ABSTRACT

Waste water samples were collected from one of wood industry in Pending Industrial Estate, Kuching. The sample was passed through a cellulose thimble and the eluate was then collected in 500 mL capacity separatory funnel. The water sample (eluate) was then extracted by liquid-liquid extraction using dichloromethane at pH 8. This extract contains base/neutral extractable compounds. Subsequently, the water sample was then extracted at pH 2. This extract contains acid extractable compounds. The particulate remained in thimble was also extracted on Soxhlet extractor using dichloromethane. The extracts represent compounds in particulate matter. All the extracts were then analysed on capillary gas chromatography/mass spectrometry (GC/MS). Several priority organic pollutants listed by the U.S EPA were detected in the waste water sample from wood industries. This compounds including halogenated compounds, phthalates, phenols, alcohols, aldehydes, ketones, ethers, esters, acid groups and, aliphatic and aromatic hydrocarbons which the sources are considered from the additives that were used in the mill processes and naturally from raw material (wood).

Key words: Effluent, organic compound, wood industry.

ABSTRAK

Sampel air kumbahan telah dikumpulkan dari sebuah industri perkayuan di kawasan perindustrian Pending, Kuching. Sampel air ini dituras menggunakan timbel selulosa dan hasil turasan dikumpukan dalam 500 mL corong pemisah. Hasil turasan kemudian diekstrak menggunakan kaedah pengestrakkan cecair-cecair dengan pelarut diklorometana pada pH 8. Ekstrak mengandungi sebatian organik yang boleh terekstraks dalam keadaan bes/neutral. Hasil turasan seterusnya diekstrak pada pH 2 dan ekstrak mengandungi sebatian yang boleh terekstraks dalam keadaan asid. Partikel yang termendap di dalam timbel selulosa juga diekstrak menggunakan kaedah pengestrakan Soxhlet dengan pelarut diklorometana. Ekstraks ini mengandungi bahan organik dalam partikel terampai. Kesemua ekstraks dianalisis menggunakan kromatografi gas/spektrometri Jisim. Beberapa sebatian organik yang disenaraikan sebagai pencemar utama oleh U.S EPA telah dikenalpasti dalam ekstrak dari air kumbahan. Ini termasuklah sebatian berhalogen, ftalat, fenol, alkohol, aldehida, keton, ester, eter, kumpulan asid serta hidrokarbon alifatik dan aromatik yang dipercayai berpunca daripada bahan additif yang digunakan dalam pemprosesan kayu dan mungkin wujud secara semulajadi daripada bahan mentah (kayu).

Kata kunci: Bahan organik, industri kayu, kumbahan

CHAPTER 1

INTRODUCTION

1.1 Wood Industry in Sarawak

Sarawak is a state in East Malaysia with 10 million hectares of forest on its 12.3 hectares of land, and dominates the Malaysian forestry sector. This forestry sector has been an important foreign-exchange earner for Sarawak's economy as well as in Malaysia as a whole, after petroleum and gas-related products. It started with the export of round logs in the 1950's and 40 years later, log export still dominates.

This wood industry includes the manufacturing of sawntimber, panel products and wooden furniture. Wood industry can be divided to two categories: primary wood industry and secondary wood industry (Bramwell, 1976). Primary wood industry is consisting of firms that manufacture logs and pulpwood into value added wood product. This primary wood industry consists of three types; sawmills and plywood mills which are produced sawntimber and panel products such as veneer, plywood, particleboard, fibreboard and laminated veneer lumber, mouldings and builders' carpentry and joinery (BCJ). Secondary wood industry is consisting of firms that manufacture dimensional and reconstituted wood products into value added wood product consist of furniture and cabinet manufacturers such as door and chair. Usually, the famous timber species used as raw materials such as meranti, nyatoh, chengal, keruing, kempas, jelutong, ramin, balau, merbau and rubberwood and these are obtained from natural forests, forest plantations and rubber plantations.

Sarawak is the world's largest exporter of tropical logs, mostly to the Japan, Korea and Taiwan markets (Tropical Timbers, 1996). The level of exports has been decreased slightly over recent years, with the South Pacific, especially Papua New Guinea (Asian Timbers, 1996). The fiberboard from Sarawak was exported to China, Japan and Saudi Arabia, and by this Malaysia is the 10^{th} largest exporter of MDF in the world. Besides that exports of mouldings and BJC are mostly to USA, Japan, Australia and United Kingdom.

Additionally, wood industry is one of the most important industries of countries. Since the technology has been added to the modern mills to further improve their outputs and productions, it can increase the economy of countries by export the product (Williams, 1989). For example, China exports their wooden furniture to many countries including the United State and Japan. The growth of these industries also cause a social impact, which is when the out migration move to this industrial area to find a job and the effect is existence of mixed society with varies of religion and people of nation in this area (Bliss and Bailey, 2002).

The wood industry is a growing sector that requires a large amount of water and energy, and the main environmental issues are emissions to water and air, and also energy consumption. However, the common problems related to this industry are the wastewaters that can be released to the environment or even remain after conventional treatment.

The effluents of this wastewater exhibit characteristic of hazardous waste (organic compound) which is mainly corrosivity and toxicity because they contain considerable amounts of fibers and chemicals (Suntio et al., 1988). These compounds come from the raw materials (wood extractives) or additives, which are used during the wood processing such as wood preservation processes (Jukka and Jaakko, 1994). Wood industry effluents discharged into freshwater, estuarine and marine ecosystem causes water pollutions, alter aquatic habitat, affect aquatic life and may present a risk to human health.

Some example of the organic compounds that has been found in the effluent of wood industries such as pentachlorophenol (Haloui and Vergnaud, 1995), sodium pentachlorophenate (Bouzon et al., 1996), 2-(thiocyanomethylthio)-benzotiazole, methylene-bis-thiocyanate and 2, 2 dibromo-3-nitrilpropionamide (Lacorte et al., 2003).

These chemicals are released either into air or water when the sample comes into contact with water and leading to a dangerous pollution (Maklnen et al., 1993) and tedious problems of decontamination (Dahab et al., 1991).

1.2 Environmental Problem / Impacts Associated with Wood Industry

The several problems from the wood industry pollutions such as volatile organic compounds (VOC's) play a significant role in the chemical reactions that form ozone. Ozone is not emitted directly into the atmosphere. It is formed when emissions of nitrogen oxides and VOC's react in the presence of sunlight (Ann, 1997). While beneficial in the upper atmosphere, ozone in the lower atmosphere can cause a variety of health problems such as damages lung tissue, reduces lung function, and adversely sensitizes the lungs to other irritants (Ann, 1997).

Organic Halides which are compounds are formed as a result of reaction between residual lignin from wood fibres and iodine or chlorine compounds during the preservation processes. Many of these compounds are recalcitrant and have long-half life periods and some of them show tendency to bioaccumulate in fish tissue. This may present a risk to human health if large amounts of fish exposed to these substances are consumed (Savant and Ranade, 2005).

Exposure to dioxin and furan can cause skin disorders, cancer, and reproductive effects. These pollutants can also affect the immune system (Carrere & Lohmann, 1996). Creosote can cause the skin to become unusually sensitive to sunlight. The skin may darken more readily, and become sunburned more easily. Creosote also contains compounds called polynuclear aromatic hydrocarbons (PAHs). So, inhaling high levels of creosote may potentially harm the kidneys and nervous system. These chemicals have been known to cause cancer in animals and human beings (Milton, 1986).

1.3 Objectives of the Project

The main objectives of this project is to extract the organic compounds from waste water released from wood industry, and to identify the organic compounds in base/neutral extractable fraction, acid extractable fraction and particulate matter using gas chromatography/mass spectrometry (GC/MS). The other objective is to predict the source of organic compounds that is presented in wastewater of wood industry.

CHAPTER 2

LITERATURE REVIEW

2.1 Wood Preservation

Wood preservation can be interpreted broadly to cover protection from fire, chemical degradation, mechanical wear and weathering. It also can be interpreted as a wood treatment method or process using chemicals that can prevent the biodegradation which is cause by biological attack such as fungi, insect, and borers (Walker, 1993), and therefore to extend the range of applications and the service life of the wood. By design, the chemicals used to protect wood must be toxic to the target organisms, but they may also affect non-target organisms and the environment.

2.1.1 Preservation Processes

Malaysian woods usually treated by three types of treatment processes; Bethell (full cell) treatment proceses, Vacuum processes and Oscillating pressure processes.

2.1.1.1 Bethell (full cell) processes

This is the simplest and most common of the vacuum-pressure processes. The full cell process is used for most of the pressure treatments using chromated copper arsenate (CCA) and pentachlorophenol-based (PCP) preservatives, and a good proportion of the treatments with creosotes (Walker, 1993).

2.1.1.2 Vacuum processes.

Typically tri-n-butyl tin oxide (TBTO) or tri-n- butyl tin napthenate (TBTN) is used together with an insecticide as a preservative during this process (Walker, 1993).

2.1.1.3 Oscillating pressure processes

This pressure treatment use water borne salts such as copper-chrome arsenate (CCA) as a chemical preservative (Walker, 1993). This method utilizes repeated applications of high pressure and vacuum to force preservatives into green wood.

2.1.2 Preservatives Formulations

The preservatives used are approved by Pesticides Board of Malaysia such as Tar oil Preservative (creosote), Light Organic Solvents Preservative (LOSP) and Water-borne preservatives (Lim et al., 2005)

2.1.2.1 **Tar oil Preservative** (Lim et al., 2005)

Tar oil preservatives such as creosotes is the oldest timber preservatives used and still provides excellent protection to timber in a variety of end uses. Creosote is a black oily liquid which is produced by the distillate of coal tar. This distillate consists principally of liquid and solid aromatic hydrocarbon and contains quantities of tar acid such as phenol and naphtols, and bases such as pyridines and quinolines. Creosote is insoluble in water and is resistant to leaching. The oily nature of the preservatives protects the timber against weathering and splitting in service.

2.1.2.2 Light Organic Solvents Preservative (LOSP)

LOSP are a group regarded mainly as fungicides, the major toxicants being pentachlorophenol and closely-related tetrachlorophenol which are produced by the chlorination of phenol; Tributyl tin oxide which is manufactured by organotin compounds; and Metallic naphthenates such as copper and zinc naphthenates which are prepared by combining soluble metal salts and napthenic acid were widely used for treating lumber in sawmills (Hilditch and Mendes, 1987).

The most effective and widely used fungicides and insecticides that have been used in timber preservation are like pyrethroids, lindane and dieldrin, organophosphates and organochlorines (Lim et al., 2005).

2.1.2.3 Water-borne preservatives

It also called arsenical preservatives. This preservative divided into three types which are Anti-sapstain, boron types and copper chrome arsenate (CCA) (Walker, 1993).

2.1.2.3.1 Anti-sapstain (Wong et al., 1995)

Chemical treatments to prevent fungal degrade of timber during seasoning have been employed for many years. The most important active chemical types likely to be found in sapstain control registered in Malaysia such as chlorinated phenol, thiocyanates, benzothiazole, organo-metallic compounds, triazoles, alkyl ammonium compounds, Iodine based-compounds, phenols and carbamates. Sodium pentachlorophenate (NaPCP) is the one of anti-sapstain widely used in every country. However, it is banned by the Malaysian Government from January 2000 regarded as a highly toxic chlorinated phenol.

2.1.2.3.2 **Boron types** (Dickinson and Murphy, 1989; Lim et al., 2000)

This preservative based on boric acid or sodium borates are effective in protecting timber against insect attack. The preservatives are usually the disodium octaborate tetrahydrate type and used to treat freshly sawn timber.

2.1.2.3.3 Copper Chrome Arsenates (CCA)

This preservative widely used in Malaysia for treatment of roof and ceiling components (Wong and Tsang, 2001). CCA offer fungicidal and insecticidal activity by combining salts of copper, chromium and arsenic (Walker, 1993). However, CCA use Ammoniacal Copper Quat (ACQ) and Copper-Azole as a chemical alternative (Lim et al., 2005).

2.2 Chemical Classes and Application of Preservative Containing Compounds.

Some preservatives have similar properties based on their chemical structure such chemicals belong to the same chemical class and frequently have similar toxicological modes of action. Table 1 show the classes of compound and their applications which are found in preservative.

Table 1: The classes of compound which are found in preservative (Jensen et al., 2001).

Chemical Classes	Applications
Alkyl phthalate	Insecticides and insect repellents.
Azole/ Triazoles	Fungicides (anti-sapstain)
Benzimidazole	Fungicides
Carboxamide	Fungicudes
Thiocyanate	Anti-sapstain formulations.
Chlorinated phenol	Microbiocides and fungicides.
Diacylhydrazine	Insecticides.
Dicarboximide	Fungicides.
Dithiocarbamate	Fungicides.
Halogenated organic	Fungicides (anti-sapstain)
N-Methyl carbamate	Pesticides.
Organoarsenic	Chemical warfare agents.
Organochlorine	Insecticides
Organophosphorus	Pesticides.
Organomercury	Insecticides.
Phenol	Pesticides
Petroleum derivative	Insecticides. Eg. Creosotes
Pyrazole	Insecticide.
Pyrethroid	Synthetic insecticides.
Quaternary ammonium	Microbiocides
Silicone	Antifoaming agents and emulsifiers.
Substituted benzene	Fungicides.
Benzothiazoles	Anti-sapstain.

2.3 Effluent from Wood Industry

The effluents from wood industry will become a threat to the environment since they consist of chemicals and organic compounds from various processes. The types of organic compounds in effluents depend on the raw material, the chemical process, and the additives used (Lacorte et al., 2003).

These effluents have been found to contain more than 200–300 different organic compounds (Fortin et al., 1998; Houk, 1992; Pérez-Alzola and Santos, 1997). In effluent of wood industry mill didecyl-dimethylammonium chloride, o-ortho phenol, and oxine copper (Sarlin et al., 1999). Other organic compounds that are also found such as 2, 2 dibromo-3-nitrilpropionamide and 2-(thiocyanomethylthio)-benzotiazole, wood extractive includes resin and fatty acids, sterols, steryl, alcohol, triglycerides and lignan that dissolve in water (Lacorte et al., 2003). Polychlorinated dibenzo-para-dioxin (PCDD) and Polychlorinated dibenzo-furan (PCDF) also found in effluent of pulp and paper mill (Harris and Elliot, 2000). Dioxin and furan compounds have been detected in some effluents of wood mill, along with polychlorinated dibenzothiophene (Munawar et al., 2000), and these compounds also have been reported in waste water effluents from wood industry in Masan Bay, Korea (Im et al., 2002).

According to Merja et al. (2001), some of organic compounds were occurred such as chlorophenols in effluent of sawmill and plywood mill. Wood treatment is the main source of these compounds. Chlorophenols consisted of 2, 3, 4, 6-tetrachlorophenol, 2, 4, 6-

trichlorophenol and pentachlorophenol (Lampi et al., 1992). These chemicals were used to preserve the wood against fungal attack, and Gutiérrez et al. (2002) reported the found phenol compounds from Chilean sawmills. The other antifungal compounds such as 2-(thiocyanomethylthio)-benzotiazole (TCMTB), methylene-bis-thiocyanate (MBT), bis (trimethylsilyl) trifluoroacetamide (BSTFA), trimethylchlorosilane and 2, 2 dibromo-3-nitrilpropionamide (DBNPA) also found in effluent of these mills (Lacorte et al., 2003).

Chemical compounds such as Dichloromethane, Chromium, Cadmium, Iron, Aluminum, Bis-(2-ethylhexyl) phthalate, Zinc, Di-n-butylphthalate and Benzene was found from the effluent of Wood Preservation Industries Ltd. Plant which is located at Tracy, Canada (Cooper, 1994). According to Otson (1991), dibutyl phthalate was detected in the effluent of wood mill in New York City. The source of this pollution was from the water draining off a former drying area for treated wood.

CHAPTER 3

MATERIALS AND METHOD

3.1 General Background of the Study Site

The wood mill selected for this study is one of wood industry in Pending Industrial Estate, Kuching. This mill occupies ten acres area and is situated at the side of Sungai Sarawak. The main product of this mill is sawn timber. This sawn timber is for export and local sale. The major market of this export includes Thailand, Taiwan, South Korea, Japan and Netherland.

This industry used vacuum and pressure technique to obtain deep penetration of permeable timbers. This treatment requires large heavy gauge cylindrical pressure vessel up to 2 X 30 m in size.

3.2 Sample Collection, Handling and Storage

Wastewater samples were collected using 2.5 liter amber bottles from several locations in wood industry. All of samples were iced or refrigerated at 4°C from the time of collection until extraction. This is to minimize the change that might occur such as chemical and physical reactions and biological degradation during the storage (Kent and Payne, 1988).

3.3 Extraction

Prior to extraction wastewater samples were filtered through a cellulose thimble. The filtrate was collected in 500 mL separatory funnel and represent water sample. The remains in cellulose thimble represent particulate matter. Water samples were extracted by liquid-liquid extraction and particulate matters were extracted by Soxhlet extraction.

3.3.1 Acid and Base/ Neutral Extraction

The extractions of organic compounds from effluent samples were carried out using liquid-liquid extraction according to USEPA (1986) protocol. This extraction protocol is designed to extract acid and base-neutral extractable compounds from the effluent. Briefly, 500 mL water samples were placed in separatory funnel. The pH of samples was checked with wide-range pH paper and adjusted to pH 11 with sodium hydroxide solution. Then, 30 mL dichloromethane was added to the separatory funnel and shaked for 30 seconds to rinse the inner surface. The organic layer was allowed to separate from the water phase for a minimum of 10 minutes. The organic bottom layer was collected in a 250 mL Erlenmeyer flask. The extraction procedures were repeated for a second time by added 30 mL of dichloromethane, and the extract was then combined in Erlenmeyer flask. The third extraction was performed in a same manner and the combined extracts were labeled as the base/neutral fraction, and then vapourized using rotor vapour. The residue was added with 1 ml dichloromethane and the samples were ready to be analysed using GC/MS. For the acidic extraction, the pH adjusted to less than 2 by using sulfuric acid. The step of acid extraction is the similar to base-neutral extraction.