UNIVERSITI PUTRA MALAYSIA

EFFECTIVENESS OF PYROLIGNEOUS ACID PYROLYSED FROM TROPICAL LIGNOCELLULOSIC BIOMASS AS BIOPRESERVATIVE

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

August 2015

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Lignocellulosic biomass are natural and abundantly available resource has been steadily gaining attention from relevant industries as feedstock for the production of chemicals, fuels and biocompatible materials due to increased concern in economic and environmental issues. The potential of being converted into usable chemicals which pyroligneous acids is one of the chemicals from the distillation of smoke generated during charcoal making. It was found to be potential use as bio-preservative due to the complex mixture of water, acetic acid, methanol, acetone, formic acid, guaiacols, catecols, syringols, vanillins, furan carboxaldehydes, isoeugenol, pyrone and more than 200 organic compounds including phenolic compounds, which are pyrolytic products of lignin and hemicellulose. This study focuses on development of pyroligneous acid as bio-preservative against wood biodegradable agents. Pyroligneous acids derived from different types of lignocellulosic biomass at temperature of; 300°C, 400°C and 500°C. The chemical compounds were then analysed using Fourier Transform Infrared (FT-IR) Spectroscopy and Gas chromatography – mass spectrometry (GC-MS). The results showed that pyroligneous acids derived with 3 temperature ranges were slightly different in chemical compositions, but significantly different in the contents of each chemical component. A total 24, 23 and 22 compounds were identified from the Rubberwood, OPT and Mix Hardwood pyroligneous acid, respectively. Ketones, organic acids, aldehydes, esters, phenols and its derivatives were found in the pyroligeneous acids where acetic acid and phenol were the primary compounds in the pyroligneous acids. For the efficacy of pyroligneous acid test, rubberwood test block was immersed in pyroligneous acid for 24 h at room temperature. Treated rubberwood test block were later tested against mold (*Penicillium chrysogenum*), white rot fungus (*Pycnoporous sanguineus*) and subterranean termites (*Coptotermes curvignathus*) according to ASTM standard methods. Results showed that Pyroligneous acids pyrolysed from sawdust of rubberwood, oil palm trunk and mixed hardwood are effective against biodegradable agents. The test blocks treated with all pyroligneous acids produced from different temperatures are equally effective against the mold, decay fungi and termites. Compounds 2-methoxy-phenol and 4-ethyl-2-methoxy-phenol contributed to inhibit *Penicillium chrysogenum*, compounds 4-ethyl-2-methoxy-phenol contributed to inhibit *Pycnoporus sanguineus* while compounds acetic acid and phenol in pyroligneous acids

found to be active chemicals in controlling termite attacks. Therefore, further studied had been carry out using OPT and Rubberwood pyroligneous acid pyrolysed at 500°C with impregnation method using different concentration of 100%, 50% and 30% of pyroligneous acid. Results showed that dilution of pyroligneous acid were effective against mold and decay fungi while only had mild effectiveness against termites. Rubberwood and OPT pyroligneous acids at 500ºC in dip-treatment process gave the best antimicrobial properties while Mix hardwood showed the best performance in antitermites properties. All the pyroligneous acid used in dip-treatment process showed equal antifungal properties. Concentration 50% Rubberwood and 30% OPT pyroligneous acids were effective against mold inhibition and decay fungi with impregnation process compared to 100% concentration pyroligneous acids with dip-treatment process. However, concentration of pyroligneous acids in impregnation and dip-treatment process showed mild effective to termites attacked.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan Ijazah Doktor Falsafah

KEBERKESANAN ASID PYROLIGNEOUS PYROLISIS DARIPADA LIGNOSELULOSA BIOMAS TROPIKA SEBAGAI BIO-PENGAWET

Oleh

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Lignoselulosa biomas adalah sumber semula jadi dan boleh didapati dengan banyaknya. Dengan peningkatan perhatian dalam isu-isu ekonomi dan alam sekitar, ia telah semakin mendapat perhatian daripada industri berkaitan sebagai bahan mentah untuk pengeluaran bahan kimia, bahan api dan bahan biocompatible. Salah satu potensi yang menukarkannya menjadi bahan kimia yang berguna iaitu asid pyroligneous, dimana ianya salah satu bahan kimia yang terjana daripada penyulingan asap semasa pembuatan kayu arang. Ia didapati potensi sebagai bio-bahan pengawet disebabkan kerumitan sebatian air, asid asetik, metanol, aseton, asid formik, guaiacols, catecols, syringols, vanillins, karbohidrat furan, isoeugenol, pyrone dan lebih daripada 200 sebatian organik termasuk sebatian fenolik, yang merupakan produk pirolisis lignin dan hemiselulosa. Kajian ini memberi tumpuan kepada pembangunan asid pyroligneous sebagai bio-pengawet terhadap agen biodegradasi kayu. Asid Pyroligneous diperolehi dari pelbagai jenis lignoselulosa biomas pada suhu 300°C, 400°C dan 500°C. Sebatian kimianya dianalisis dengan menggunakan Fourier Transform Infrared (FT-IR) Spectroscopy dan Gas chromatography – mass spectrometry (GC-MS). Hasil kajian menunjukkan bahawa asid pyroligenous diperolehi daripada 3 julat suhu adalah sedikit berbeza dalam komposisi kimia, tetapi berbeza dengan ketara dalam kandungan setiap komponen kimia. Sebanyak 24, 23 dan 22 kompaun telah dikenal pasti daripada asid pyroligenous Kayu Getah, Batang Kelapa Sawit dan Campuran Kayu Keras masing-masing. Keton, asid organik, aldehid, ester, fenol dan terbitannya ditemui dalam asid pyroligeneous di mana asid asetik dan fenol adalah bahan utama dalam asid pyroligenous. Blok kayu getah direndam dalam asid pyroligneous selama 24 jam pada suhu bilik untuk menguji keberkesanan asid pyroligneous. Blok kayu getah yang telah dirawat kemudiannya diuji dengan pulapok (*Penicillium chrysogenum*.), kulat (*Pycnoporous sanguineus*) dan anai-anai (*Coptotermes curvignathus*) mengikut Piawaian ASTM. Hasil kajian menunjukkan bahawa asid Pyroligneous yang dihasilkan daripada habuk kayu getah, batang kelapa sawit dan campuran kayu keras berkesan terhadap agen biodegradasi kayu. Blok kayu yang dirawati dengan asid pyroligneous yang dihasilkan daripada suhu yang berbeza didapati adalah sama berkesan terhadap kulat, pulapok dan anai-anai. Sebatian 2-methoxy-fenol dan 4-etil-2-methoxy-fenol menyumbang untuk menghalang *Penicillium chrysogenum*, sebatian 4-etil-2-methoxy-fenol menyumbang untuk menghalang *Pycnoporus sanguineus* manakala sebatian asid

asetik dan fenol yang terkandung dalam asid pyroligenous didapati mengawal serangan anai-anai. Oleh itu, kajian lanjutan dijalankan dengan menghasilkan asid pyroligneous daripada batang kelapa sawit dan kayu getah pada suhu 500°C dan dirawat dengan kaedah tekanan dengan kepekatan asid pyroligneous 100%, 50% dan 30%. Keputusan menunjukkan bahawa pencairan asid pyroligneous adalah berkesan terhadap kulat dan pulapok manakala hanya keberkesanan yang sederhana terhadap anai-anai. Asid pyroligneous daripada Kayu Getah dan Batang Kelapa Sawit pada suhu 500ºC dalam proses celup-rawatan memberikan ciri-ciri antikulat terbaik manakala Campuran kayu keras menunjukkan keberkesanan terhadap anai-anai. Semua asid pyroligenous yang digunakan dalam proses celup-rawatan menunjukkan sifat antikulat yang sama. Kepekatan asid pyroligenous 50% Kayu Getah dan 30% Batang Kelapa Sawit adalah berkesan terhadap kulat dan pulapok dengan proses impregnasi berbanding 100% kepekatan asid pyroligenous dengan proses celup-rawatan. Walau bagaimanapun, kepekatan asid pyroligenous dalam proses impregnasi dan celup-rawatan menunjukkan keberkesanan yang sederhana terhadap anai-anai.

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation and gratitude to my supervisory committee, for all the construction comments, guidance, ideas and supervision that enabled the completion of this research project.

My appreciation also to my dearest friends for their indirect involvement in helping me complete this research study.

Last but not least, I would like to thank my parents and for their enormous love, support in completing this research study.

I certify that a Thesis Examination Committee has met on 13 August 2015 to conduct the final examination of Lee Soon Heng on his thesis entitled "Effectiveness of Pyroligneous Acid Pyrolysed from Tropical Lignocellulosic Biomass as Biopreservative" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
FT-IR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas chromatography – mass spectrometry
LSD	Least Significant Difference
MX HW	Mix Hardwood
OPT	Oil Palm Trunk
P.A	Pyroligneous Acid
RT	Room Temperature
RW	Rubberwood
SAS	Statistical Analysis System

CHAPTER 1

INTRODUCTION

1.1 Background

Lignocellulosic biomass is referring to plant biomass which is built up by cellulose, hemicellulose and lignin (Perez, 2011). Lignocellulosic biomass can be coming from wide range of source; trees to agricultural residues. Therefore it is considered the most abundant material in the world. Every year, there are about 2 x 10^{11} tons of lignocellulosics biomass are produced as waste in the world (Perez, 2011). This includes the wood residue from primary and secondary wood products mills such as sawmills, wood and bark from pulp and paper mills, panel mills, crafts and furniture. Other example of lignocellulosics biomass waste includes residue of demolition, FRQVWUXFWLRQ GLVFDUGHG ZRRG SURGXFWV DQG DJULF

Lignocellulosic biomass can be produced into many valuable products. Previous study IURP +¶QJ VKRZHG WKDW OLJQRF ellulosic biomass are capable produced into wood composites product such as plywood, wood plastic composite and laminated veneer lumber without any modifications on the resin formulation. He also found that, lignocellulosic materials have wide potential as chemical derivatives either for food or for energy (Chin, 2010). In his study, he found that fermentation of lignocellulosic biomass to ethanol is an alternative route to energy feedstocks which helps covering the depleting source of fossil fuels (Chin, 2010; Bhattacharyya *et al.*, 2013).
Lignocellulosic biomass also has potential in the chemical derivation to produce usable products through bioconversion techniques. In theory, the components of wood can be converted into any desired chemicals; the chemicals which can be in practice derived from wood depend greatly on its chemical composition. One of the chemicals that can be derived from lignocellulosic biomass is pyroligneous acid through pyrolysis method. In this study, the pyroligenous acid was produced from two major lignocellulosic biomasses available in Malaysia. The two main lignocellulosic biomass sources in Malaysia which are wood residues from wood working industry and oil palm trunks that removed during the oil palm replanting activities. The oil palm trunks were not only underutilized but also causes pollution as well (Ratnasingam *et al*., 2008).

Pyroligneous acid appears in dark and reddish-brown colour. The chemical composition of pyroligneous acid includes acetic acid, methanol, acetone, wood oils and tars (Lee *et al.*, 2011; Ninomiya *et al.*, 2004). Wood vinegar is another term for pyroligneous acid. Currently, pyroligneous acid is mainly used as fertilizer additives, deodorization agents and also as a natural aid for mild pain relief and detoxification. It also helps in sterilizing and promotes healing for minor wounds.

For years, public had put their special attention to the workability of pyrolysis of biomass since it helps reducing environmental pollution especially that arising from wastes accumulation and open field burning (Bonelli *et al.*, 2001). It is useful for vermin examination, deodorant and soil improvement. However, further study on the characteristics to establish new functionality such as new biocides against wood biodegradation would be greatly helpful (Lee *et al.*, 2011; Kartal, 2004). Among different potential uses of pyroligneous acid, many research organizations have put their special attention on developing the pyroligneous acid into wood preservatives (Suzuki *et. al.*, 1997 & Mourant *et. al.*, 2005).

1.2 Statement of problem and justification

In the world economy, wood plays an important role as a renewable resource. However, wood is subject to deterioration by mold, insects like termites, and wood degrading fungi. To avoid deterioration of wood during storage, manufacturing, transportation or when in service, it needs to be protected. Protection of wood can be generally realized by doing preservation it. Wood preservation can increase the durability and resistance to organisms that cause deterioration with different chemical and processes.

Currently there are several commercial wood preservatives which are in the form of oil-borne and water-borne. These are typically toxic, not environmental friendly and also not renewable. Due to the public concern, people are looking into more environmental friendly alternative wood preservative. One of the solutions is by introducing natural chemical derived wood preservative from plants, which is pyroligneous acid that produced from pyrolysis process of lignocellulosic biomass. Pyroligneous acid from pyrolysis process of wood is believed to prevent the wood from termite and fungal attack due to its complex structure.

Pyroligneous acids have a potential source of valuable chemicals that can be developed as a new wood preservative against biological degradable (Lee, 2010). Mohan *et al.* (2007) stated that the pyroligneous acid can be used as preservatives for timber in wet condition while Jung (2007) stated that it could inhibit the growth of pathogenic fungus, *Alternaria mali*, which is known as the agent of Alternaria blotch of apple plants.

Pyroligneous acid could also be used as a fungicide for wood preservative as Bruce and Highley (1991) stating that it is useful for controlling the wood decay Basidiomycetes. Lee (2010), Yatagai *et al.* (2002) and Sameshima *et al.* (2002) have done the correlation of termiticidal activity with acetic acid and phenolic contents in the pyroligneous acid produced from charcoal production. From research of Nakai, *et al.* (2007) it is found that the resistance of wood against brown-rot fungi can be strengthened by pyroligneous acid from pyrolysis of sugi and acacia wood. Femi-Ola (2008) stated that many researchers are now focused towards the alternative non toxic and biological methods of controlling termites. Therefore, the production of these chemical products from pyroligneous acid could become economically viable and profitable.

As mentioned early, the pyroligneous acid is the product produced from high temperature carbonization of lignocellulosic biomass. However, the content of chemical compounds in pyroligneous acid depends on the biomass chemical composition mainly the three major components, i.e. cellulose, hemicellulose and lignin. The interaction of the three major components during pyrolysis show different reactivity depending on temperature condition of decomposition of each component (Lee *et al.*, 2010; Diem *et al.*, 2005). The overall pyroligneous acid conversion level related with interactions between the components and minus amounts of mineral matter that naturally present in whole biomass samples which catalyze numerous reactions taking place during pyrolysis and affect the final content of pyroligneous acid (Lee *et al*., 2010; Bonelli *et al*., 2001; Liu *et al.*, 2008).

The main chemical compounds of pyroligneous acids include methanol, allylalcohol, acetic acid, acetone, acetaldehyde, methyl acetone, furan and furfural, and formic, propionic and butyric acids (Tiilikkala *et al*., 2010). Pyroligneous acids may also contain various phenolic compounds, fermentable sugars, furan compounds, organic acids, etc. The degradation of lignin and wood sugars is generally forming phenolic compounds and organic acid are believed to be derived from acetyl groups in the hemicelluloses.

Velmurugan *et al.* 2009 showed that the pyrolysis of bamboo and broad-leaved trees produce acids (mainly acetic acid) and phenols, which have great antifungal properties that is found useful in wood treatment. Salim *et al.* (2014) showed that 4-ethyl-2-methoxyphenol, 2, 6-dimethoxyphenol, guaiacol and cresol, in pyroligneous acids showed good antifungal activity.

Therefore, in this study the effectiveness of pyroligenous acid produced from ruuberwood waste, mixed hardwood waste and oil palm trunk at three different temperatures as wood preservative were evaluated on rubberwood block for mold, decay fungi and termites biodegradation.

1.3 Objective

The main objective of this study is to evaluate the efficacy of pyroligneous acid pyrolysed from lignocellulosic biomass as wood bio-preservative against mold, fungus and termites.

The specific objective:-

1 To study the physical and chemical compositions of pyroligneous acid derived from different types of lignocellulosic biomasss.

2 To determine the effectiveness of rubberwood treated with pyroligneous acid pyrolysed from different lignocellulosic biomass and temperature against mold (*Penicilium chrysogenum*).

3 To determine the effectiveness of rubberwood treated with pyroligneous acid pyrolysed from different lignocellulosic biomass and temperature against decay fungi (*Pycnoporous sanguineus*).

4 To determine the effectiveness of rubberwood treated with pyroligneous acid pyrolysed from different lignocellulosic biomass and temperature against ternites (*Coptotermes curvignathus*).

5 To enhance the effectiveness of pyroligneous acid as wood preservative using impregnation method on rubberwood block.

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