MODIFICATION OF LIGNIN CONTENT IN WOOD FIBER BY MICROWAVE HEATING AND LACCASE TREATMENT

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A thesis submitted in fulfillment of the
requirement for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
Universiti Malaysia Pahang

DECEMBER 2010

ABSTRACT

Oxidoreductases and by microwave heating can be applied for bonding of fiberboards. The objectives of this research are to modify the lignin content of wood fibers by using enzymatic treatments and by microwave heating treatments to make binderless boards and to determine the use of laccase treatment and by microwave heating can give promise and possibilities for industrial bonding and modification of lignin. In this research, the fiberboards were prepared from four different treatments which are untreated, UF-resin treated, microwave heating treated and laccase treated 6U/g fiber boards. Hot pressing at constant 200°C and 4 minutes pressing was done to form the boards. For each treatment the boards were tested for modulus of elasticity (MOE), modulus of rupture (MOR) and internal bond strength (IB). From the results obtained, the microwave heating treated boards displayed quite comparable in average mechanical property within the UF-resin treated (standard) boards meanwhile for laccase treatment of fibers, it displayed the lowest MOR and MOE values. As a conclusion, the microwave heating treatment shows promise and possibilities for industrial bonding and modification of lignin content in wood fiber. However, the laccase treatment can be potentially improved through extensively studies in future regarding on the use of laccase for adhesion enhancement in binderless wood boards because it had been proved on recent studies that laccase used resulting in boards with good mechanical properties without toxic synthetic adhesives. For recommendation, in future, research regarding wood modification in lignin content by microwave heating and enzyme treatment could be optimized and enhance by variances of a number of process parameters such as temperature, time pressing, pressure and moisture content.

ABSTRAK

Oxidoreductases dan pemanasan ketuhar boleh digunakan untuk ikatan papan. Tujuan kajian ini adalah untuk mengubah kandungan lignin fiber kayu dengan menggunakan enzim dan pemanasan ketuhar untuk membuat papan *binderless* dan menentukan penggunaan enzim laccase dan pemanasan ketuhar dapat memberikan janji dan kemungkinan untuk ikatan industri dan pengubahsuaian lignin. Dalam kajian ini, fiber kayu disediakan daripada empat kaedah berbeza iaitu tanpa tanpa rawatan, dirawat, penggunaan UF-resin, pemanasan ketuhar dan penggunaan 6U laccase / g fiber. Pemanasan pada suhu tetap 200 °C selama 4 minit dilakukan untuk menghasilkan papan. Setiap papan diuji untuk ujian kelikatan (MOE), ujian kekuatan (MOR) dan kekuatan ikatan dalaman (IB). Dari hasil yang diperoleh, papan yang dihasilakn daripada pemanasan ketuhar papan sebanding dengan papan yang dihasilkan daripada resin-UF sedangkan untuk papan daripada kaedah laccase memberikan nilai MOR dan MOE terendah. Sebagai kesimpulan, rawatan pemanasan ketuhar menunjukkan hasil positif dan penggunaan dalam industri untuk pengubahsuaian kandungan lignin dalam serat kayu dapat dilakukan. Namun, kaedah laccase berpotensi untuk dipertingkatkan melalui kajian secara meluas pada masa depan mengenai penggunaan laccase untuk peningkatan ikatan dalam papan kayu Binderless kerana telah terbukti penggunaan laccase dapat menghasilkan papan dengan sifat mekanik yang baik tanpa menggunakan bahan kimia yang berbahaya. Untuk penambahbaikan, di masa depan, kajian mengenai pengubahsuaian kandungan lignin dalam fiber kayu oleh pemanasan ketuhar dan rawatan enzim mesti dioptimumkan dan melibatkan parameter proses yang lain seperti suhu, tekanan panas, tekanan dan kandungan kelembapan.

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LIST OF ABBREVIATIONS

ABTS	2,2-azinobis-(3-ethylbenzenthiazoline-6-sulfonic acid)
HAA	Hydroxyanthranilic
HDF	High-density fiberboard
HBT	1-hydroxybenzotriazole
IB	Internal bonding
LMS	Laccase-mediator
LiP	Lignin peroxidase
MC	Moisture content
MDF	Medium-density fiberboard
MOE	Modulus of elasticity
MOR	Modulus of rupture
MUF	Melamin-urea-formaldehyde
MnP	Manganese peroxidase
NHA	N-hydroxyacetanilide
OSB	Oriented strand board
PB	Particleboard
PF	Phenol-formaldehyde
UF	Urea-formaldehyde
UV	Ultraviolet
VA	Violuric acid

LIST OF NOMENCLATURES

V	Volume
M	Mass
ρ	Density
O_2	Dioxygen
H_2O_2	Hydrogen peroxide
PhOH	Phenolic hydroxyl
PhO	Phenoxy
g	Gram
U/mg	Unit activity of enzyme

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CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

Lignin comprises as much as 40 percent of wood's mass, therefore the development and modification for the use of lignin is an attractive and environmentally intelligent goal. Lignin's random and non-crystalline network structure makes it a very thermodynamically stable biopolymer (Glasser 1981).

Wood composites are a class of materials that generally consist of solid fragments of wood that are reconstituted in a form fit for a designated end-use by some sort of adhesion process. Plywood, fiberboards, particleboard, oriented strand board (OSB), and wood plastic composites are all members of this class of composites (J. Youngquist, 1999). Over time, wood composites have been reconstituted from ever-smaller wood fragments, progressing from plies to strands to fibers to fine 'flour' measuring only microns in size. Wood composites are capturing ever-larger markets, partially in response to reduction in the supply of solid, large dimension timber (S. Shook, I. Eastin, 2001). Composites in general are materials that combine the high strength and stiffness characteristics of a fiber (or particle) with the ductility of a (continuous) matrix (J.E. Gordon, G. Jeronimidis, 1980). In many man-made composites the fiber matrix interface is the weakest point resulting in ‘fiber pull-out’ and failure before the fiber reaches its true strength potential (B. Harris, 1980). Many wood composites also suffer from the high density that is the result of thermal processing under high-pressure conditions (A.R. Sanadi, D.F. Caulfield, R.E. Jacobson, 1997). The ideal wood-like composite would combine the features of a high-strength and high stiffness (hollow) fiber embedded in a continuous matrix from which it never (under any condition of moisture or temperature) separates inter-facially, and with which it produces a lightweight material (G.M. Bond, R.H. Richman, W.P. McNaughton, 1995).

Bonding of lignocellulosic material is essential for the manufacture of particleboard, fiberboard, oriented strandboard, laminated wood products and plywood. Bonding of wood fibers or particles can be achieved by high pressures and temperatures, a phenomenon known as auto-adhesion. The effect can be used for making binderless boards and panels, e.g. masonite boards, but compared to boards made with synthetic adhesives the mechanical properties are inferior. The auto-adhesion of beech wood (*Fagus sylvatica*) fibers can be enhanced by a pretreatment of the fibers with a phenol oxidase enzyme (Felby et al., 1997 and Felby et al., 2002).

Bonding of wood fibers and particles by adhesives can be accomplished by forming a resinous matrix in which the particles or fibers are bonded together, e.g. by mechanical entanglement or covalent cross-linking (Claus Felby et al., 2002).

In current commercial bonding process, an adhesive is spread or sprayed on the surface of the material. Procedures have been proposed to create adhesion through formation of wood-to-wood chemical bonds, but have not met commercial acceptance (D Yelle et al., 2004).

The concept of using lignin-oxidizing enzymes for bonding applications is based on the reactivity of phenoxy radicals in the plant cell wall. In vivo, oxidoreductases such as laccase catalyze polymerization of lignin through cross-linking of phenoxy radicals and thus it may be possible to utilize a similar type of reaction for bonding of lignocellulosic materials in vitro (Claus Felby et al., 2002). Kharazipour et al. (1993) also described a procedure for bonding wood fragments together in the manufacturing of a composite product. A commonality in their procedures for bonding wood fragments is the activation of the middle lamella lignin of the wood cell wall through incubation with phenol-oxidizing enzymes. Using this technique, molded products were created without additional bonding chemicals.

In addition, the use of laccase as an oxidative enzyme for this research is applies due to its versatility applications which is enzymatic treatment conditions are often milder, less damaging to the fiber, and are environmentally friendly compared to chemical treatments which involve harsh reaction conditions, loss of desirable components, and potential use of hazardous chemicals.

Furthermore, the mechanism of microwave application on wood fiber for heating is based on the characteristics of water molecules, which are highly polar. Besides, wood contains a significant amount of water, which makes it a good candidate for microwave heating. When microwave is applied, water molecules absorb the electromagnetic energy, which causes violent vibration and friction among water molecules, which produces heat. Wood fiber as a dielectric material also absorbs microwave energy to some extent and converts the electromagnetic energy into heat (James Deng 2005).

In addition, the microwave heating is very different from hot platen heating. The characteristics of microwave heating are fast heating speed, reasonably good uniformity, swift and accurate process control and high flexibility. Some earlier works include the study of wood drying using microwave (Egner 1965 and Walters 1972), experimental work on dielectric characteristics of Douglas-fir under microwave (James and Hamill 1965) and studies of adhesive bonding and treatment of wood composite products with microwave heating (Matsuda and Mori 1975 and Kawase and Hayakawa 1974) due to many unique advantages of microwave.

Regarding wood products made with the increasingly expensive petroleum-derived adhesives, manufacturers of medium-density fiberboard (MDF) and particleboard (PB); structural panels such as plywood and oriented strandboard (OSB); solid-wood joints, are keen to reduce production costs and harmful formaldehyde emissions from the adhesives, and to improve product recyclability.

In addition, the adhesive components are derived from petroleum, which is increasingly more expensive (Sellers T, 2001, Maloney TM, 1996) in North America alone, the total amount of wood adhesive solids used for wood composites was around 1.8 Mt (Sellers T, 2001). Therefore, meeting these challenges calls for innovative approaches to minimize the amount of binder, e.g. masonite boards, while ensuring product quality. Another important topic related to wood products is the chemical modification of their surface and bulk properties to improve their durability, enhance their properties strength, range of application, and compatibility with other materials for use in hybrid products such as wood–plastic composites. The cost of pulping may also be an issue for wood products such as fiberboards whose manufacturing process includes pulping.

In its search for solutions to the above-discussed challenges, the goal of this research are to use enzymatic treatment and by microwave heating of wood fibers before their pressing into composite boards such as MDF and as a means for making boards without petroleum-derived wood adhesives and to promote a more environmentally friendly, less expensive alternative for bonding of wood in the wood composite industry.

1.2 PROBLEM STATEMENT

Wood composite boards such as MDF and PB such as chipboard are commonly used for interior building and furnishing (Sellers T 2001, Maloney TM 1996, Youngquist JA 1999). The thermosetting adhesives used in MDF and PB, mainly UF but also melamin-urea-formaldehyde (MUF) and phenol-formaldehyde (PF), account for ~10% of the board mass.

Many grades of high-density fiberboards (HDF boards, hardboards) also require a certain amount of binder. Formaldehyde is used in glues in composite wood products such as medium density fiberboard or MDF and particle-board which are generally recognised as being the highest formaldehyde-emitting composite wood product (used for kitchen and bathroom cupboards and drawers, and wardrobes); particleboard (used as sub-flooring and shelving and in cabinetry and furniture); and plywood paneling (used for decorative wall covering and used in cabinets and furniture).

Occupational exposure to formaldehyde by inhalation is mainly from three types of sources: thermal or chemical decomposition of formaldehyde-based resins, formaldehyde emission from aqueous solutions (for example, embalming fluids), and the production of formaldehyde resulting from the combustion of a variety of organic compounds (for example, exhaust gases).

Formaldehyde can be toxic, allergenic, and carcinogenic. In addition, the health-hazards of formaldehyde (carcinogenic to humans) emissions during board production and end-use of fiberboard products made with amino resins (UF and MUF) are a concern among consumers and manufacturers (Sellers T 2001, Youngquist JA 1999). Because formaldehyde resins are used in many construction materials it is one of the more common indoor air pollutants. At concentrations above 0.1 ppm in air formaldehyde can irritate the eyes and mucous membranes, resulting in watery eyes. Formaldehyde inhaled at this concentration may cause headaches, a burning sensation in the throat, and difficulty breathing, as well as triggering or aggravating asthma symptoms. Formaldehyde has also been shown to have short-term health effects, including burning sensations in the eyes and throat, nausea, and difficulty in breathing.

Formaldehyde is also the primary cause of methanol's toxicity, since methanol is metabolised into toxic formaldehyde by alcohol dehydrogenase. Formaldehyde is converted to formic acid in the body. Emission of harmful formaldehyde from adhesives is currently causing significant health concerns. If this unwanted formaldehyde is spread widely, exposure to its toxicity and volatility will course major problem and will be resulting in the health diseases of human.

1.3 OBJECTIVES

The research was conducted to achieve the following objectives:

(1) To modify the lignin content of wood fibers by the use of laccase enzymes and by microwave heating to make binderless wood boards.

(2) To determine the use of laccase treatment & microwave heating can gives promise & possibilities for industrial bonding & modification of lignin.

1.4 SCOPES OF STUDY

In order to achieve the objectives, the following scopes have been identified.

(i) Reviewed on the literature review on the latest development and related study on lignin modification in wood fiber.

(ii) A pre-treatment of the fibers with the laccase treatment and microwave heating followed hot pressing to made boards.

(iii) Tested the board mechanical properties.

(iv) Analyzed data.

(v) Thesis report writing.

1.5 RESEARCH CONTRIBUTIONS

Modifications of lignin content in the woods using oxidative laccase enzymatic treatment and by microwave heating are beneficial to the environment and society. There are several benefits which are:

(i) Contribute to the personnel protection in preventing the harmful emission substances from adhesives which is reduces health hazards for production personnel.

(ii) Promote a more environmentally friendly, less expensive alternative for bonding of wood in the wood composite industry which is preserving and protecting environment.

Both economical and health benefits could thus be obtained from binderless (synthetic resin-free) production processes. Moreover, the “mega-trends” of favoring renewable raw materials and waste elimination (Sellers T, 2001) are compatible with binderless composite boards.

CHAPTER 2

LITERATURE REVIEW

2.1 Chemical composition and content of lignin

The three major constituents of plant biomass are lignin (20% in wood), cellulose (50%) and hemicellulose (25%) (Bobleter, 1994). It is relatively hydrophobic and aromatic in nature. The degree of polymerisation in nature is difficult to measure, since it is fragmented during extraction and the molecule consists of various types of substructures which appear to repeat in a haphazard manner. Variance types of lignin have been described depending on the means of isolation.

Lignin fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components, especially in tracheids, sclereids and xylem. It is covalently linked to hemicellulose and thereby crosslinks different plant polysaccharides, conferring mechanical strength to the cell wall and by extension the plant as a whole. It is particularly abundant in compression wood but scarce in tension wood.

Lignin is an amorphous polymer which functions as a cementing material in wood cells; it comprises approximately 20–32% of the dry wood mass. A study by Boeriu et al. (2004); Chakar and Ragauskas (2004) stated lignin is a natural polymeric product arising from an enzyme initiated dehydrogenative polymerisation of the three primary precursors shown in Fig.2.1. It is an integral part of lignocellulosic materials with the relative amount present varying over the approximate range of 10–30%.

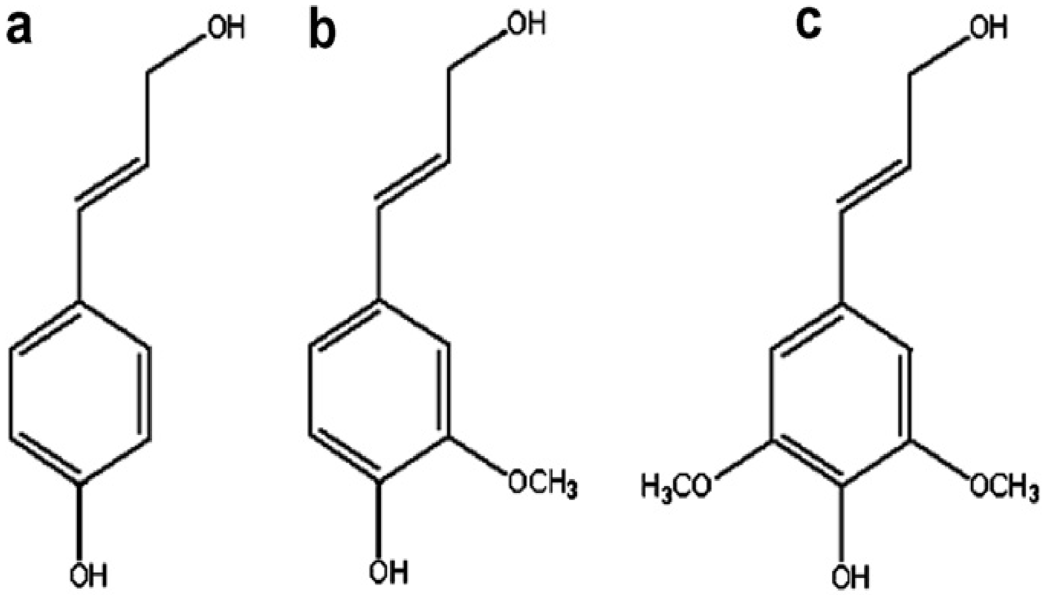

Fig.2.1. Lignin precursors: (a) p-coumaryl alcohol, (b) coniferyl alcohol and (c) sinapyl alcohol

Lignin may be divided into three broad classes which are soft wood, hard wood and grass lignin, according to their composition in structural units (Adler, 1977 and Roberts, 1996). A typical soft wood lignin, also called guaiacyl or coniferous lignin is made up of coniferyl alcohol units. Soft wood lignin isolated by different methods and from different species is very similar in their structure and a molecular model of a typical soft wood lignin molecule is shown in Fig. 2.2. The molecule shown has a molar mass of 1692, which is very close to the number average molar mass of alkali (Kraft) lignin commercialised by Aldrich. On the other hand, lignin is highly polydisperse and significant amounts of molecules up to 100 times larger are also present. Hard wood or dicotyledonous angiosperm lignin is made up of coniferyl and sinapyl alcohol units. For a grass lignin which is an annual plant or monocotyledonous angiosperm lignin is made up of coniferyl, sinapyl and p-coumaryl units.