UNIVERSITI PUTRA MALAYSIA

OPTIMIZATION OF GLYOXALATION FOR ALKALI LIGNIN USED AS BULKING AGENT IN WOOD

ANG AIK FEI

FH 2016 9

OPTIMIZATION OF GLYOXALATION FOR ALKALI LIGNIN USED AS BULKING AGENT IN WOOD

By

ANG AIK FEI

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

April 2016

DEDICATION

I specially dedicate this thesis to

My Supervisor
Prof. Dr. Zaidon Bin Ashaari

My Mother
Kua Ai Lian

My Father
Ang Boon Lip

My Wife
Gan Peg Kee

My Daughters
Ang Min Xuan & Ang Yu Xuan

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

OPTIMIZATION OF GLYOXALATION FOR ALKALI LIGNIN USED AS BULKING AGENT IN WOOD

By

ANG AIK FEI

April 2016

Chairman : Zaidon Ashaari, PhD
Faculty : Forestry

Bulking treatment through the impregnation of low molecular weight phenol formaldehyde (LmwPF) resin is a promising method to enhance the dimensional stability of wood. The development of bulking agent that made of modified alkali lignin, the glyoxalated alkali lignin is crucial to mitigate the concentrations of petrochemical derived phenol and carcinogenic formaldehyde. The objective of this study was to enhance the structural homogeneity and chemical reactivity of alkali lignin through sequential organic solvents fractionation and glyoxalation, and to enhance the dimensional stability of jelutong (*Dyera costulata*) wood using glyoxalated alkali lignin incorporated with low molecular weight phenol formaldehyde resin as bulking agent.

Low molecular weight lignin feedstock was obtained through base catalysed depolymerisation (BCD) treatments from an alkali lignin (OL) with a weight-average molecular weight (M_w) of 11646 g/mol at different combined severity factors. The homogeneity of the OL and BCD treated lignins was altered through sequential fractionation using organic solvents with different Hildebrand solubility parameters i.e. propan-1-ol, ethanol and methanol. The yield of OL and BCD treated lignins dissolved in propan-1-ol (F1), ethanol (F2), and methanol (F3) and their molecular weight distributions and chemical structures were determined and characterized by Gel Permeation Chromatography (GPC), Fourier transform infrared (FT-IR) spectroscopy and ^{13}C-nuclear magnetic resonance (NMR) spectroscopy. The reactivity of the obtained low molecular weight lignin feedstock was then enhanced through glyoxalation using non-volatile and non-toxic dialdehyde, namely glyoxal, instead of formaldehyde. The proportion ratio of glyoxal to sodium hydroxide (NaOH) used in the glyoxalation process was optimised using response surface methodology (RSM) and central composite design (CCD). The glyoxalated alkali lignin (GL) synthesised using the optimum proportion ratio of glyoxal to NaOH was then incorporated with LmwPF resin to prepare bulking agent for wood bulking treatment. Oven dried jelutong (*Dyera costulata*) wood was evacuated under vacuum and then followed by soaking in 15, 20 and 25% concentrations of GL-LmwPF (67% solid of GL:33% solid of LmwPF based on the total solute content) and LmwPF resins, respectively at ambient temperature for 24 h. The impregnated wood was then curing at 180 °C for 30 min. The resin weight percent gain (WPG) and dimensional stability in terms of antiswelling efficiency (ASE), moisture excluding efficiency (MEE) and water absorption (WA) as well as leachability of bulking agents for GL-LmwPF treated wood were determined and compared with untreated wood and wood treated solely with LmwPF resin. The formaldehyde release for both GL-LmwPF and LmwPF treated wood were also determined.

BCD treatments did not increase the yield of an OL dissolved in propan-1-ol or ethanol but did increase the yield of OL dissolved in methanol. Repolymerization of OL occurred during the BCD treatment. Lower molecular weight, more homogeneous OL tended to dissolve in propan-1-ol and ethanol, but their overall soluble lignin yields were low. The OL dissolved in methanol had higher molecular weight, was less homogeneous, and had a bulkier structure than OL dissolved in propan-1-ol or ethanol. ^{13}Carbon-NMR and FT-IR spectroscopy analyses confirmed that F3 in OL exhibits optimum yield and appropriate chemical structures as well as molecular weight distributions for resin synthesis. For glyoxalation of alkali lignin, FT-IR spectroscopy revealed that lower molecular weight of lignin polymers was formed due to the crosslinking of lignin molecules *via* methylene (CH_2) bridges through the condensation reaction. RSM and CCD showed that the reactivity of GL reached highest when optimum amounts of glyoxal and NaOH, i.e., 0.222 and 0.353 mole, respectively, were used in the glyoxalation process. The WPG of GL-LmwPF treated wood was lower than LmwPF treated wood. GL-LmwPF treated wood exhibited positive ASE but the values were lower compared to LmwPF treated wood. The MEE and WA of GL-LmwPF treated wood were also inferior than LmwPF treated wood and untreated wood. GL-LmwPF resin was leached from treated wood whereas no leaching was found for LmwPF resin after 3 leaching cycles in distilled water. The formaldehyde release of GL-LmwPF resin treated wood was 25.76% lesser than wood treated with LmwPF resin. Wood treated with 25% GL-LmwPF resin yielded highest ASE value compared to 15 and 20% GL-LmwPF treated wood. Hence, wood treated with 25% GL-LmwPF resin together with external coatings could be used in several end applications such as parquet flooring, paneling and furniture component.

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

PENGOPTIMUMAN GLYOXALASI UNTUK LIGNIN ALKALI DIGUNAKAN SEBAGAI EJEN PUKAL DALAM KAYU

Oleh

ANG AIK FEI

April 2016

Pengerusi : Zaidon Ashaari, PhD
Fakulti : Perhutanan

Rawatan pukal melalui pengisitepuan fenol formaldehid resin (LmwPF) berberat molekul rendah adalah satu kaedah yang berkesan untuk meningkatkan kestabilan dimensi kayu. Pembangunan ejen pukal yang diperbuat daripada lignin alkali yang diubahsuai iaitu lignin alkali *glyoxalated* adalah penting untuk mengurangkan kepekatan fenol yang diperolehi daripada petrokimia dan formaldehid yang berkasinogenik. Objektif kajian ini adalah untuk meningkatkan keseragaman struktur dan kereaktifan kimia lignin alkali melalui pemeringkatan berurutan dengan menggunakan pelarut organik dan glyoxalasi, dan untuk meningkatkan kestabilan dimensi kayu jelutong (*Dyera costulata*) menggunakan lignin alkali *glyoxalated* yang digabungkan dengan resin fenol formaldehid berberat molekul rendah sebagai ejen pukal.

Bahan mentah lignin berberat molekul rendah diperoleh melalui rawatan *base catalyzed depolymerisation* (BCD) daripada lignin alkali (OL) berberat molekul (mw) 11646 g/mol pada gabungan faktor tahap kekuatan yang berbeza. Kehomogenan struktur OL dan lignin-lignin yang dirawat dengan BCD dikawal melauli pemeringkatan berurutan dengan menggunakan pelarut organic yang mempunyai parameter keterlarutan Hildebrand yang berbeza iaitu propan-1-ol, etanol dan methanol. Hasil OL dan lignin-lignin yang dirawat dengan BCD yang terlarut dalam propan-1-ol (F1), etanol (F2), dan metanol (F3) dan taburan berat molekul serta struktur kimia mereka ditentukan dengan *Gel Permeation Chromatography* (GPC), spektroskopi *Fourier transform infrared* (FT-IR) dan spektroskopi ^{13}C-nuklear resonans magnetik (NMR). Kereaktifan bahan mentah lignin berberat molekul rendah yang diperolehi kemudiannya dipertingkatkan melalui proses *glyoxalation* dengan menggunakan dialdehyde yang tidak meruap dan tidak toksik, iaitu glyoxal, daripada formaldehid. Nisbah bahagian glyoxal kepada natrium hidroksida (NaOH) yang digunakan dalam proses *glyoxalation* dioptimumkan dengan menggunakan kaedah *response surface methodology* (RSM) dan *central composite design* (CCD). Lignin alkali *glyoxalated* (GL) yang disintesis dengan nisbah kadar glyoxal kepada NaOH yang optimum kemudiannya digabungkan dengan resin LmwPF untuk penyediaan ejen pukal bagi rawatan pukal kayu. Kayu-kayu jelutong yang telah dikeringkan di dalam oven didedahkan di bawah vakum dan kemudiannya masing-masing direndamkan dalam resin GL-LmwPF (67% pepejal GL: 33% pepejal LmwPF berdasarkan jumlah kandungan bahan larut) dan LmwPF berkepekatan 15, 20 dan 25% pada suhu ambien selama 24 jam. Kayu-kayu yang telah diisitepuan kemudian dimatangkan pada suhu 180 °C selama 30 minit. Kenaikan peratus berat resin (WPG) dan kestabilan dimensi dari segi *antiswelling efficiency* (ASE), *moisture excluding efficiency* (MEE) dan *water absorption* (WA) serta larut lesap bagi resin-resin LmwPF dan GL-LmwPF ditentukan dan dibandingkan dengan kayu yang tidak dirawat dan kayu dirawat dengan resin LmwPF. Perlepasan formaldehid dari kayu yang dirawat dengan kedua-dua resin GL-LmwPF dan LmwPF juga telah ditentukan.

Rawatan BCD tidak meningkatkan hasil OL yang terlarut dalam propan-1-ol atau etanol tetapi meningkatkan hasil OL yang terlarut dalam methanol. Repolimersasi OL berlaku semasa rawatan BCD dijalankan. OL dengan berat molekul yang lebih rendah, struktur yang lebih seragam cenderung untuk melarut dalam propan-1-ol dan etanol, tetapi secara keseluruhannya hasil lignin yang terlarut dalam larutan-larutan tersebut adalah rendah. OL yang terlarut dalam metanol mempunyai berat molekul yang lebih tinggi, strukturnya adalah kurang seragam dan lebih mampat daripada OL yang terlarut dalam propan-1-ol atau etanol. Analisis spektroskopi ^{13}Carbon-NMR dan FT-IR mengesahkan bahawa F3 dalam OL mempamerkan hasil yang optima dan struktur kimia serta taburan berat molekul yang sesuai untuk sintesis resin. Untuk proses *glyoxalation* lignin alkali, spektroskopi FT-IR menunjukan bahawa pembentukan polimer lignin dengan berat molekul yang lebih rendah adalah disebabkan oleh penyilangan antara molekul-molekul lignin melalui pembentukan lingkaran metilena (CH_2) secara tintak balas condensasi. RSM dan CCD menunjukkan bahawa kereaktifan GL mencapai tertinggi apabila jumlah glyoxal dan NaOH yang optimum, iaitu, 0.222 dan 0.353 mol, masing-masing digunakan dalam proses glyoxalasi. WPG untuk kayu yang dirawat dengan GL-LmwPF adalah lebih rendah daripada kayu yang dirawat dengan LmwPF. Kayu yang dirawat dengan GL-LmwPF mempamerkan ASE positif tetapi nilai-nilainya adalah lebih rendah berbanding dengan kayu yang dirawat dengan LmwPF. MEE dan WA untuk kayu yang dirawat dengan GL-LmwPF adalah lebih lemah daripada kayu yang dirawat dengan LmwPF dan juga kayu yang tidak dirawat. Larut lesap resin GL-LmwPF dari kayu yang dirawat berlaku sedangkan larut lesap resin LmwPF tidak berlaku selepas 3 kitaran larut lesap dalam air suling. Perlepasan formaldehid dari kayu yang dirawat dengan resin GL-LmwPF adalah 25.76% lebih rendah daripada kayu dirawat dengan resin LmwPF. Kayu yang dirawat dengan 25% kepekatan resin GL-LmwPF menghasilkan nilai ASE yang tertinggi berbanding dengan kayu yang dirawat dengan kepekatan 15 dan 20% resin GL-LmwPF. Oleh itu, kayu dirawat dengan 25% kepekatan resin GL-LmwPF diliputi dengan penyalut luar boleh digunakan dalam beberapa aplikasi akhir seperti lantai parket, panel dan komponen perabot.

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude and appreciation to my supervisor, Prof. Dr. Zaidon Ashaari for his guidance, comments, and encouragement on the entire project. I also would like to express my appreciation to my co-supervisor, Assoc. Prof. Dr. Edi Suhaimi Bakar and Assoc. Prof. Dr. Nor Azowa Ibrahim for their helpful comments and assistance.

A special acknowledgement goes to the staff of the Faculty of Forestry, En. Rahmat Ismail, En. Zamani Mohd Daud, Pn. Maizatul Akhmar Johari, Cik Fatimah Mohamed. Apart from this, I would also like to thanks other staff from Faculty of Science, Pn. Zaidina Mohd Daud, En. Mohamad Johadi Iskandar Che Jamil, Pn. Nor Azlina Shari, Pn. Rusnani Amiruddin and Pn. Shareena Safiai.

I am also indebted to my beloved parents and my brothers for their full support and continuous prayer for my success in completing my research project paper. My warmest gratitude also goes to my friends especially Nur Nabilah Abd. Khalid, Puteri Nur Khairunnisha Ismail and Nurliyana Mohd Yaakob who kindly helped me to complete my project on time.

Special thanks to Universiti Putra Malaysia (UPM) for providing the Research University Grant Scheme (RUGS).

Last but not least, I would like to express my sincere thanks to those who are involved either directly or indirectly in completing this project.

I certify that a Thesis Examination Committee has met on 6 April 2016 to conduct the final examination of Ang Aik Fei on his thesis entitled "Optimization of Glyoxalation for Alkali Lignin Used as Bulking Agent in Wood" 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.

Members of the Thesis Examination Committee were as follows:

Jegatheswaran a/l Ratnasingam, PhD
Professor
Faculty of Forestry
Universiti Putra Malaysia
(Chairman)

Luqman Chuah Abdullah, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

H Ng Paik San, PhD
Associate Professor
Faculty of Forestry
Universiti Putra Malaysia
(Internal Examiner)

Mehmet Hakki Alma, PhD
Professor
Kahramanmaraş Sütçüimam University
Turkey
(External Examiner)

ZULKARNAIN ZAINAL, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 25 May 2016

The thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirements for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Zaidon Ashaari, PhD
Professor
Faculty of Forestry
Universiti Putra Malaysia
(Chairman)

Edi Suhaimi Bakar, PhD
Associate Professor
Faculty of Forestry
Universiti Putra Malaysia
(Member)

Nor Azowa Ibrahim, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

Declaration by graduate student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any other institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and Innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software.

Signature: ________________________ Date: ___________________

Name and Matric No.: __Ang Aik Fei & GS30052

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature:
Name of Chairman of Supervisory Committee: Dr. Zaidon Ashaari

Signature:
Name of Member of Supervisory Committee: Dr. Edi Suhaimi Bakar

Signature:
Name of Member of Supervisory Committee: Dr. Nor Azowa Ibrahim

TABLE OF CONTENTS

Page

CHAPTER

1 INTRODUCTION

2 LITERATURE REVIEW

3 MATERIALS AND METHODOLOGY

4 RESULTS AND DISCUSSION

5 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

LIST OF TABLES

LIST OF FIGURES

Figure **Page**

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
ASE	Antiswelling Efficiency
BC	Bulking Coefficient
BCD	Base Catalysed Depolymerisation
CCD	Central Composite Design
CPF	Control PF
DMDHEU	Dimethyloldihydroxyethyleneurea
DMSO-d_6	Deuterated Dimethyl Sulfoxide
EFB	Empty Fruit Bunch
EMC	Equilibrium Moisture Content
FT-IR	Fourier Transform Infra-Red
GBI	Green Building Index
GL	Glyoxalated Alkali Lignin
GL-LmwPF	Glyoxalated Alkali Lignin-Low Molecular Weight Phenol Formaldehyde
GPC	Gel Permeation Chromatography
IAQ	Indoor Air Quality
IARC	International Agency for Research on Cancer
IB	Internal Bonding
IMC	Initial Moisture Content
LEED	Leadership in Energy and Environmental Design
LmwPF	Low Molecular Weight Phenol Formaldehyde
LPF	Lignin Substituted PF
ML	Methanol-Fractionated Alkali Lignin
PEO	Polyethylene Oxide

PT	Press Time
MALDI-TOF	Matrix-Assisted Laser Desorption/Ionization Time-of-Flight
MC	Moisture Content
MEE	Moisture Excluding Efficiency
MDF	Medium Density Fibreboard
MF	Melamine Formaldehyde
NMR	Nuclear Magnetic Resonance
OL	Alkali Lignin
OSB	Oriented Strand Board
PAM	Pertubuhan Akitek Malaysia
PF	Phenol Formaldehyde
PPM	Part per Million
RH	Relative Humidity
RSM	Response Surface Methodology
S	Swelling Coefficient
SDS	Sodium Dodecyl Sulfate
SI	Severity Index
TGA	Thermogravimetry Analysis
UF	Urea Formaldehyde
VOCs	Volatile Organic Compounds
WA	Water Absorption
WHO	World Health Organization
WPG	Weight Percent Gain

CHAPTER 1

INTRODUCTION

1.1 General Background

Wood chronically is a good material to be used for many applications because of its many excellent material properties. The natural beauty and high strength at low density of wood make it is the first choice of material to use in many applications such as roof truss, column, beam, wall cladding, flooring and so on compared to other materials. Although wood possess the excellent properties as mentioned above, but the drawbacks of wood such as the dimensional instability when it is exposed to various atmospheric conditions, susceptibility to biological attack and changes in appearance when exposed to weathering condition limits the potential end-uses of wood.

In fact, the drawbacks of wood can be enhanced through wood modification treatments. Wood modification treatment is a means of altering the material to overcome or ameliorate one of more of its advantages. Wood modification treatments involve the action of a chemical, biological or physical agent upon the material, resulting in a desired property enhancement during the service life of the modified wood (Hill 2006a). Wood modifications either by bulking, internal coating or croslinking have shown promising results to upgrade low quality timbers for potential applications (Ashaari et al. 1990a and 1990b; Nicholas and Williams 1987; Rowell and Youngs 1981). Some of the modified wood such as phenol formaldehyde resin-treated wood (*Impreg* and *Compreg*) and heat treated-compressed wood (*Lignostone* and *Lignofol*) have been introduced and commercialized since many years ago (Rowell and Konkol 1987).

One of the examples of wood modification using bulking principle is impregnation modifications. Impregnation or diffusion of wood with a single chemical or combination chemicals into wood cell walls followed by polymerization of the chemicals is the most adequate method to enhance the properties of wood with this implication. Impregnation of low molecular weight phenol formaldehyde (LmwPF) compound in the wood followed by full curing under heat may enhance the dimensional stability and strength properties of the treated material (Ang 2010; Furuno et al. 2004; Sham et al. 2004; Ryu et al. 1991; Rowell and Konkol 1987).

However, the utilization of LmwPF resin as bulking agent also brought some disadvantages such as phenol is derived from non-renewable petrochemicals while formaldehyde is a known carcinogen. By using so called ‘green’ materials, the strong exploitation of fossil resources can be mitigated, reduce the amount of carbon dioxide that enters the atmosphere and take upon the responsibility of using earth’s resources in a sustainable manner, thus improving resource management, indoor air quality (IAQ), and generally the overall performance and efficiency of human kind on earth. In Malaysia, the launching of green building rating tool, Green Building Index (GBI) in 2009 by the Pertubuhan Akitek Malaysia (PAM) was an approach to promote sustainability in the built environment and raise awareness among developers, architects, engineers, planners, designers, contractors and the public about environmental issues and our responsibility to the future generations. This was a message to show that the awareness to protecting the environment through energy savings, water savings and a healthier indoor environment is getting more important in Malaysia.

1.2 Problem Statement and Justification

Wood is an anisotropic material, which means it swells and shrinks to a different extent in the three anatomical directions–longitudinal (vertical direction), tangential (parallel to annual growth rings), and radial (perpendicular to the annual growth rings). Swelling of wood in contact with moisture exerts very large forces. When wood in use swells, the forces developed can cause serious damage. As mentioned earlier, the dimensional instability of wood can be enhanced through bulking treatment i.e. impregnation of low molecular weight phenol formaldehyde (LmwPF) compound (bulking agent) in the wood followed by full curing under heat which yielded treated products with cell walls bulked with insoluble resin polymer.

Although the impregnation modification with LmwPF resin has been studied extensively in past few decades ago (Paridah et al. 2006; Furuno et al. 2004; Wan Ariffin et al. 1992; Kajita and Imamura 1991), but the study of using lignin based-phenolic resin as bulking agent to enhance the properties of wood is rather poor. Phenol is derived from petrochemical benzene and formaldehyde from methanol that is prepared from natural gas. The availability of petrochemicals is finite as it is non-renewable resource and the prices of raw materials for LmwPF resin would increase because the fuel consumption increases as the world's population grows (Sellers, 1985). Formaldehyde has been classified as a known carcinogen by the International Agency for Research on Cancer (IARC), a division of the World Health Organization (WHO). The emission of free formaldehyde from the resin during impregnation process and service life of the treated products will causes health problems to the consumers (Soljacic and Katovic 1988). It has been reported that the formaldehyde emission from LmwPF resin impregnated wood reduced when the wood is impregnated with lower concentration of LmwPF resin (Nur Izreen et al. 2011; Rabi'atol Adawiah et al. 2012). However, it is anticipated that the effectiveness in enhancing some the properties of wood would become inferior if using lower concentration of LmwPF resin as the effectiveness in enhancing the dimensional stability of wood through this method is very much associated with the ultimate cell wall bulking effect (ultimate polymer of chemicals deposited in cell wall) of the impregnated wood (Deka and Saikia 2000; Ang 2010; Rabi'atol Adawiah et al. 2012; Leemon et al. 2015).

The polyphenolic nature of lignin makes it a potential substitute for phenol in the production of ordinary formaldehyde-based resin. In addition, lignin is the most abundant natural and renewable organic polymer in the world after cellulose. Large quantities of isolated lignin can be recovered from various pulping or biomass conversion processes. Therefore, lignin is an inexpensive raw material that potential for the production of environmentally friendly thermosetting resin by substituting the phenol in the ordinary formaldehyde based thermosetting resins (Alonso et al. 2004; Khan and Ashraf 2007; Cetin and Ozmen 2002; El Mansouri et al. 2006; Cavdar et al. 2008). Therefore, impregnation of wood with partial glyoxalated alkali lignin (GL) substituted-LmwPF resin as bulking agent thus offers advantages by reducing the free formaldehyde emission with using lesser neat LmwPF resin while retaining the ultimate WPG in the impregnated wood as majority of the solid content deposited in the impregnated wood (especially in the cell walls) was comprised of natural and renewable lignin polymer.

To process lignin into various end products, it would be advantageous to use material with a more homogenous structure, chemistry and purity (Stewart 2008). The homogeneity of lignin can be enhanced by sequential fractionation in different organic solvents (Wang et al. 2010; Li et al. 2012). The heterogeneity of lignin can be reduced because different parts of the lignin molecule have different hydrogen-bonding capacity (Hildebrand solubility parameter) in different organic solvents. Low-molecular weight lignin fragments are dissolved in organic solvents with weak or moderate hydrogen-bonding capacities with a wider range of Hildebrand solubility parameters than the higher-molecular weight lignin fragments (Schuerch 1952).

Apart from this, lignins also offer no advantages in terms of chemical reactivity. The low reactivity of lignins is the main obstacle limits their utilization in the production of resins (Vishtal and Kraslawski 2011). Hence, the reactivity of lignins needs to be enhanced in order to increase the possibility of using lignins as feedstock for the production of resins. Hydrolysis of lignin in an alkaline medium has been shown to increase the reactivity of lignin by liberating lower molecular weight phenolic compounds which possess more reactive sites and reduced steric hindrance effect (Cheng et al. 2013; El Mansouri et al. 2006; Thring 1994). Apart from this, depolymerisation of lignin macromolecule into lower molecular weight fragments is also important as one of the requirements for wood bulking treatment is that the molecular weight of bulking agents used should be low to ensure the penetration of bulking agents into wood cell walls (Norimoto 2000). It has been reported that hydroxymethylation is also one of the chemical modification methods applied to enhance the reactivity of lignin toward crosslinking agents such as formaldehyde (Lin et al. 2010; Mu et al. 2009; Malutan et al. 2008; Zhao et al. 1994). Hydroxymethylation enhances the reactivity of lignin by introducing reactive functional groups to the lignin molecules. Instead of using toxic and volatile formaldehyde as crosslinking agent in hydroxymethylation, non-toxic and non-volatile dialdehydes such as glyoxal also has been used as a replacement for formaldehyde (Navarrete et al. 2012; El Mansouri et al. 2011). Glyoxal can be obtained as a by-product from the generation of hydrogen peroxide required by manganese-dependent peroxidase enzymes (Kersten 1990; Hirayama et al. 1984).

Although the modifications of lignin to enhance its structural homogeneity and chemical reactivity may slightly increase the cost of processing, the cost of processing can be reduced by monitoring the concentration of chemicals used by developing the optimum treatment method. Furthermore, the treated products are very potential for commercialization because it is Green Building Index (GBI) and Leadership in Energy and Environmental Design (LEED) complaint material. The treated products could sell with better price as it is value-added product that renders superior performance under service life. The needs of developing thermosetting resin from renewable raw materials as bulking agent for impregnation modification are crucial in order to ensure that the sustainability of thermosetting resins raw materials for this modification.

1.3 Main Objective

The objective of this study was to enhance the structural homogeneity and chemical reactivity of alkali lignin through sequential organic solvents fractionation and glyoxalation, and enhance the dimensional stability of jelutong (*Dyera costulata*) wood using glyoxalated alkali lignin (GL) incorporated low molecular weight phenol formaldehyde (LmwPF) resin as bulking agent.

1.3.1 Specific Objectives

1. To obtain optimal yield of alkali lignin with more homogeneous structure through base catalysed depolymerisation (BCD) and sequential organic solvents fractionation treatments.

2. To optimise the ratios of glyoxal to sodium hydroxide used in the glyoxalation process based on the relative intensity of methylene (CH_2) bridge using response surface methodology (RSM).

3. To determine the molecular weight distributions and thermal stability of glyoxalated alkali lignin (GL).

4. To identify the functional groups in low molecular weight phenol formaldehyde (LmwPF) resin and GL-LmwPF admixture resin.

5. To evaluate the effectiveness of using GL-LmwPF admixture resin as bulking agent to enhance the dimensional stability of jelutong (*Dyera costulata*) wood.

REFERENCES

Abatzoglou N, Chornet E, Belkacemi K, Overend RP. Phenomenological kinetics of complex systems: The development of a generalized severity parameter and its application to lignocellulosics fractionation. Chemical Engineering Science 47 (5):1109-1122 (1992).

Abdelwahab NA, Nassar MA. Preparation, optimization and characterization of lignin phenol formaldehyde resin as wood adhesive. Pigment & Resin Technology 40 (3):169-174 (2011).

Alonso MV, Oliet M, Pérez JM, Rodríguez F, Echeverría J. Determination of curing kinetic parameters of lignin–phenol–formaldehyde resol resins by several dynamic differential scanning calorimetry methods. Thermochimica Acta 419:161-167 (2004).

Amarullah M, Bakar ES, Zaidon A, Sahri MH, Febrainto F. Reduction of formaldehyde emission from phenol formaldehyde treated oil palm wood through improvement of resin curing state. Journal of Tropical Wood Science and Technology 8 (1):9-14 (2010).

Ang AF. Properties and decay resistance of mahang (*Macaranga sp.*) treated with phenolic resin and acrylic monomer using vacuum-pressure process [Dissertation]. Serdang: Universiti Putra Malaysia; 2010. 155p.

Arshanitsa A, Ponomarenko J, Dizhbite T, Andersone A, Gosselink RJA, Putten JVD, Lauberts M, Telysheva G. Fractionation of technical lignins as a tool for improvement of their antioxidant properties. Journal of Analytical and Applied Pyrolysis 103:78-85 (2013).

Ashaari Z, Barnes HM, Lyon DE, Vasishth RC, Nicholas DD. Effect of aqueous polymer treatments on wood properties. Part I: Treatability and dimension stability. IRG/WP/3610 (1990a).

Ashaari Z, Barnes HM, Lyon DE, Vasishth RC, Nicholas DD. Effect of aqueous polymer treatments on wood properties. Part II: Mechanical properties. IRG/WP/3611 (1990b).

Ballerini A, Despres A, Pizzi A. Non-toxic, zero emission tannin-glyoxal adhesives for wood panels. Holz Als Roh-Und Werkstoff 63 (6):477-478 (2005).

Baysal E, Ozaki SK, Yalinkilic MK. Dimensional stabilization of wood treated with furfuryl alcohol catalysed by borates. Wood Science and Technology 38:405-415 (2004).

Bezerra MA, Santelli RE, Oliveira EP, Villar LS, Escaleira LA. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. Talanta 76 (5):965-977 (2008).

Box GEP. The exploration and exploitation of response surfaces: Some general considerations and examples. Biometrics 10 (1):16-60 (1954).

Cavdar AD, Kalaycioglu H, Hiziroglu S. Some of the properties of oriented strandboard manufactured using kraft lignin phenolic resin. Journal of Materials Processing Technology 202:559-563 (2008).

Cetin NS, Ozmen N. Use of organosolv lignin in phenol-formaldehyde resins for particleboard production. Part I: Organosolv lignin modified resins. International Journal of Adhesion and Adhesives 22:477-480 (2002).

Chakar FS, Ragauskas AJ. Review of current and future softwood kraft lignin process chemistry. Industrial Crops and Products 20 (2):131-141 (2004).

Chang HT, Chang ST. Moisture excluding efficiency and dimensional stability of wood improved by acylation. Bioresource Technology 85:201-204 (2002).

Chen Y, Frihart CR, Cai Z, Lorenz LF, Stark NM. Lignin-based phenol formaldehyde resins from purified CO_2 precipitated kraft lignin (PCO_2KL). In: International Conference on Wood Adhesives: proceedings: 2013 Oct 9-11; Toronto. p.601-10.

Cheng SN, Yuan ZS, Leitch M, Anderson M, Xu CB. Highly efficient de-polymerization of organosolv lignin using a catalytic hydrothermal process and production of phenolic resins/adhesives with the depolymerized lignin as a substitute for phenol at a high substitution ratio. Industrial Crops and Products 44:315-322 (2013).

Deka M, Saikia CN. Chemical modification of wood with thermosetting resin: effect on dimensional stability and strength property. Bioresource Technology 73:179-181 (2000).

Drumond M, Aoyama M, Chen CL, Robert D. Substituent effects on C-13 chemical shifts of aromatic carbons in biphenyl type lignin model compounds. Journal of Wood Chemistry and Technology 9 (4):421-441 (1989).

Effendi A, Gerhauser H, Bridgwater AV. Production of renewable phenolic resins by thermochemical conversion of biomass: A review. Renewable and Sustainable Energy Reviews 12 (8):2092-2116 (2008).

El Mansouri NE, Farriol X, Salvadó, J. Structural modification and characterization of lignosulfonate by a reaction in an alkaline medium for its incorporation into phenolic resins. Journal of Applied Polymer Science 102 (4):3286-3292 (2006).

El Mansouri NE, Pizzi A, Salvado J. Lignin-based wood panel adhesives without formaldehyde. Holz als Roh- und Werkstoff 65 (1):65-70 (2007a).

El Mansouri NE, Pizzi A, Salvado J. Lignin-based polycondensation resins for wood adhesives. Journal of Applied Polymer Science 103 (3):1690-1699 (2007b).

El Mansouri NE, Yuan QL, Huang FR. Study of chemical modification of alkaline lignin by the glyoxalation reaction. BioResources 6 (4):4523-4536 (2011).

EN 717-3. Wood-based panels. Determination of formaldehyde release. Part 3: Formaldehyde release by the flask method European Committee for Standardization, Brussels, Belgium; 1996.

Erdocia X, Prado R, Corcuera MÁ, Labidi J. Base catalysed depolymerisation of lignin: Influence of organosolv lignin nature. Biomass and Bioenergy 66:379-386 (2014).

Freudenberg K, Neish AC. Constitution and biosynthesis of lignin. New York: Springer-Verlag; 1968. 129p.

Furuno T, Imamura Y, Kajita H. The modification of wood by treatment with low molecular weight phenol-formaldehyde resin: a properties enhancement with neutralized phenolic-resin and resin penetration into wood cell walls. Wood Science and Technology 37:349-361 (2004).

Henriksson G, Li G, Zhang L, Lindström ME. Lignin Utilization. In: Crocker M, editor. Cambridge: Royal Society of Chemistry; 2010. pp. 223-262.

Hill CAS. Modyfying the properties of wood. In Wood modification: Chemical, thermal and other processes. West Sussex: John Wiley & Sons, Ltd; 2006a. p. 19-44.

Hill CAS. Impregnation modification. In Wood modification: Chemical, thermal and other processes. West Sussex: John Wiley & Sons, Ltd; 2006b. p. 149-173.

Hirayama T, Yamada N, Nohara M, Fukui S. The existence of the 1,2-dicarbonyl compounds glyoxal, methyl glyoxal and diacetyl in autoxidised edible oils. Journal of the Science of Food and Agriculture 35 (12):1357-1362 (1984).

Holtman KM, Chang H, Jameel H, Kadla JF. Quantitative ^{13}C NMR characterization of milled wood lignins isolated by different milling techniques. Journal of Wood Chemistry and Technology 26 (1):21-34 (2006).

Hu L, Pan H, Zhou Y, Zhang M. Methods to improve lignin's reactivity as a phenol substitute and as replacement for other phenolic compounds: A brief review. BioResources 6 (3):3515-3525 (2011).

Inoue M, Norimoto M, Tanahashi M, Rowell RM. Fixation of compressed wood using melamine-formaldehyde resin. Wood and Fiber Science 25 (4):404-410 (1993).

Johnson SE, Kamke FA. Characteristics of phenol-formaldehyde adhesive bonds in steam injection pressed flakeboard. Wood and Fiber Science 26 (2):259-269 (1994).

Johnson SE, Kamke FA. Quantitative analysis of gross adhesive penetration in wood using fluorescence microscopy. Journal of Adhesion 40 (1):47-61 (1992).

Kadam KL, Chin CY, Brown LW. Continuous biomass fractionation process for producing ethanol and low-molecular-weight lignin. Environmental Progress and Sustainable Energy 28 (1):89-99 (2009).

Kajita H, Imamura Y. Improvement of physical and biological properties of particleboards by impregnation with phenolic resin. Wood Science and Technology 26:63–70 (1991).

Kamke FA, Lee JN. Adhesive penetration in wood—a review. Wood and Fiber Science 39 (2):205-220 (2007).

Kersten PJ. Glyoxal oxidase of Phanerochaete chrysosporium: its characterization and activation by lignin peroxidase. In the National Academy of Sciences of the United States of America: proceedings: 1990 April. p.2936–40.

Khan MA, Ashraf SM. Studies on thermal characterization of lignin substituted phenol formaldehyde resin as wood adhesives. Journal of Thermal Analysis and Calorimetry 89 (3):993-1000 (2007).

Khan MA, Ashraf SM, Malhotra VP. Eucalyptus bark lignin substituted phenol formaldehyde adhesives: A study on optimization of reaction parameters and characterization. Journal of Applied Polymer Science 92 (6):3514-3523 (2004).

Kunaver M, Medved S, Čuk N, Jasiukaitytė, E, Poljanšek, I, Strnad T. Application of liquefied wood as a new particle board adhesive system. Bioresource Technology 101(4):1361-1368 (2010).

Leemon NF, Ashaari Z, Uyup MKA, Bakar ES, Tahir PM, Saliman MAR, Ghani MA, Lee SH. Characterisation of phenolic resin and nanoclay admixture and its effect on *impreg* wood. Wood Science and Technology 49 (6):1209-1224 (2015).

Lei H. Synthetic and natural materials for wood adhesive resins [dissertation]. France (Nancy 1): University Henri Poincare; 2009. 144p.

Lei H, Pizzi A, Du GB. Environmentally friendly mixed tannin/lignin wood resins. Journal of Applied Polymer Science 107 (1):203-209 (2008).

Li J, Henriksson G, Gellerstedt G. Lignin depolymerisation/repolymerization and its critical role for delignification of aspen wood by steam explosion. Bioresource Technology 98 (16):3061-3068 (2007).

Li X, Li Y, Zhong Z, Wang D, Ratto JA, Sheng K, Sun XS. Mechanical and water soaking properties of medium density fibreboard with wood fibre and soybean protein adhesive. Bioresource Technology 100 (14):3556-3562 (2009).

Li MF, Sun SN, Xu F, Sun RC. Sequential solvent fractionation of heterogeneous bamboo organosolv lignin for value-added application. Separation and Purification Technology 101:18-25 (2012).

Lin ZX, Ouyang XP, Yang DJ, Deng YH, Qiu XQ. Effect of hydroxymethylation of lignin on the properties of lignin-phenol-formaldehyde resins. World Sci-Tech R&D 32 (3):348-351 (2010).

Mai C, Milstein O, Hüttermann A. Chemoenzymatical grafting of acrylamide onto lignin. Journal of Biotechnology 79 (2):173-183 (2000).

Malutan T, Nicu R, Popa VI. Contribution to the study of hydroxymethylation reaction of alkali lignin. BioResources 3 (1):13-20 (2008).

Mancera C, Ferrando F, Salvadó J, El Mansouri NE. Kraft lignin behaviour during reaction in an alkaline medium. Biomass and Bioenergy 35 (5):2072-2079 (2011).

McDonough TJ. The chemistry of organosolv delignification. Tappi Journal 76 (8):186-193 (1993).

Michelle AJ, Watson AJ, Higgins HG. An infra red spectroscopic study of delignification *Eucalyptus regnans*. Tappi 48 (9):520-532 (1965).

Mohamad Ibrahim MN, Ghani AM, Nen N. Formulation of lignin phenol formaldehyde resins as a wood adhesive. The Malaysian Journal of Analytical Sciences 11 (1):213-218 (2007).

Mu YB, Wang CP, Zhao LW, Chu FX. Study on composite adhesive of hydroxymethylated lignosulfonate/phenol-formaldehyde resin with low free formaldehyde. Chemistry and Industry of Forest Products 29 (3):38-42 (2009).

Myers RH, Montgomery DC. Response Surface Methodology: Process and product optimization using designed experiments. New York: John Wiley and Sons; 2002.

Navarrete P, Mansouri HR, Pizzi A, Tapin-Lingua S, Benjelloun-Mlayah B, Rigolet, S. Synthetic-resin-free wood panel adhesives from low molecular mass lignin and tannin. Journal of Adhesion Science and Technology 24 (8):1597-1610 (2010).

Navarrete P, Pizzi A, Pasch H, Delmotte L. Study on lignin-glyoxal reaction by MALDI-TOF and CP-MAS ^{13}C NMR. Journal of Adhesion Science and Technology 26 (8-9):1069-1082 (2012).

Navarrete P, Pizzi A, Rode K, Vignali M, Pasch, H. MALDI-TOF study of oligomers distribution for stability-durable spray-dried glyoxalated lignin for wood adhesives. Journal of Adhesion Science and Technology 27 (5-6):586-597 (2013).

Nenkova S, Vasileva T, Stanulov K. Production of phenol compounds by alkaline treatment of technical hydrolysis lignin and wood biomass. Chemistry of Natural Compunds 44 (2):182-185 (2008).

Nicholas DD, Williams AD. Dimensional stabilization of wood with dimethylol compounds. IRG/WP/3412 (1987).

Norimoto M. Chemical modification of wood. In: Hon DNS, Shiraishi N, editors. Wood And Cellulosic Chemistry. New York: Marcel Dekker; 2000. p. 573-598.

Norimoto M, Gril J. Structure and properties of chemically treated woods. In: Shiraishi N, Kajita H, Norimoto M, editors. Recent research on wood and wood-based materials. Barking: Elsevier; 1993. p. 135 – 54.

Nur Izreen FA, Zaidon A, Rabi'atol Adawiah MA, Bakar ES, Paridah MT, Mohd Hamami S, Anwar UMK. Enhancing the properties of low density hardwood *Dyera costulata* through impregnation with phenolic resin admixed with formaldehyde scavenger. Journal of Applied Sciences 11:3474–3481 (2011).

Ohmae K, Minato K, Norimoto M. The analysis of dimensional changes due to chemical treatments and water soaking for hinoki (*Chamaecyparis obtusa*) wood. Holzforschung 56 (1):98-102 (2002).

Olarte MV. Base-catalyzed depolymerization of lignin and hydrodeoxygenation of lignin model compounds for alternative fuel production [dissertation]. Atlanta: Georgia Institute of Technology; 2011. 213p.

Pan X, Lachenal D, Neirinck V, Robert D. Structure and reactivity of spruce mechanical pulp lignins IV: ^{13}C-NMR spectral studies of isolated lignins. Journal of Wood Chemistry and Technology 14 (4):483-506 (1994).

Paridah MT, Ong LL, Zaidon A, Rahim S, Anwar UMK. Improving the dimensional stability of multilayered strand board through resin impregnation. Journal of Tropical Forest Science 18 (3):166-172 (2006).

Pearl IA. The chemistry of lignin. New York: Marcel Dekker; 1967. 339p.

Poljanšek I, Krajnc M. Characterization of phenol-formaldehyde prepolymer resins by in line FT-IR spectroscopy. Acta Chimica Slovenica 52:238-244 (2005).

Pouteau C, Cathala B, Dole P, Kurek B, Monties B. Structural modification of kraft lignin after acid treatment: characterization of the apolar extracts and influence on the antioxidant properties in polypropylene. Industrial Crops and Products 21 (1):101-108 (2005).

Purba TP, Zaidon A, Bakar ES, Paridah MT. Effects of processing factors and polymer retention on the performance of phenolic-treated wood. Journal of Tropical Forest Science 26 (3):320-330 (2014).

Rabi'atol Adawiah MA, Zaidon A, Nur Izreen FA, Bakar ES, Mohd Hamami S, Paridah MT. Addition of urea as formaldehyde scavenger of low molecular weight phenol formaldehyde treated compreg wood. Journal of Tropical Forest Science 24:265–274 (2012).

Ramires EC, Megiatto JD Jr, Gardrat C, Castellan A, Frollini E. Biobased composites from glyoxal-phenolic resins and sisal fibres. Bioresource Technology 101 (6):1998-2006 (2010).

Robert D. Carbon-13 nuclear magnetic resonance spectroscopy. In: Lin SY, Dence CW, editors. Methods in Lignin Chemistry. New York: Springer-Verlag; 1992. p. 250-73.

Roberts VM, Fendt S, Lemonidou AA, Li X, Lercher JA. Influence of alkali carbonates on benzyl phenyl ether cleavage pathways in superheated water. Applied Catalysis B: Environmental 95 (1-2):71-77 (2010a).

Roberts VM, Knapp RT, Li X, Lercher JA. Selective hydrolysis of diphenyl ether in supercritical water catalyzed by alkaline carbonates. ChemCatChem 2 (11):1407-1410 (2010b).

Roberts VM, Stein V, Reiner T, Lemonidou A, Li X, Lercher JA. Towards quantitative catalytic lignin depolymerisation. Chemistry - A European Journal 17:5939-5948 (2011).

Rowell RM, Banks WB. Water repellency and dimensional stability of wood. Gen. Tech. Rep. FPL-50. Madison, WI: U.S. Department of Agriculture, Forest Service, Forest Product Laboratory. Wisconsin (1985).

Rowell RM, Ellis WD. Determination of dimensional stabilization of wood using the water-soak method. Wood and Fiber Science 10 (2):104-111 (1978).

Rowell RM, Konkol P. Treatments that enhance physical properties of wood. Gen. Tech. Rep. FPL-GTR-55. Madison, U.S. Department of Agriculture, Forest Service, Forest Product Laboratory. Wisconsin. (1987).

Rowell RM, Youngs RL. Dimensional stabilization of wood in use. U.S. For. Serv., For. Prod. Res. Note FPL -0243. Forest Product Laboratory, Wisconsin. (1981).

Ryu JY, Takahashi M, Imamura Y, Sato T. Biological resistance of phenol-resin treated wood. Mokuzai Gakkaishi, 37 (9):852-858 (1991).

Saito T, Perkins JH, Vautard F, Meyer HM, Messman JM, Tolnai B, Naskar AK. Methanol fractionation of softwood kraft lignin: Impact on the lignin properties. ChemSusChem 7 (1):221-228 (2014).

Schuerch C. The solvent properties of liquids and their relation to the solubility, swelling, isolation and fractionation of lignin. Journal of the American Chemical Society 74 (20):5061-5067 (1952).

Sellers TJ. Plywood and adhesive technology. New York: Marcel Dekker, Inc; 1985.

Shams MI, Yano H, Endou K. Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin I: effects of pressing pressure and pressure holding. Wood Science 50:337-342 (2004).

Shojaeimehr T, Rahimpour F, Khadivi MA. A modelling study by response surface methodology (RSM) and artificial neutral network (ANN) on Cu^{2+} adsorption optimisation using light expended clay aggregate (*LECA*). Journal of Industrial and Engineering Chemistry 20:870-880 (2014).

Singh M, Kumar V. Preparation and characterization of melamine–formaldehyde–polyvinylpyrrolidone polymer resin for better industrial uses over melamine resins. Journal of Applied Polymer Science 114 (3):1870-1878 (2009).

Soljacic I, Katovic D. The effect of heating on the release of formaldehyde from durable-press finished fabrics. Coloration Technology 104 (10):384-386 (1988).

Stamm AJ. Wood and cellulose science. New York: Ronald Press; 1964. 549p.

Stamm AJ, Baechler RH. Decay resistance and dimensional stability of five modified woods. Forest Products Journal 10:22-26 (1960).

Stamm AJ, Seborg RM. Resin-treated plywood. Industrial and Engineering Chemistry 31 (7):897-902 (1939).

Stewart D. Lignin as a base material for materials applications: Chemistry, application and economics. Industrial Crops and Products 27 (2):202-207 (2008).

Sun RC, Tomkinson J, Jones GL. Fractional characterization of ash-AQ lignin by successive extraction with organic solvents from oil palm EFB fibre. Polymer Degradation and Stability 68 (1):111-119 (2000).

Tejado A, Peña C, Labidi J, Echeverria JM, Mondragon I. Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis. Bioresource Technology 98 (8):1655-1663 (2007).

Thring RW. Alkaline degradation of ALCELL® lignin. Biomass and Bioenergy 7 (1-6):125-130 (1994).

Thring RW, Breau J. Hydrocracking of solvolysis lignin in a batch reactor. Fuel 75 (7):795-800 (1996).

Toledano A, Serrano L, Labidi J. Process for olive tree pruning lignin revalorization. Chemical Engineering Journal 193-194:396-403 (2012).

Vishtal A, Kraslawski A. Challenges in industrial applications of technical lignins. BioResources 6 (3):3547-3568 (2011).

Wahab NHA, Tahir PM, Yeoh BH, Ashaari Z, Yunus NYM, Uyup MKA, Shahri MH. Adhesion characteristics of phenol formaldehyde pre-preg oil palm stem veneers. BioResources 7(4):4545-4562 (2012).

Wan Ariffin WT, Koh MP, Mustafa MT. Improved rattan through phenolic resin impregnation - a preliminary study. Journal of Tropical Forest Science 5 (4):485-491 (1992).

Wang K, Lam F. Quadratic RSM models of processing parameters for three-layer oriented flakeboards. Wood and Fibre Science 31 (2):173-186 (1999).

Wang M, Leitch M, Xu C. Synthesis of phenol–formaldehyde resole resins using organosolv pine lignins. European Polymer Journal 45 (12):3380-3388 (2009).

Wang JX, Shen J, Lei CS, Feng Q. Volatile organic compound and formaldehyde emission from *Populus davidiana* wood treated with low molecular weight urea-formaldehyde resin. Journal of Environmental Biology 35 (5):989-994 (2014).

Wang K, Xu F, Sun, R. Molecular characteristics of kraft-AQ pulping lignin fractionated by sequential organic solvent extraction. International Journal of Molecular Sciences 11 (8):2988-3001 (2010).

Xiang Q, Lee YY. Oxidative cracking of precipitated hardwood lignin by hydrogen peroxide. Applied Biochemistry and Biotechnology 84-86:153-162 (2000).

Yuan TQ, He J, Xu F, Sun RC. Fractionation and physico-chemical analysis of degraded lignins from the black liquor of *Eucalyptus pellita* KP-AQ pulping. Polymer Degradation and Stability 94 (7):1142-1150 (2009).

Zabaleta AT. Lignin extraction, purification and depolymerization study [dissertation]. Donostia-San Sebastián: University of the Basque Country; 2012. 280p.

Zaidon A, Kim GH, Paridah MT, Bakar ES, Rushdan I. Optimisation of the processing variables for high polymer loading in compressed wood using response surface methodology. Journal of Tropical Forest Science 24 (2):241-248 (2012).

Zhao Y. Development of Bio-Based Phenol Formaldehyde Resol Resins using Mountain Pine Beetle Infested Lodgepole Pine Barks [dissertation]. Canada: University of Toronto; 2013. 169 p.

Zhao LW, Griggs BF, Chen CL, Hse CY. Utilization of softwood kraft lignin as adhesive for the manufacture of reconstituted wood. Journal of Wood Chemistry and Technology 14 (1):127-145 (1994).