PRODUCTION OF CELLULOSE ACETATE FROM *Acacia mangium* FOR WOOD COATING LACQUER

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THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE DEGREE OF MASTER OF SCIENCE

FACULTY OF SCIENCE AND NATURAL RESOURCES
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2016

DECLARATION

I hereby declare that this submission is my own work and that, to the best of my knowledge and beliefs, contains no material previously publishes or written by another person nor material except where due acknowledgement has been made by text.

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DEGREE	: **MASTER OF SCIENCE (FORESTRY)**
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ACKNOWLEDGEMENTS

I would like to take this opportunity to express my sincere appreciation and heartfelt gratitude to the following, who shared their knowledge, expertise, encouragements, and cooperation, by guiding me through this hardship that I have gotten myself voluntarily partaking to, with a couple of nudges from dad, in which people would call it in high admiration and dissolute indifference, Master's degree.

I would like to acknowledge our School of International Tropical Forestry (SITF), in which is now known as the Faculty of Science and Natural Resources (Forestry Complex), Universiti Malaysia Sabah, who inexhaustibly provided me with a shed (and air conditioners) to fight off the heat from the tiresome weathers, chemicals that burns through shoes, the knight-in-shining manpower, as well as materials to dwell with in conducting this research project. A shout out to my thesis supervisor, Miss Ismawati Palle, who had unknowingly agreed on supervising a monstrosity of a person that is I, to the end of my master's. Your kindness and affliction will forever haunt my dreams, just like your 5 a.m. text messages. To Dr. Liew Kang Chiang, my constant tormentor but in a fatherly sort of way co-supervisor, thank you for always keeping me sharp and on my feet with your quizzing eyebrows.

The deepest sense of gratitude especially to my mother and father, Mrs. Masneh Jain and Mr. Gilbert Laimon, for all the morale and financial support to the daughter that you made further her studies unwillingly. Best mandatory order ever. Thank you to my three favorite laboratory assistant, Mr. Azli Sulid, Mr. Abdul Airin, and Mr. Mohd. Rizan, for their aid in handling machines and apparatus, as well as knowledge and advices, for this project. To my fellow comrades, Elizabeth James, Julia Ak Nelson, Sitti Suraidah Anas, Hue Su Wah, Ellyza Syazzana, Dr. Benny Yeong, and many more, thank you and I wish you all the worst in enduring the torture.

I would also like to express my overall heartfelt gratitude to the rest of my family and friends for the never-ending support especially in the physical/mental contribution. Without you guys, I would never have made it, or even if I did made it, I would have been bald and super conceited. Thank you for not making me bald, especially, and gripped my legs so that I would not fly to the sun. Lastly, I would also like to thank those unnamed contributors in their cooperation and participation, directly and indirectly, in successfully helping me finish my upward climb to my (academic) K2 Mountain.

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26th January 2016

ABSTRACT

Cellulose acetate (CA) is a semi-synthetic industrial fiber that has a wide-range of application that includes materials for molded goods and fabrics, as well as filter membrane, cigarette tow, and coating. This study focuses on the production of coating from *Acacia mangium*-produced cellulose acetate. It covers the selection of the *A. mangium* fibers for development into the intermediate CA, followed by the optimum condition for the production of CA, and finally the performance of the end product of the *Acacia mangium*-based CA for wood coating. The fiber characteristic of the *A. mangium* wood and pulp fiber was determined and compared, where the pulp fiber was shown to potentially be a better material in the development of CA due to the higher cellulose composition of nearly 100% of percentage difference if compared to the wood fibers. Structurally, the pulp also displays better fibrillated structure and slightly higher derived value compared to the wood fiber for thefiber dimensions, with percentage difference not more than 10% for most. The selected form of pulp fiber underwent acetylation process through the reaction with acetic anhydride and acetic acid, where certain condition was manipulated, which includes the pretreatment process, amount of catalyst, pulp particle size, and reaction time to obtain the optimum condition. The result shows the pretreated *A. mangium* pulp fiber of 200-mesh size that underwent 36 hours of acetylation, with the highest catalyst usage of 0.10 ml earned the most ideal DS of 2.81, in the development of coatings. The formation of the acetate lacquer coating loosely follows the U.S. patent no. 2426379 that includes the fusion of melamine formaldehyde and ethyl acetate. The performance of the *A. mangium* cellulose acetate (AMCA) lacquer was evaluated and compared with a control lacquer that was produced from a commercial CA (CCA), based on the mechanical and physical performance. The AMCA lacquer is proven to be on par or better than that of CCA lacquer with better staining resistance and lower water absorption rate for the physical, and a higher durability for the impact, abrasion, and hardness test for the mechanical performance. These properties further justify the ergonomics of the most abundant organic compound on Earth, which is the cellulose, as an alternative for petroleum-based products while indicating the feasibility of a wide-range unconventional product development of the *A. mangium* species as a whole.

ABSTRAK

PENGHASILAN SELULOSA ASETAT DARI PULPA Acacia mangium UNTUK LAKUER PENYALUT KAYU

Selulosa asetat (CA) adalah fiber industri separa sintetik yang mempunyai aplikasi yang luas termasuk bahan untuk acuan produk dan tekstil, selain daripada membran turas, puntung rokok, dan penyalut. Kajian ini memberi tumpuan terhadap penghasilan penyalut daripada CA yang diperbuat daripada Acacia mangium. Ia merangkumi pemilihan serat A. mangium untuk fabrikasi pengantara CA, diikuti dengan keadaan yang optimum untuk penghasilan CA, dan akhirnya prestasi produk akhir CA berasaskan A. mangium bagi penyalut kayu. Ciri-ciri fiber kayu dan pulpa dari A. mangium telah ditentukan dan dibandingkan, yang mana fiber pulpa menunjukkan potensi yang lebih baik dalam penghasilan CA kerana komposisi selulosa yang tinggi iaitu melebihi 100% perbezaan jika dibandingkan dengan fiber kayu. Dari segi struktur, pulpa mempunyai struktur fibril yang lebih baik dan nilai yang lebih tinggi berbanding serat kayu untuk dimensi serat, dengan peratusan perbezaan tidak melebihi 10% bagi hampir semua nilai. Fiber pulpa yang telah dipilih seterusnya melalui proses asetilasi, melalui tindakbalas dengan asetik anhidrida dan asid asetik dimana beberapa keadaan telah dimanipulasi, termasuk proses pra-rawatan, jumlah pemangkin, saiz partikel pulpa, dan masa tindakbalas untuk memperolehi keadaan optimum. Keputusan menunjukkan pra-rawatan fiber pulpa A. mangium dengan saiz jaringan partikel 200 yang bertindakbalas selama 36 jam dengan penggunaan pemangkin tertinggi berjumlah 0.10 ml telah memperoleh nilai tahap penggantian (DS) yang paling ideal untuk pembentukan penyalut, iaitu 2.81. Manakala, pembentukan penyalut lakuer asetat seterusnya telah mengikuti paten A.S. bernombor 2426379 yang melibatkan percampuran melamin formaldehid dan juga etil asetat. Prestasi lakuer A. mangium selulosa asetat (AMCA) telah dinilai dan dibandingkan dengan lakuer kawalan yang diperbuat daripada CA komersil (CCA), berdasarkan dengan prestasi mekanikal dan fizikal. Prestasi lakuer AMCA terbukti setanding atau lebih baik daripada CCA lakuer dengan daya rintangan yang lebih baik terhadap kesan kotor serta kadar penyerapan air yang rendah untuk ciri fizikal, dan ketahanan yang tinggi untuk ujian impak, kekerasan, dan lelasan untuk prestasi mekanikal. Dapatan kajian perkembangan lakuer asetat ini mengukuhkan lagi kebolehgunaan sebatian organik terbanyak di muka bumi ini iaitu selulosa sebagai alternatif kepada produk berasaskan petroleum, selain menunjukkan kesesuaian bahan mentah ini untuk perkembangan produk bukan konvensional bagi spesies A. mangium.

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LIST OF ABBREVIATIONS

AMCA	*Acacia mangium* cellulose acetate
ASH	Action on smoking and health
CA	Cellulose acetate
CCA	Commercial cellulose acetate
CMC	Carboxymethyl cellulose
DBH	Diameter breast height
DP	Degree of polymerization
DS	Degree of substitution
EIA	Ethiopian embassy
GAMA	Global Acetate Manufacturers Association
LCD	Liquid crystal display
MDF	Medium density fiberboard
MOE	Modulus of elasticity
MOR	Modulus of rupture
RE	Rate of efficiency
TAPPI	Technical Association of the Pulp and Paper Industry
WPG	Weight percentage gained

LIST OF EQUATIONS

LIST OF SYMBOLS

±	Plus minus
μm	Micrometre

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Plants play a constitutive role in the functioning of the ecosystem. Apart from conducting a colossal part in the carbon cycle, plants are also one of the main contributors to the most abundant organic compound on Earth, the cellulose. According to VarshneyandNaithani (2011),there are about 10^{11} to 10^{12} tons of cellulose are synthesized annually through photosynthesis, as cellulose is one of the main component in plants besides hemicellulose and lignin, comprising of approximately 45 to 50% of all carbon in vegetation (Haygreen and Bowyer, 1989). Usually being extracted through processes such as pulping or cellulose purification, cellulose is extensively used as raw materials in paper production (Villar, Revilla, Gomez, Carbajo and Simon, 2009) and lignocellulosic bioethanol production (Limayem and Ricke, 2012).

The unique structure of cellulose enables it to be one of the more easily modified elements, as it is constituted of long chains of glycosidic units with unlimited hydroxyl groups. With the promise of a never-ending supply and high modification potential, cellulose has a high potential in the development of bio-based material engineering such as one of the promising but far long ago established, cellulose derivatives. Derivatives by definition are imitative materials, which is based from a natural element or source such as cellulose, where the properties are profoundly improved from its original form through the process of chemical alterations. As for cellulose derivatives, it includes processes such as etherification and esterification to obtain the targeted trait or characteristics in forming a new and improved product, which individually incorporates chemical reactions with alkaline and acidic reagents, respectively. Among the cellulose derivatives available includes carboxymethyl cellulose (CMC) and ethyl cellulose for ethers, and cellulose acetate for esters (Granström, 2009).

For this study, cellulose acetate was produced from *Acacia mangium* for the production of acetate lacquer. Cellulose Acetate (CA) is one of the cellulose derivatives, specifically ester, which is produced through the substitution of hydroxyl group by acetyl groups provided from acetic acids. The procedures in fabricating the CA are slightly modified following previous studies to obtain the optimum condition and providing lower cost alternative procedures that includes different types of pretreatments, reaction time, catalyst, and mesh size. Meanwhile the selection of *A. mangium* is based on Pinto, Evtuguin, and Neto (2005), where it shows an impressive composition of cellulose with an overall composition of over 45% in dry weight, hence is chosen to be the main source of cellulose for the project as an alternative of the cellulose-filled cotton.

According to Saka (2004), there are a number of other selections for the source of cellulose, which typically includes cotton and wood pulps. The production of CA can be derived from most plants, but is highly recommended for plants with a high composition of α-cellulose. There has been a number of previous researches done on the production of cellulose acetate from a wide range of plant species, such as agricultural biomass that includes sugarcane bagasse (Shaikh, Pandare, Nair, and Varma, 2009), corn fiber, rice hulls and wheat straw (Biswas, Saha, Lawton, Shogren, and Willett, 2006) and cotton byproducts (Cheng, Dowd, Selling, and Biswas, 2010), as well as hard and soft wood. Mainly the wood species suitability for the derivation of cellulose refers similarly to the production of pulp for paper itself, similarly following the suitable species such as birch and spruce for softwood (Laine, 2005) as well as Yemane (Palaypayon and Batalon, 2002) and Batai (Bunye, 1990) for tropical hardwoods.

Due to the production of CA from biodegradable materials, it is one of the long lasting derivatives with numerous developments since more than a century ago. There are four (4) main categories of CA products, which include fibers for textile application, tough and moldable materials for plastics, film for tapes and coatings, and as effective filter for beverages and cigarette filters (Rustemeyer, 2004). Properties such as hypoallergenic, high water absorption, and mold/mildew resistant are among the excellent qualities of CA for the utilization as a raw material for the textile industry. Meanwhile, properties such as thermoplasticity, highly soluble in solvents, and bondable in plasticizers, makes it a suitable substance for the film and membrane industry, with an additional biodegrability trait due to the development from natural renewable resources (Fischer, Thummler, Volkert, Hettrich, Schmidt, and Fischer, 2008).

One of the oldest products for CA is lacquer, which used to be called dope during World War I. Acetate lacquer is a type of glossy clear coating that forms a film on the surface of the area through the evaporation of the solvents, differentiating itself from naturally derived resin-based lacquers. The film formation mechanism differs from the resin-based lacquers due its dependability towards solvent, where crosslinking among monomers happens with the evaporation of solvents. It is highly used in the finishing act in the wood industry as a barrier from the exposure of weather and pests, and considered as a beautifier of the products. Lacquer produced from CA namely will adapt the better qualities of the CA itself such as the hypoallergenic and resistance to molds, and proven to be of an advantage even more than other cellulose esters such as Nitrocellulose that was usually used to produce nitrate films, but due to its flammability, was developed into gun powders instead (Gettens and Stout, 2012).

1.2 Problem Statement and Justification

The extricable resources of the Earth are reckonable, in spite of the disputes over its depletion rate, especially to the non-renewable resources such as petroleum. Based on the Peak theory by Marion King Hubbert, the rate of petroleum production of the reserve over time would resemble a bell curve for any given geographical area, in which anticipates an exponential growth, followed by an overall peak petroleum production before encountering a decline of oil capacity right after. The said theory successfully predicted the peak oil production for the 48 states of the United States of America, which peaked in 1970, within the estimated 1966 – 1972 augured year (Towler, 2014).

With the act of depleting resources became fully aware, the demands for bio-based products; be it chemicals, materials, and energy are envisioned to be fully in amplified demands, hence, rigorously metamorphose the material industries, notably in the petroleum alternatives industry such as plastics and biofuels, stemming from the proposition of sustainability and green energy. Developments in alternative productions such as soy-based biodiesels (Tomei and Upham, 2009) and plasticizers (Galli, Nucci, Pirola, and Bianchi, 2014) have garnered attention in the chemical engineering world due to its perceptible improvements to the environmental impact and workers' safety.

Likewise, the consumers of the world are also becoming more aware in the advantages in using biodegradable products or machines that emit lower carbon dioxide emission or high carbon sinkage. Alternatives to coating products with paraffin wax, which is a petroleum-based derivative, are expected to be in high demands such as the starch-based (Rohula, Kawiji, Andre, and Andik, 2013) and lignin-based (Narapakdeesakul, Sridach, and Wittaya, 2013) coatings. With a higher demand for alternatives, succeeding action will also increase the demands of renewable resources, subsequently increasing the supply for these bio-based materials resources such as trees and other vegetation.

As in Malaysia, we are naturally blessed with a rich condition that is most suitable in deciduous as well as some of the coniferous trees, in other words, sustainably rich in resources. Exploiting the perfect condition for timber plantations, production of fast-growing woods with inferior quality has resulted to some unwanted implications in utilization of it as solid wood. With the intention of developing the usability of plantation timbers that has an unfortunately low desirability factor, it is more feasible and cost effective for its development in the cellulose-based application and industrialization (Varmola, 2002).

In Sabah alone, *Acacia mangium* has been steadily producing logs for industrial use since the early 1990s. With more than 4 000 000 m^3 of plantation log production in 2011, *A. mangium* is one of the major contributor in the Sabah timber supply with a fourth of the count, consequently providing a promising supply of cellulose (Sabah Forestry Department, 2012). With only an approximately 3% of the overall production exported, the majority of the *A. mangium* usage are used as materials for the downstream processing in Sabah, hence a number of potential of the fast growing timber as raw material for other fiber or cellulose products has also been carried out such as for acetylated Medium Density Fiberboards (Unchi, 1996), pulp for papermaking (Lee, 2004) and particleboards (Sarmin, Zakaria, Kasim, and Shafie, 2013). Apart from the Thus, this study will be focusing on improving the potential application of timber as fiber or cellulose based, specifically the feasibility of *Acacia mangium* to be developed into a bio-based ester material, specifically cellulose acetate (CA) in being consequently developed into wood coating lacquer.

1.3 Objectives

The focus of this study was to produce cellulose acetate from *Acacia mangium* pulp, and then subsequently develop it into wood laminating lacquer. It follows four objectives, which includes;

1. To determine and compare the chemical composition and fiber dimensions between the *Acacia mangium* pulp and wood fiber.

2. To evaluate the effect of the manipulated condition towards the degree of substitution, weight percentage gained, and rate of efficiency in the production of cellulose acetate from *Acacia mangium*.

3. To identify and characterize the spectroscopy of the cellulose acetate produced.

4. To evaluate and compare the properties of the basic and applied lacquer between the *Acacia mangium* acetate lacquer and a commercial cellulose acetate lacquer.

CHAPTER 2

LITERATURE REVIEW

2.1 *Acacia mangium*

Acacia mangium (Figure 2.1)is a leguminous tree species from the family of Fabaceae. Native of Australia, Indonesia and Papua New Guinea, which is also widely grown exotically in countries such as Malaysia, South Africa and Vietnam. *A. mangium*is originally planted in the Malesian region such as Thailand and Papua New Guinea as an ornamental, however due to its fast growing and utilization potential properties, significant areas of plantations has been established in numerous countries such as India, Indonesia and Malaysia (Hegde, Palanisamy, and Jae, 2013). In Sabah alone, the FSC certified forest plantation, which includes SAFODA and Sabah Softwood Bhd., covers up more than 40 000 hectares that is dominantly populated by *Acacia mangium* (Sabah Forestry Department, 2012).

Being a single-stemmed evergreen tree, *A. mangium* can grow up to 25-35 m in height with a straight bole, reaches roughly up to six (6) meters increment in height and 15 cm in diameter breast height (DBH) per year. The bark surface is rough, rutted longitudinally and differs in colors, from the range of pale grey-brown to brown, while the sapwood and heartwood may have distinct color from each other. The former is often white or yellowish white and the latter is yellowish brown to golden-brown when fresh, but oxidized to dull brown when exposed longer. It is a light hardwood that has the density ranges from 400-480 kg/m^3 (Sahri, Ibrahim, and AbShukor, 1993), giving it good reputation as a fast growing timber species with considerably good form and utilization potential.

Figure 2.1: *Acacia mangium* tree sapling.

Acacia mangium is a durable tree species that can endure extreme conditions such as the wide variety of soil types, low soil fertility and acidic pH soil as low as 3.8. It can also tolerate extreme weather such as heavy rainfall and drought, with significant difference in growth rate. This species was also successfully planted on areas of shifting cultivation colonized by *Imperatacylindrica* grass such as in Indonesia (Otsamo, 2001). Apart from its tolerability, the utilization of the species as timber is also favorable, as it can be easily sawn, drilled, polished and turned. The dimensional stability is within a satisfactory range state, with green to air-dried shrinkage of 6.4% in the tangential section and 2.7% in radials (Kader and Sahri, 1992). *A. mangium*has one of the highest moisture content in assorted age groups, in the heartwood more than sapwood with the highest reaching up to 253% and 149% respectively (Lim, Gan, and Choo, 2003), substantially increasing its MOR and MOE in its dried state (Table 2.1).

Table 2.1: Mechanical Properties of *Acacia mangium* wood

Properties	*Acacia mangium*	
	Green	Air-dry
Modulus of Rupture (MPa)	37.8	58.4
Modulus of Elasticity (MPa)	9579	11671
Compression Parallel to Grain	30.7	43.5
Cleavage (radial)(N/mm)	12.02	12.65
Cleavage (tangential)(N/mm)	15.05	16.20

Source: Lim *et al.* (2003)

2.1.1 Utilization

Similar to other lignocellulosic materials, the utilization of *A. mangium* wood can be divided into three main categories; which includes timber, fiber, and pulp. Each category is significant to its own field, wherein the timber sector, *A. mangium* is an important source of wattle timber, which is usually used for boat building and constructions but not for structural timber as it has low susceptibility towards pest and contains undesirable knots and flutes. It also has potential for non-structural timber, which includes molding, furniture (Figure 2.2) and veneers, as well as for firewood and charcoal due to its calorific value of 4800–4900 Kcal/kg (Orwa, Mutua, Kindt, Jamnadas, and Anthony, 2009).

In the form of macerated fiber or particles, *A. mangium* fiber has long been used as a material in the production of engineered woods, which includes particleboards and fiberboards, due to its fast-growing properties. Production of pulp from its fiber are also feasible due to it low tolerance towards bleaching, enabling it to provide a bright pulp for papermaking hence making it grown primarily for this industry in Sabah, Sumatra, and Vietnam (Hegde*et al*., 2013).