THE STUDY OF SUGARCANE BAGASSE PYROLYSIS DERIVED OIL FOR BIO-BASED ADHESIVE

by

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LIST OF ABBREVIATIONS

BPF	Bio-Based Phenol Formaldehyde
C	Carbon Element
DSC	Differential Scanning Calorimetry
EVA	Ethylene Vinyl Acetate
GCMS	Gas Chromatography Mass Spectrometer
HHV	High Heating Value
LVL	Laminated Veneer Lumber
MF	Melamine Formaldehyde
NaOH	Sodium Hydroxide
OFAT	One-Factor-At-A-Time
OSB	Oriented Star and Board
O_2	Oxygen
PF	Phenol Formaldehyde
PVA	Polyvinyl Acetate
PRF	Phenol Resorcinol Formaldehyde
RF	Resorcinol Formaldehyde
TGA	Thermogravimetric Analysis
UF	Urea Formaldehyde
UTM	Universal Testing Machine
ZSM-5	Zeolite Socony Mobil-5

LIST OF SYMBOLS

℃	Celcius
min	Minute
wt%	Weight Percentage
°C/min	Celcius per minute
hr	Hour

Kajian ke atas Hasilan Minyak Pirolisis Hampas Tebu Untuk Pelekat Berasaskan Bio

ABSTRAK

Resin fenolik adalah polimer termoset yang terbentuk daripada pemeluwapan fenol dan formaldehida berasaskan petroleum. Resin ini kebanyakannya digunakan dalam industry kayu kerana kekuatan ikatan yang tinggi, kestabilan kimia, rintangan haba dan rintangan air. Bagaimanapun, disebabkan ketidakstabilan harga minyak, harga fenol juga terjejas dan menyebabkan pembatasan penggunaan resin PF. Biomas lignoselulosa kelihatan seperti pengganti hebat kerana ia mempunyai struktur yang sama seperti resin PF komersial. Oleh itu, matlamat kajian ini adalah untuk menghasilkan dan mencirikan hasil bio-minyak tertinggi yang diperolehi daripada pirolisis katalitik dan bukan katalitik hampas tebu. Keadaan untuk mensintesis resin fenolik berasaskan bio ditentukan dari proses pengoptimuman resin formaldehida fenol menggunakan kaedah satu faktor-pada-satu-masa (OFAT). Keadaan optimum ditentukan dengan membandingkan kesan pembolehubah seperti nisbah molar F/P, masa dan nisbah pemangkin (NaOH/P) pada sifat fizikal dan kekuatan mekanikal resin PF. Keadaan optimum yang dikenal pasti bagi sintesis resin PF digunakan dalam pengeluaran resin fenolik berasaskan bio di mana bio-minyak pada nisbah berat yang berbeza (10, 20, 30, dan 40% berat) dicampurkan dengan resin PF komersial. Kesan kadar penggantian pada sifat-sifat dan kekuatan mekanik resin BPF ditentukan berdasarkan perbandingan dengan data Standad Kebangsaan Cina (GB / T14732-2006) untuk resin PF. Piawaian ini dipilih kerana saiz piawai papan lapis adalah sesuai untuk dilaksanakan menggunakanMesinUjian Universal. Keputusan menunjukkan bahawa hasil bio-minyak tertinggi diperolehi daripada pirolisis katalitik pada suhu 500˚C iaitu 21.4% berat. Pengkhususan fisiologi kimia bio-minyak menunjukkan bio-minyak mempunyai potensi untuk digunakan sebagai pelekat. Keadaan optimum untuk mensintesis resin formaldehida fenol adalah pada nisbah molar F/P (2.0), masa (3 jam), dan nisbah pemangkinNaOH/P (0.6). Keputusan prestasi ikatan resin fenolik berasaskan bio menunjukkan bahawa tahap penggantian bio-minyak maxima sehingga 20% sahaja yang memberi prestasi yang baik dan setanding apabila dibandingkan dengan Standad Kebangsaan Cina untuk resin PF. Kajian ini dijalankan memandangkan tidak banyak kajian yang menumpukan pada pengeluaran pelekat berasaskan bio menggunakan bio-minyak yang diekstark dari tebu. Penemuan keseluruhan menunjukan bahawa bio-minyak yang diekstrak dari tebu mempunyai potensi untuk digunakan sebagai pelekat berasaskan bio.

The Study of Sugarcane Bagasse Pyrolysis Derived Oil for Bio-Based Adhesive

ABSTRACT

Phenolic resins are thermosetting polymers that are formed from the condensation of petroleum-based phenol and formaldehyde. This resin is mostly utilized in wood industry due to their high bonding strength, chemical stability, heat resistance and water resistance. However due to the fluctuation of oil price, the price of phenol is also affected which constrained the application of PF resin. Lignocellulose biomass seems like a great replacement as it has quite similar structure as the commercial PF resin. Hence, the aim of this study is to produce and characterize the highest yield of bio-oil gained from catalytic and non-catalytic pyrolysis of sugarcane bagasse. The conditions for synthesizing bio-based phenolic resin are determined from the optimization process of Phenol Formaldehyde (PF) resin using one-factor-at-a-time (OFAT) method. The optimum condition was determined by comparing the effect of the manipulating variables such as F/P molar ratio, time and catalyst ratio on the physical properties and mechanical strength of the PF resin. The identified optimum conditions for synthesis of PF resin were applied in the production of bio-based phenolic resin where bio-oil at different weight ratios (10, 20, 30, and 40 wt.%) were mixed with the commercial PF resin. The effect of substitution rate on the properties and mechanical strength of the BPF resin is determined based on the comparison with the Chinese National Standard (GB/T14732-2006) data for PF resin. This standard was chosen due to the plywood standard size was compatible to be done using the Universal Testing Machine. The results shows that highest yield of bio-oil was gained from catalytic pyrolysis at temperature of 500°C which was 21.4 wt%. Physiochemical characterizations of the bio oil shows bio-oil has potential to be used as adhesive. The optimum condition to synthesize phenol formaldehyde resin is at F/P molar ratio of (2.0), time (3 hour), and NaOH/P molar ratio of (0.6). The results of bio-based phenolic resins bonding performance shows that the level of bio-oil substitution up to 20% at most provide a good performance and comparable to the Chinese National Standard PF resin. This study was carried out considering there were not much studies focusing on the production of bio-based adhesive using bio-oil extracted from sugarcane bagasse. Overall, findings show that bio-oil extracted from sugarcane bagasse has a potential to be used as bio- based adhesive.

CHAPTER 1 : INTRODUCTION

1.1 Background

In recent years, the forest industry has become one of the major industries in the world. Composite elements like plywood, flake board, strand board and lumber have high demands especially in manufacturing industry. Phenol Formaldehyde (PF) resins is an adhesive that is conventionally used in the manufacturing of these composite wood products. PF resin is a synthetic polymer gained from the reaction between phenol and formaldehyde. However, phenol used in this process comes from petrochemical sources. The depletion of petroleum and environmental issues has resulted in the search for alternative resources as a replacement for petroleum based phenol. Lignocellulose biomass seem like a promising alternative energy sources as it can be converted into bio-oil which is rich with phenolic compound (Brosse, Ibrahim, & Rahim, 2011).

Biomass is a biological components developed from living or recently living organisms. It can produce heat in the energy context, as an alternative to fossil fuels (Akhtar & Amin, 2011). Utilization of lignocellulose biomass such as crop residues, grasses, sawdust, wood chip, oil palm empty fruit bunch, trunk, and frond seems like a potential source for future low cost bio-based adhesive production. Lignocellulose biomass primarily consists of natural polymers hemicelluloses, cellulose and lignin. Table 1.1 shows the content of lignocellulose materials which varies with every species (Gani & Naruse, 2007).

Table 1.1: Composition of lignocellulose materials (Gani & Naruse, 2007)

<table>
<tr><th colspan="2">Lignocellulose materials</th><th>Lignin (Wt. %)</th><th>Cellulose (Wt. %)</th><th>Hemicellulose (Wt. %)</th></tr>
<tr><td colspan="2">Forestry residues/wastes</td><td>20-35</td><td>40-45</td><td>15-35</td></tr>
<tr><td colspan="2">Agriculture residues/wastes</td><td>10-20</td><td>34-39</td><td>20-25</td></tr>
<tr><td colspan="2">Paper waste</td><td>8-18</td><td>62-75</td><td>12-20</td></tr>
<tr><td rowspan="2">Softwood</td><td>Wood</td><td>25-30</td><td colspan="2">66-72</td></tr>
<tr><td>Bark</td><td>40-55</td><td colspan="2">30-48</td></tr>
<tr><td rowspan="2">Hardwood</td><td>Wood</td><td>18-25</td><td colspan="2">74-80</td></tr>
<tr><td>Bark</td><td>40-50</td><td colspan="2">32-45</td></tr>
<tr><td colspan="2">Eastern White Pine Dust</td><td>28.4</td><td>40.2</td><td>21.9</td></tr>
<tr><td colspan="2">Cornstalk</td><td>24.7</td><td>26.7</td><td>21.0</td></tr>
</table>

Previous researches show that high amount of lignin in agricultural waste is an excellent element for the synthesis of bio-based adhesive (Moubarik, 2014; Zhang, Tu, & Paice, 2011). The abundance and high amount of lignin content in lignocellulose materials makes it suitable to be used in the production of adhesive. Lignocellulose materials can be converted into bio-oil by thermochemical methods, such as pyrolysis and liquefaction. Figure 1.1 shows the product generation from biomass conversion via bio-refinery concept (Capareda, 2002).

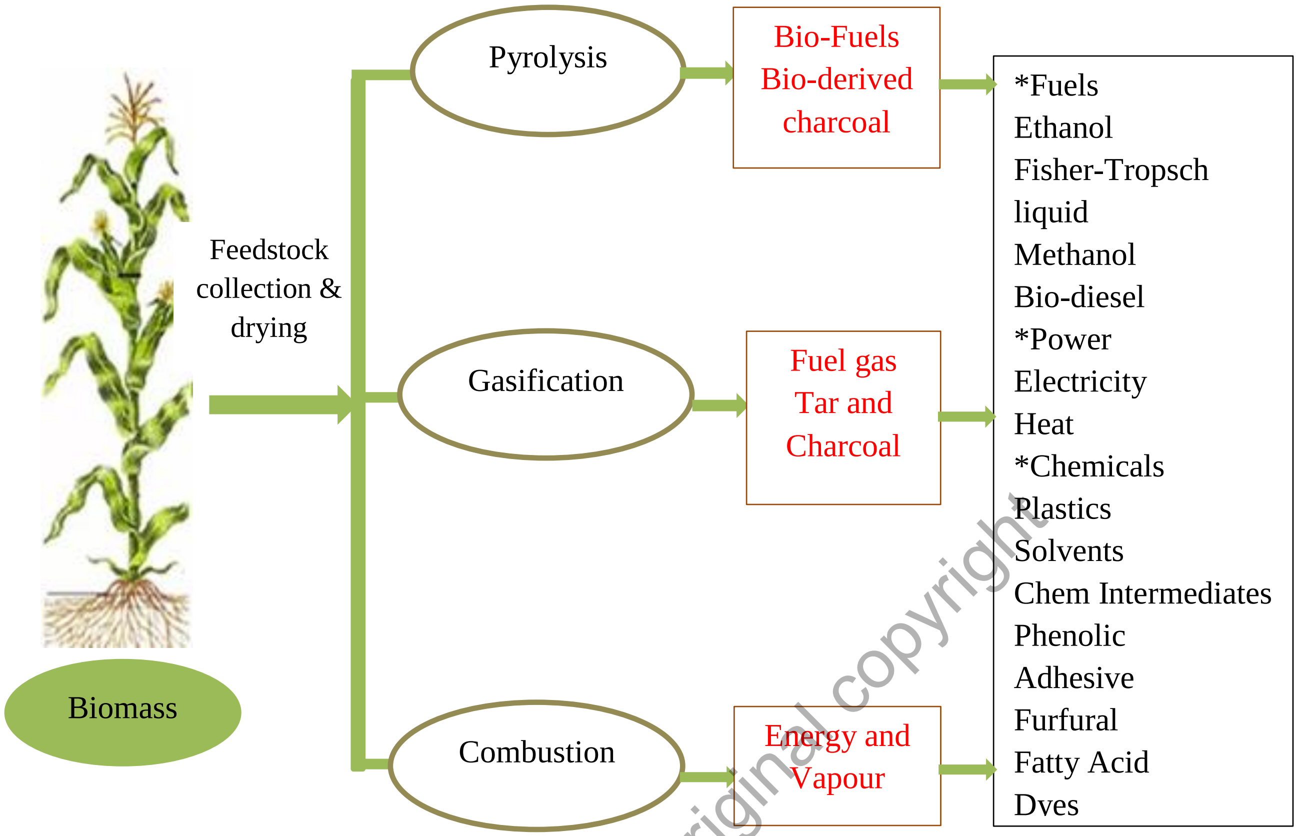

Figure 1.1: Product generation from biomass conversion via biorefinery concept (Capareda, 2002).

In this study, sugarcane bagasse was used as biomass feedstock to produce bio-oil using pyrolysis method. The bio-oil obtained will be further optimized into adhesive. Most studies about bio-oil have emphasized its usage in transportation, fertilizers, agrichemicals and food flavourings (Mathias, Grédiac, & Michaud, 2016). However, to date there have been scarce of study on the synthesis of adhesive using whole bio oil. Hence, the aim of this research work is to characterize the physicochemical properties of bio-oil, optimize the synthesis of PF resin and determine level of bio-oil substitution in the production of Bio-Based Phenol Formaldehyde (BPF) resin.

1.2 Problem statement

Phenol formaldehyde (PF) resin has been widely used as wood adhesive for production of various wood composites due to their excellent bonding strength, water resistance and durability. Phenol is a primary component of resin used in the wood adhesive industry which is derived from fossil fuel resources (petroleum and coal).

The cost of producing phenol formaldehyde resin is high as it depends on the petroleum price. The current value of PF resin in market is at $10 billion/tonne globally, and has an annual market value of $4.5 billion/tonne to $6 billion/tonne (Siddiqui et al., 2017). Besides that, the extraction process of phenol from petroleum can be dangerous to the environment and also human health. Phenol is known for its toxicity and carcinogenic effect which is dangerous to human health. In terms of the environment, the used of bio-oil from biomass as substitution for petroleum based phenol seems like a great alternative as it helps to reduce the carbon footprint. In addition the biodegradability of renewable materials such as cellulose is higher compared to synthetic materials (Ghorbani et al., 2016).

Lignocellulose biomass is renewable natural resource that is composed mainly of organic polymers such as cellulose, hemicelluloses and lignin. Although lignocellulose biomass is burned to generate energy in some industry, but most of it is discarded as waste. The phenolic structure of lignin in lignocellulosic biomass is quite similar with the commercial phenol, so it can be used as a partial substitute for phenol in the production of PF resin.

This method had been emerging as a reliable technique because it is from renewable materials which are abundant and thus lowering the cost of production. Studies on utilization of biomass as precursor for synthesis of PF resin by using pyrolysis method is still limited. Thus, this research will be focusing on production and characterization of bio-oil from sugarcane bagasse as well as to optimize the synthesis of PF resin and determine level of bio-oil substitution in the production of Bio-Based Phenol Formaldehyde (BPF) resin.

1.3 Research objectives

The three objectives that have been outlined for this research work are as follows:

I. To characterize the pysical and chemical properties of the highest bio- oil yield derived from sugarcane bagasse.

II. To optimize Phenol Formaldehde (PF) resin prepared at different operating conditions consists of formaldehyde/phenol (F/P) ratio, catalyst (NaOH/Phenol) ratio and duration.

III. To determine level of bio-oil substitution in the synthesis of Bio-Based Phenol Formaldehde (BPF) resin.

1.4 Scope of research

In this research, bio-oil was extracted from sugarcane bagasse using catalytic and non-catalytic pyrolysis method where the products mostly consist of bio-oil, bio-char and permanent gases, such as hydrogen, carbon monoxide, and carbon dioxide.

Catalytic and non-catalytic pyrolysis was conducted in catatest bed reactor with temperature range of 400-550˚C at atmospheric pressure and heating rate of 50˚C/min. The catalyst used in this research was zeolite ZSM-5. The highest bio-oil yield achieved among catalytic and non-catalytic pyrolysis will be selected to be characterized further.

Preparation of PF resin was carried out by batch polymerization process at different operating condition such as F/P molar ratio, NaOH/P molar ratio and duration. Each parameter is manipulated by using one-factor-at-time (OFAT) method. Each time a factor is manipulated the physical properties which consist of pH value, viscosity, and gel time and also mechanical strength of the PF resin will be tested to determine the optimum conditions for the preparation of the PF resin.

The optimum conditions determined from the preparation of PF resin will be incorporated in the synthesis of Bio-based Phenolic (BPF) resin. BPF resin is prepared by mixing various amounts of PF resin and bio-oil weight ratios. The level of bio-oil substitution is determined by comparing the shear strength value with Chinese National Standard shear strength for the commercial PF resin. This standard was chosen due to the plywood standard size is compatible to be done using the Universal Testing Machine. The shear strength of BPF resin which was applied on plywood was tested using Universal Test Machine (UTM). Physical characteristic of the resin such as pH value, viscosity and gel time was also determined.

Although this research was carefully prepared, however there are still limitations and shortcomings.

First of all, the research was conducted at constant conditions which were atmospheric pressure, heating rate (50°C/min) and particle size of biomass (0.6mm). Secondly, the type and amount catalyst (0.2 g zeolite ZSM-5) used in the reactor is also fixed which is based on previous research by Imran, Bramer, Seshan, & Brem, (2016).

1.5 Thesis organization

Chapter 1 is the introduction which consist the background of study, problem statement, research objective and scope of research. Chapter 2 is literature review which mainly describes the review for entire study which includes biomass in Malaysia, sugarcane bagasse, biomass conversion and adhesive. Chapter 3 is methodology where this part explained the materials and methods used to conduct the analysis, material preparation, data collection in order to achieve the objectives listed. Chapter 4 is result and discussion of the results obtained from the study of the research objectives. Chapter 5 elaborate the conclusion based on the results obtained during the study. The ideas for further study are listed in the future work section. Overall 5 chapters, a list of references and appendixes are included in this thesis.

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

This chapter elaborates on the current knowledge including substantive findings, as well as theoretical and methodological contributions of adhesive and bio-oil.

2.2 Adhesive

Adhesive is known as glue, cement or paste that can be applied to one surface, or both surfaces, of two separate items that binds them together and resists their separation (William, 2009). Phenol formaldehyde (PF) resin is one of adhesives that are mostly used in manufacturing building materials such as plywood, windows and frames, architectural doors, and fibreglass insulation. Phenol which is used in the synthesis of PF resin is extracted from petroleum; hence the price of PF resin is quite high as it depend the petroleum price. The supply of PF resin is enough until today, but scarcity of petroleum products can affect the future cost and availability of PF resin. Thus, it is vital to explore other alternative as a replacement for these petroleum based raw materials such as renewable sources (Khan, Ashraf,& Malhotra, 2004).

2.3 Types of Adhesive

Wood adhesive exist in two forms, synthetic and natural adhesive as shown in Table 2.1. Synthetic adhesive are adhesive that are made from petrochemicals derived raw materials. There are two types of synthetic adhesive which are thermoplastic and thermosetting resin.

Table 2.1: Classification of Wood Adhesives (Conner & Bhuiyan, 2017)

Class	Resin type	Typical adhesive system
Synthetic		
Thermosetting	Amino	Urea-formaldehyde (UF) Melamine formaldehyde (MF) Melamine-urea-formaldehyde (MUF)
	Phenolic	Phenol-formaldehyde (PF) Resorcinol-formaldehyde (RF) Phenol-resorcinol-formaldehyde (PRF)
	Isocyanate	Diphenylmethane-4,4'-discocyanate (MDI)
	Epoxy	Bisphenol A-based epoxy resins
	Elastomeric	Styrene butadiene rubber (SBR)
Thermoplastic	Vinyl	Polyvinyl acetate (PVAc) Polyvinyl alcohol (PVA)
	Hot-melts	Ethylene vinyl acetate (EVA)
Natural	Protein	Casein Soybean Blood Animal

Thermoplastic resins are polymer which get soften when contact with heat and solidify upon cooling to room temperature. Polyvinyl acetate (PVAc) is one of the major wood adhesive used in this category. Polymer which has lower molecular weight and viscosity than most of thermoplastic are hot-melts polymer. Example for this type of adhesive is Ethylene vinyl acetate (EVA). Thermosetting resins are formed when polymers are cross-linked during cure. These polymers are insoluble and do not soften on heating when it has been cured. Examples of these adhesives include amino resins, phenolic resins, epoxy resins, and isocyanates (Conner & Bhuiyan, 2017).

Natural adhesive are synthesized from organic sources. Natural adhesive is generally known as bio- based adhesives. Due to an increasing environmental awareness and the growing need to decrease dependence on petroleum resources, much attention has been paid to the possibilities of synthesising polymeric materials from bio-based, renewable resources. Renewable materials have historically been used as adhesives longer than synthetic polymers, but have been replaced in many applications because of the cheaper production or superior characteristics of synthetic equivalents. One example is the adhesive used on the back of stamps. It was historically based on natural gums such as gum arabic, but has now been largely replaced by polyvinyl acetates due to their superior adhesion and water resistance (Dian Lopez & Montalvo, 2015).

Protein is biopolymers that already have adhesive characteristics. Examples of these biopolymers are casein, soybean, blood and animal.

2.4 Phenol Formaldehyde (PF) Resin

Phenol formaldehyde resins or phenolic resins are synthetic polymers obtained by the reaction of phenol or substituted phenol with formaldehyde. The chemical structure of the raw material, the molar ratio of formaldehyde to phenol (F/P), process duration, and the catalyst ratio are the main factors governing the type of resin (Hu, Zhao & Cheng, 2014).

Research done by Lee et al., (2003); Nakos et al., (2001); Amen Chen et al., (2002) shows that the preparation of phenolic resin is usually conducted at F/P molar ratio range of 1.8 to 2.2, catalyst ratio of 0.5 to 0.7 and duration of 1 to 4 hour. The optimum conditions for the preparation of phenolic resin are commonly determined by studying the properties of the resin such as pH, viscosity and gel time (Hu et al., 2014).

2.5 Applications of Phenolic Resin

Phenolic resins are commonly used in the industry. The advantages of phenolic resin are it allows substrates to joint with different type of sizes and shapes. Furthermore, the application of phenolic resin as bonding material does not cause any deformation to the materials. Besides that, PF resin also reduces the manufacturing cost and improves the aesthetics feature of the product (Conner et al., 2017).

The applications of PF resin globally is shown in Figure 2.1. Phenolic composite materials cover a wide range of industries including wood adhesive, moulding compound, insulation, laminates, paper impregnation and coatings. Phenolic resin is used widely in moulding compound which also known as Bakelite. It is favourably used for various purposes due to the excellent water resistance, heat resistant and dimensional stability (Srebrenkoska, Bogoeva Gaceva, & Dimeski, 2009). However phenolic resin has been used mainly as wood adhesive in the structural of wood-based composites such as plywood, oriented star and board (OSB) and laminated veneer lumber (LVL).

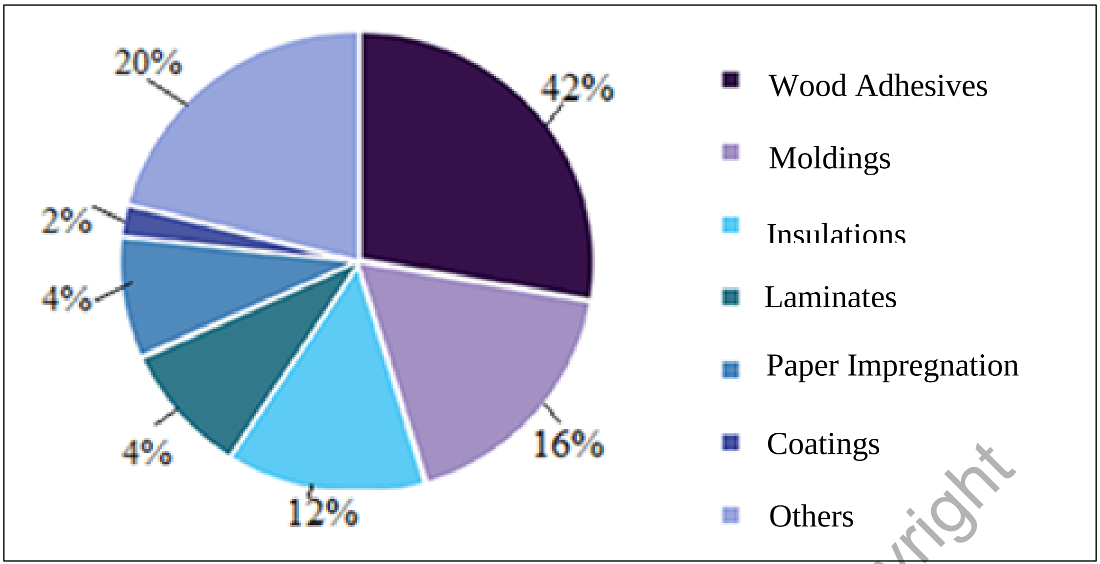

Figure 2.1.: Global Phenolic Resin Market Trends by Applications 2018
(Pang, Jiao, & Tao, 2006)

2.6 Market Survey for Phenolic Resin

The global phenolic resin market is expected to reach an estimated value of $16.0 billion/tonne by 2025. Wood adhesives are the dominant application of this resin, result of high demand from furniture, woodworking and construction industries (Lucintel, 2018). The relatively low cost and proven performance of phenol-formaldehyde and urea-formaldehyde resins has made them the most important adhesive systems for composite wood products. Nevertheless, PF resin is more suitable for exterior grade compared to Urea Formaldehyde (UF) resin due to its moisture resistance ability (Ferdosian, Pan, Gao, & Zhao, 2017).

PF resin is a petroleum-based product, whereby any significant increase in the price of crude oil will affect the price of wood adhesive. Thus, it is important to consider the future supplies of adhesives and the impact of future adhesive cost. Figure