SYNTHESIS AND CHARACTERIZATION OF BIO-PHENOLIC GLYOXAL RESINS VIA LIQUEFACTION AND RESINIFICATION OF EMPTY FRUIT BUNCH FIBRES

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Thesis submitted in fulfillment of the requirements for the award of the degree of

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SUPERVISORS' DECLARATION

I hereby declare that I have checked the thesis and in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Applied Science (Honor) Material Technology.

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STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

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DEDICATION

This thesis is dedicated to my beloved father, Ismail Bin Othman, mother, Tharwar Maisur Bt Shahar Murshid, my siblings, and my friends. Without whom none of my success could possible.

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LIST OF SYMBOLS

~	-	approximately
%	-	percent
^{o}C	-	degree celcius
g	-	grams
cm	-	centimetre
cm^{-1}	-	reciprocal centimeters
ml	-	milliliters
mg	-	miligram
h	-	hour
t	-	time
wt%	-	weight percent

LIST OF ABBREVIATIONS

EFB	-	Empty fruit bunch
TGA	-	Thermogravimetric analysis
ATR	-	Attenuated total reflection
FTIR	-	Fourier transform infrared spectroscopy
HCl	-	Hydrochloric acid
H_2SO_4	-	Sulphuric acid
H_3PO_4	-	Phosphuric acid
NaOH	-	Sulphuric Acid
KBr	-	Potassium bromide

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ABSTRACT

The fast development of oil palm industry in the country has produced substantial amount of empty fruit bunch (EFB) fibres. These waste has caused pollution to the environment. To overcome this problem, research has been made to convert EFB into bio-phenolic resin which has beneficial uses in industry. This research describes the synthesis and characterization of bio-phenolic glyoxal resins by using liquefaction of EFB fibres. EFB were liquefied in phenol with the presence of hydrochloric acid and mixture of sulphuric acid with phosphuric acid as catalyst for 2 hours at 150 ℃. The liquefied EFB and residue was characterized using FTIR to determine the functional groups present and to determine the effect of catalyst on phenol and EFB. Glyoxal is used as dialdehyde replacing formaldehyde for resinification as it is non-toxic and obtained from natural sources which make it environmental friendly. Next, after resinification process of liquefied EFB and glyoxal with the presence of sodium hydroxide, the bio-phenolic resin C and resin F were characterized using ATR-FTIR and TGA analysis. The ATR-FTIR analysis shows that resin C produced higher and strong intensity compared to resin F. TGA analysis were used to study the thermal stability and to compare the weight loss between those resins.The decomposition temperatures of sample F is 232.47℃ while the temperature of decomposition for resin C is 189.52℃. It can be concluded that glyoxal can be a successful replacement for formaldehyde in producing Bio-Phenolic resin.

ABSTRAK

Kepesatan industri menggunakan pokok kelapa sawit di negara ini telah menghasilkan lebihan serabut tandan kosong kelapa sawit (EFB). Sisa ini menyebabkan pencemaran kepada alam sekitar. Untuk mengatasi masalah ini, penyelidikan telah dibuat untuk menggunapakai EFB kepada resin bio-fenolik yang mempunyai kepelbagaian berfaedah dalam industri. Kajian ini menerangkan tentang sintesis dan pencirian resin glyoxal bio-fenolik dengan menggunakan teknik pemanasan minyak EFB. EFB telah dicairkan bersama fenol dengan kehadiran acid hydrochlorid dan asid sulfuric/acid fhosphuric sebagai pemangkin selama 2 jam pada 150 ℃. Cecair EFB serta lebihannya telah dianalisis menggunakan FTIR bagi menentukan kumpulan berfungsi yang hadir dan untuk menentukan kesan pemangkin terhadap fenol dan EFB. Glyoxal digunakan sebagai dialdehyde menggantikan formaldehid untuk resinification kerana ia tidak mengandungi bahan toksik dan diperolehi daripada sumber semula jadi yang menjadikannya mesra alam sekitar. Seterusnya, selepas proses resinification (sintesis EFB cecair dan glyoxal dengan kehadiran NaOH), bio-fenolik glyoxal resin C dan resin F dicirikan menggunakan ATR-FTIR dan TGA analisis. Analisis ATR-FTIR menunjukkan bahawa resin C menghasilkan puncak yg lebih tinggi dan keamatan yang kuat berbanding dengan resin F. TGA telah digunakan untuk mengkaji kestabilan haba antara kedua-dua resin .Masa penguraian untuk sampel F adalah 232,47 ℃ manakala suhu penguraian resin C adalah 189,52 ℃. Dapat disimpulkan dalam kajian ini bahawa glyoxal boleh menjadi pengganti yang sesuai untuk formaldehid dalam menghasilkan Bio-fenolik resin.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Oil palm tree or logically called (Elaeis guineensis) is a tropical palm which is started from Africa. The development of oil palm trees began as a moderately little scale plantation. However in less than 100 years, it became one of the most profitable agricultural commodities in the world. Malaysia's climate is suitable for the development of oil palm tree. The cultivation in Malaysia has started almost a century ago. Malaysia was acquainted by the British in mid-1870 as decoration plant. In early 1960s, the cultivation of oil palm expanded at a quick pace. It was under the administration farming broadening project to minimize the country economic reliance on rubber and tin. Up to this point, Malaysia still on the top in the world as one of the biggest exporter of palm oil (Awalludin et al. 2015). The main product from oil palm is crude palm oil which is largely used in many industries.

Despite the benefits obtain from the cultivation of oil palm tree, there is also problem arises that need to be solved by the country. The main issue in the cultivation of oil palm is the substantial amount of biomass wastes. Some examples of wastes generated after harvesting or processing are empty fruit bunches (EFB), oil palm trunks (OPT), mesocarp fiber (MF), palm oil mill effluent (POME), oil palm fronds (OPF), oil palm leaves (OPM) and palm kernel shell (Awalludin et al. 2015) (PKS). These wastes are left behind and smoldered in incinerators by palm oil mills that created pollution to the environment and offers limited value to the industry (Rahman et al. 2006).

Empty fruit bunch (EFB) fibres is the waste product commonly from oil palm industry. The chemical composition of oil palm EFB biomass contains holocellulose (cellulose and hemicellulose), lignin, extractives and ash (Rahman et al. 2006). Holocellulose are naturally from the removal of the extractives and the lignin in lignocellulosic materials. It is known to be soluble in dilute alkali. Other chemical composition of oil palm EFB is lignin which acts as a binder in supporting all cells and microfibrils in the lignocellulosis structure but it is different in chemical structures relying on the types of plant it presents (Rahman et al. 2006). Extractive and ash in oil palm EFB comes in small proportion which is less than 10% each. EFB can be converted into useful biomass such as bio-oil that can be used to produce bio-phenolic resin which gives economic advantages to the country.

Numerous research have been made on oil palm EFB to find alternative ways to beneficially utilize EFB (Yusoff 2006). Generally, EFB biomass can be converted into value-added products through several processes for example, mechanical processes, direct combustion, gasification, pyrolysis and liquefaction. This research will be focused on liquefaction technique via oil bath heating to produce bio-phenolic resin.

Liquefaction is a process by where the biomass went to complicated thermochemical reaction in a solvent medium to produce liquid product. Oil bath heating is used to assist the liquefaction process in this study instead of using microwave heating. This is because it is suitable for heating reaction mixtures and has been widely used by researchers unlike microwave assisted which is still in study as it is a new technique. The contact is intimate as the hot oil used will completely surrounds the sides and bottom of the neck flask which will results in effective heat control. In addition, oil bath is inexpensive and safer to handle without being assisted.

In this study, liquefied EFB are produced from the reaction of EBF with phenol in the presence of acidic catalyst. The effect of phenol to EFB ratio will be investigated to obtain optimum ratio that will give highest yield of liquefied EFB. The liquefied EFB is then reacts with Glyoxal. Glyoxal is a dialdehyde that is used to

replaced formaldehyde in the synthesis of phenolic resins (Ramires et al. 2010). Formaldehyde, which is one of economical important chemical has been recently classified by The International Agency for Research on Cancer (IARC) as human carcinogen which can cause leukemia with its exposure (Zhang et al. 2009). This become main reason of replacing Glyoxal to natural sources that is non-toxic and environmental friendly. The bio-phenolic glyoxal resin that is produce from this study can be beneficial used in various application such as adhesives, composites and coating materials.

1.2 STATEMENT OF PROBLEM

Over the last few decades' Malaysian palm oil industry has become one of important agriculture-based industry (Awalludin et al. 2015). The demand for palm oil from the global is high as Malaysia is one of the leading countries in producing and exporting the palm oil. With the increase of need for the palm oil, indirectly, it increase the oil palm waste from the harvesting process such as empty fruit bunches (EFB). The abundance of the EFB has caused environmental issues such as air pollution, fouling and attraction of pests.

In order to overcome the problem, a study is conducted to produce bio-phenolic resin from EFB via microwave-assisted liquefaction which can be used in industry. This bio-phenolic resin produced can be applied into various industry as it is environmental friendly and reusable. Utilization of EFB waste will reduce the wastes and it effects to environment. It also can reduce the dependency on petroleum chemical to produce PF resin.

Oil bath heating is used to assist the liquefaction process in this study. This is because the use of oil bath instead of microwave heating will help in reducing the cost and it is suitable for heating reaction mixtures. For resinification process**,** Glyoxal was used as the dialdehyde replacing the formaldehyde. This is because formaldehyde contains toxic which can effect in developing of cancer and other diseases. Research that were conducted by Michael Krzyzanowsk et al. shows that exposed of formaldehyde causes upper respiratory tract irritation (Michael K. et al.

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