UNIVERSITI PUTRA MALAYSIA

USE OF OIL PALM EMPTY FRUIT BUNCH FOR LIGNOPHENOL PRODUCTION

SHARIFAH SOPLAH BINTI SYED ABDULLAH

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By

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

February 2008

Dedicated to my husband, daughter and my extended family who have brought a new level of love, patience and understanding into my life.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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Chairman: Professor Mohd. Ali Hassan, PhD

Faculty : Engineering

Oil palm empty fruit bunch (OPEFB) is a by-product in palm oil industry and represents an abundant, inexpensive and renewable resource which has not been utilized satisfactorily. It can be categorized as lignocellulosic material due to its cellulose, hemicellulose and lignin content. Due to the reasons, this research was done to evaluate the potential of OPEFB as starting material for lignophenol production by using one step and two-step processes to compare the efficiency of the methods. The best method was further applied for the next experiment to produce lignophenols from different type of OPEFB. The separation of lignin from OPEFB is based on the phase separation reaction system at room temperature (~ 28°C) to produce lignophenol. This process composed of phenol derivative (*p*-cresol) and concentrated acid (72% sulfuric acid) where lignin is present in organic phase and carbohydrates in aqueous phase after 1 hour of stirring. From the results obtained, the two step process is the best method to

produce lignophenol due to competitive yield obtained and less chemicals used compared to one step process. The yield of lignophenol produced by one step and two step processes were 68% and 61%, respectively. Three types of OPEFB have been used, i.e. extractives free OPEFB (LP1), non-extractives free OPEFB (LP2) and OPEFB powder obtained from Sabutek Mill, Perak (LP3). The chemical composition of each OPEFB was determined prior to production of lignophenol by two step process. Basically, the lignin content in LP1 and LP2 were not so much different as compared to LP3 which has lower lignin and cellulose content. There were no difference in yield of lignophenol being produced from LP1 and LP2 which gave 61±1% respectively, whereas LP3 gave 56±1% yield based on lignin content. Lignophenol from LP1 and LP2 also appeared in white pinkish color which is comparable to the previous work. However, lignophenol from LP3 appeared in dark brown color. The sugars hydrolyzed in the phase separation system in terms of percent conversion were 89%, 99% and 97% in LP1, LP2 and LP3, respectively. The lignophenol sample from LP1, LP2 and LP3 were further analyzed and characterized by Proton Nuclear Magnetic Resonance (^{1}H-NMR), Fourier Transform Infrared Spectroscopy (FTIR), Gel Permeation Chromatography (GPC), Ultraviolet spectroscopy (UV) and thermomechanical analysis (TMA). However, LP3 could not be analyzed due to insolubility in the solvents used. From the results obtained, lignophenol from LP1 and LP2 showed similar results in structure and physical properties. The molecular weight of lignophenols from LP1 and LP2 were 5759 g mol^{-1} and 5866 g mol^{-1}, respectively. There were no significant difference in the amount of attached cresol between LP1 and LP2 which gave 26±1%. In summary, it can be concluded that OPEFB has a good potential as a starting material in lignophenol production by using two step process. Furthermore, it does not require ethanol/benzene extraction to treat the material.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

KEGUNAAN TANDAN KOSONG KELAPA SAWIT UNTUK PENGHASILAN LIGNOPHENOL

Oleh

SHARIFAH SOPLAH BINTI SYED ABDULLAH

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Tandan kosong kelapa sawit (OPEFB) adalah produk sampingan di dalam industri minyak kelapa sawit dan ia boleh didapati dengan banyak, murah dan sentiasa diperbaharui tetapi tidak digunakan dengan sebaiknya. Bahan ini dikategorikan sebagai bahan lignoselulosa kerana kandungan selulosa, hemiselulosa dan lignin di dalamnya. Berdasarkan sebab-sebab di atas, penyelidikan ini telah dilakukan untuk mengkaji potensi OPEFB sebagai bahan pemula bagi penghasilan lignophenol menggunakan dua kaedah iaitu satu langkah pertama dan dua langkah bagi membandingkan kecekapan kedua-dua kaedah. Kaedah terbaik telah diaplikasikan di dalam eksperimen yang seterusnya untuk menghasilkan lignophenol daripada pelbagai jenis OPEFB. Pengasingan lignin daripada OPEFB adalah berdasarkan sistem fasa tindakbalas pengasingan pada suhu bilik (~ 28°C) untuk menghasilkan lignophenol. Proses ini terdiri daripada phenol (*p*-cresol) dan asid pekat (72% sulfurik asid) di mana lignin akan

terpisah ke dalam fasa organik dan karbohidrat di dalam fasa akues selepas pengacauan selama satu jam. Daripada keputusan yang diperolehi, kaedah dua langkah adalah kaedah terbaik untuk menghasilkan lignophenol berdasarkan angkali hasil yang kompetitif dan penggunaan amaun bahan kimia yang sedikit berbanding kaedah satu langkah. Angkali hasil perolehan lignophenol bagi kaedah satu langkah dan dua langkah adalah 68% dan 61% masing-masing. Tiga jenis OPEFB telah digunakan iaitu OPEFB bebas ekstraktif (LP1), OPEFB tidak bebas ekstraktif (LP2) dan serbuk OPEFB daripada kilang minyak sawit Sabutek, Perak (LP3). Komposisi kimia bagi setiap sampel telah ditentukan sebelum penghasilan lignophenol menggunakan kaedah dua langkah. Secara asasnya, kandungan lignin dalam LP1 dan LP2 tidak banyak berbeza berbanding LP3 yang mempunyai kandungan lignin dan selulosa yang yeng lebih rendah. Tiada perbezaan bagi angkali hasil lignophenol yang dihasilkan daripada LP1 dan LP2 dengan nilai 61±1% masing-masing, manakala LP3 menunjukkan 56±1% angkali hasil berdasarkan kandungan lignin. Lignophenol daripada LP1 dan LP2 juga berwarna putih merah jambu sebagaimana dengan hasil daripada kajian sebelum ini. Bagamanapun, lignophenol daripada LP3 berwarna coklat gelap. Gula yang dihidrolisis dalam sistem fasa pengasingan dalam peratus penukaran adalah 89%, 99% dan 97% bagi LP1, LP2 dan LP3 masing-masing. Ketiga-tiga lignophenol sampel kemudiannya dianalisis dan ditentukan ciri-cirinya menggunakan *Proton Nuclear Magnetic Resonance* (^{1}H-NMR), *Fourier Transform Infrared Spectroscopy* (FTIR), *Gel Permeation Chromatography* (GPC), *Ultraviolet spectroscopy* (UV) and *thermomechanical analysis* (TMA). Walaubagaimanapun, LP3 tidak dapat dianalisis kerana ketidaklarutannya di dalam pelarut yang digunakan. Daripada keputusan yang diperolehi, lignophenol daripada LP1 dan LP2 menunjukkan keputusan yang sama dari segi struktur dan ciri-ciri fizikal. Berat molekul lignophenol daripada LP1 dan LP2 adalah 5759 g mol^{-1} dan 5866 g mol^{-1} masing-masing. Tiada perbezaan ketara dari segi amaun cresol yang melekat pada lignin di antara LP1 dan LP2 dengan nilai 26±1%. Secara ringkasnya, dapat disimpulkan bahawa OPEFB mempunyai potensi yang baik sebagai bahan pemula dalam penghasilan lignophenol menggunakan kaedah langkah kedua. Selain itu, ia tidak memerlukan ekstraksi ethanol/benzene untuk merawatnya.

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I certify that an Examination Committee has met on 13th February 2008 to conduct the final examination of Sharifah Soplah Binti Syed Abdullah on her Master of Science thesis entitled "Use of Oil Palm Empty Fruit Bunch for Lignophenol Production" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of Supervisory Committee were as follows:

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Date: 8 May 2008

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

SHARIFAH SOPLAH SYED ABDULLAH

Date: 27 April 2008

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^{1}H-NMR	Proton Nuclear Magnetic Resonance Spectroscopy
ADF	acid detergent fiber
ADL	acid detergent lignin
CMC	carboxymethylcellulose
DSC	differential scanning calorimetry
DTA	differential thermal analysis
EFB	empty fruit bunches
FRIM	Forest Research Institute of Malaysia
FTIR	Fourier Transform Infrared Spectroscopy
GFC	gel filtration chromatography
GPC	Gel Permeation Chromatography
H_2SO_4	Sulfuric acid
IPN	semi-interpenetrating polymer network
IR	Infrared
KBr	potassium bromide
MRSM	Maktab Rendah Sains MARA
Mn	Number average molecular weight
Mw	Molecular weight
NaOH	Natrium/sodium hydroxide
NDF	neutral detergent fiber
OPEFB	Oil palm empty fruit bunch
OPF	oil palm fronds

OPT	oil palm trunks
PNB	p-nitrobenzaldehyde
SEC	size exclusion chromatography
TG	Thermogravimetry
THF	Tetrahydrofuran
TMA	thermomechanical analysis
UKM	Universiti Kebangsaan Malaysia
UPM	Universiti Putra Malaysia
UV	Ultraviolet
v/v	volume per volume
VOCs	volatile organic compounds
w/v	weight per volume

CHAPTER 1

INTRODUCTION

Cultivation of the oil palm (*Elaeis guineensis Jacq.*) has expanded tremendously in recent years such that it is now second only to soybean as a major source of the world supply of oils and fats. Presently, Southeast Asia is the dominant region of production with Malaysia being the leading producer and exporter of palm oil (Wahid et al., 2004). It is accounting for approximately 10% of the world's oil and fat production (1998). The total area of oil palm plantations is close to 3.2 million hectares, which account for almost 50% of the land under cultivation in Malaysia (Tanaka et al., 2004).

Due to its large economic scale of the industry, enormous amount of biomass is being generated daily. About 94% of agricultural residue comes from palm oil industry. In 2004, it was estimated that 26.7 million tonnes of solid biomass produced from 381 palm oil mills in Malaysia. The solid biomass is made up of 53% oil palm empty fruit bunch (OPEFB), 32% mesocarp and 15% fiber and palm kernel shell. Therefore, disposing large tonnages of biomass generated daily is a problem for the industry (Yacob, 2005). Full exploitation of this biomass can be done by maximizing the utilization of this biomass to form products of high value which not only comply to the zero waste strategy but also generate additional profit to the palm oil industry. More than 14.4 million tonnes of OPEFB produced annually. About 65% of OPEFB is either incinerated for bunch ash or recycled back to the plantation as mulching or used as solid fuel in the boilers to generate steam and electricity for the mills (Mat Soom et al., 2004). This is only practice by the bigger plantation such as Golden Hope, Guthrie, Sime Darby and United Plantation. For old palm oil mills, the empty fruit bunch is burned in the incinerator to produce fertilizer. However, there are still plantation company that disposed the empty fruit bunches as landfill method particularly those mill without enough plantation or estates.

OPEFB, which is considered as lignocellulosics available in large quantities and has fairly high lignin content with an average of 20.5% based on an oven dried basis (Ramli et al., 2002), appears to be a potential material for lignophenol production. In recent years, lignocellulosic materials have shown interesting features to be used as raw materials for industrial material production. Lignocellulosics are renewable, available in abundance and inexpensive, offering great potential for transformation into chemical feed stocks or fuels. However, the lignocellulosics must be separated into individual components before use as chemical feedstocks (Mikame and Funaoka, 2006a).

Therefore, a new phase-separation system was originally designed by Funaoka and co-workers as a successive total utilization of lignocellulosics leading to sustainable development. Through the phase separation system, hydrophobic lignin and hydrophilic carbohydrates are subjected to selective structural conversion individually at different