Faculty of Engineering

PRETREATMENT OF LIGNOCELLULOSIC BIOMASS (EMPTY FRUIT BUNCH) BY USING IONIC LIQUIDS AS SOLVENTS

Fiouna Dok Wan

Bachelor of Engineering with Honours
(Chemical Engineering)
2013

UNIVERSITI MALAYSIA SARAWAK

Grade: ____________

Please tick (√)

Final Year Project Report [√]

Masters [ ]

PhD [ ]

DECLARATION OF ORIGINAL WORK

This declaration is made on the 20 day of May 2013.

Student's Declaration:

I, FIOUNA DOK WAN (23501), DEPT. OF CHEMICAL ENGINEERING AND ENERGY SUSTAINABILITY, FACULTY OF ENGINEERING hereby declare that the work entitled, PRETREATMENT OF LIGNOCELLULOSIC BIOMASS (EMPTY FRUIT BUNCH) BY USING IONIC LIQUIDS AS SOLVENTS is my original work. I have not copied from any other students' work or from any other sources except where due to reference or acknowledgement is made explicitly in the text, nor has any part been written for me by another person.

20 MAY 2013 — Date submitted

FIOUNA DOK WAN (23501) — Name of the student (Matric No.)

Supervisor's Declaration:

I, SHANTI FARIDAH SALLEH (DR) hereby certifies that the work entitled, PRETREATMENT OF LIGNOCELLULOSIC BIOMASS (EMPTY FRUIT BUNCH) BY USING IONIC LIQUIDS AS SOLVENTS was prepared by the above named student, and was submitted to the "FACULTY" as a partial fulfillment for the conferment of BACHELOR OF ENGINEERING WITH HONOURS (CHEMICAL ENGINEERING), and the aforementioned work, to the best of my knowledge, is the said student's work.

Received for examination by: SHANTI FARIDAH SALLEH (DR) Date: 20 MAY 2013

(Name of the supervisor)

I declare this Project/Thesis is classified as (Please tick (√)):

☐ **CONFIDENTIAL** (Contains confidential information under the Official Secret Act 1972)*

☐ **RESTRICTED** (Contains restricted information as specified by the organisation where research was done)*

☑ **OPEN ACCESS**

Validation of Project/Thesis

I therefore duly affirmed with free consent and willingness declare that this said Project/Thesis shall be placed officially in the Centre for Academic Information Services with the abiding interest and rights as follows:

- This Project/Thesis is the sole legal property of Universiti Malaysia Sarawak (UNIMAS).
- The Centre for Academic Information Services has the lawful right to make copies for the purpose of academic and research only and not for other purpose.
- The Centre for Academic Information Services has the lawful right to digitalise the content for the Local Content Database.
- The Centre for Academic Information Services has the lawful right to make copies of the Project/Thesis for academic exchange between Higher Learning Institute.
- No dispute or any claim shall arise from the student itself neither third party on this Project/Thesis once it becomes the sole property of UNIMAS.
- This Project/Thesis or any material, data and information related to it shall not be distributed, published or disclosed to any party by the student except with UNIMAS permission.

Student's signature: ____________ (20 MAY 2013)

Supervisor's signature: ____________ (20 MAY 2013)

Current Address:
96, SUMMERVILLE VILLA, JALAN TUN HUSSEIN ONN, 97000 BINTULU, SARAWAK

Notes: * If the Project/Thesis is **CONFIDENTIAL** or **RESTRICTED**, please attach together as annexure a letter from the organisation with the period and reasons of confidentiality and restriction.

[The instrument is duly prepared by The Centre for Academic Information Services]

APPROVAL SHEET

This final year report which entitled **"Pretreatment of Lignocellulosic Biomass (Empty Fruit Bunch) by using Ionic Liquids as Solvents"** was prepared by Fiouna Dok Wan (23501) as a partial fulfilment for the Degree of Bachelor of Chemical Engineering is hereby read and approved by:

DR SHANTI FARIDAH SALLEH
(Supervisor)

20 MAY 2013
Date

PRETREATMENT OF LIGNOCELLULOSIC BIOMASS (EMPTY FRUIT BUNCH) BY USING IONIC LIQUIDS AS SOLVENTS

FIOUNA DOK WAN

Thesis is submitted to

Faculty of Engineering, Universiti Malaysia Sarawak

In Partial Fulfilment of the Requirements

for the Degree of Bachelor of Engineering

Chemical Engineering (With Honours)

2013

This thesis is dedicated to my late grandmother for her everlasting love,
and to my beloved parents,
who have given me the opportunity of an education.

ACKNOWLEDGEMENT

First of all, the author is grateful to The God Almighty for His blessings upon the author throughout her life. It is with immense gratitude that the author acknowledges the support and encouragement from her Final Year Project Supervisor, Dr Shanti Faridah Salleh. Without her guidance and continuous supervision, this thesis would not have been possible. The author also owes her deepest gratitude to her Final Year Project Coordinators, Mr Nazeri Abdul Rahman and Madam Nur Syuhada Ahmad Zauzi for providing her with necessary information and support in completing her thesis. Deepest appreciation to her lecturers for the knowledge and experiences that have been shared with her. She is also indebted to the technicians of Chemical Engineering & Energy Sustainability Department for their assistance. Special thanks to Faculty of Engineering, Universiti Malaysia Sarawak for providing all the facilities and opportunities in order to complete her thesis. She would also like to extend her gratitude to her family and friends for their continuous support, love and faith in her along the way. Last but not least, she would also like to place on record, her sense of gratitude to one and all who, directly or indirectly, have lent their helping hand in completing her thesis.

ABSTRAK

Pada zaman ini, isu tenaga dan isu alam sekitar merupakan isu besar yang dihadapi oleh masyarakat sejagat. Tenaga masa kini yang berasaskan bahan api fosil tidak akan cukup untuk menampung keperluan masyarakat dan bahan api ini merupakan penyumbang besar kepada pencemaran. Oleh hal yang demikian, sumber tenaga alternatif terutamanya sumber yang boleh diperbaharui mula digunakan. Antara sumber yang boleh menggantikan bahan api fosil adalah biomas lignoselulosa, yang boleh ditemui dalam jumlah yang banyak daripada sumber perhutanan, pertanian dan perbandaran. Malaysia merupakan salah satu negara yang mengeluarkan sisa biomas dalam kandungan yang besar, dan salah satu daripadanya adalah Tandan Kosong (TK) kelapa sawit. TK mampu menjadi sumber pengeluaran tenaga bio yang bagus. Namun begitu, struktur lignoselulosa TK merupakan satu halangan sebelum sakarifikasi biomas dapat dilaksanakan. Kehadiran hemiselulosa dan lignin menyukarkan selulosa untuk larut. Oleh hal yang demikian, pra-rawatan perlu dilakukan untuk melarutkan struktur selulosa dalam TK. Kajian penyelidikan ini bertujuan untuk mengenalpasti kebolehan tiga jenis Cecair Ionik iaitu *1-butyl-3-methylimidazolium Chloride ([BMIM]Cl)*, *1-ethyl-3-methylimidazolium Acetate ([EMIM]OAc)* dan *1-ethyl-3-methylimidazolium Diethyl Phosphate ([EMIM]DEP)* untuk melarutkan komponen di dalam biomas lignoselulosa, iaitu TK melalui proses pra-rawatan. Kajian ini dilaksanakan pada suhu bawah 100 °C dan masa, 6 jam dan 10 jam. Analisis TK dilakukan dengan menggunakan *Fourier Transform Infrared Spectroscopy* dan *Thermogravimetric Analyzer*.

Kata kunci – Biomas Lignoselulosa, Cecair Ionik, Tandan Kosong, Selulosa

ABSTRACT

At this age, energy and environmental issues have been major issues that are faced by the community globally. The current fossil-fuel based energy will not be enough to sustain the needs of the society and it has been a major contributor of pollution. Thus, alternative sources of energy especially the renewable sources are started to be utilised. Among the sources that could replace fossil fuels is lignocellulosic biomass, which could be found in abundant from forestry, agriculture and municipal sources. Malaysia is one of the countries that produce large amount of biomass waste, and one of them is Empty Fruit Bunch (EFB). EFB could be a good source for bioenergy production. However, the lignocellulosic structure of the EFB has been a great obstacle before the saccharification of the biomass could be done. The presence of hemicelluloses and lignin has made it hard for the solubilisation of cellulose to occur. Therefore, pretreatment should be conducted to dissolve the cellulose structure in the EFB. This research study aims to identify the ability of three types of Ionic Liquids namely, 1-butyl-3-methylimidazolium Chloride ([BMIM]Cl), 1-ethyl-3-methylimidazolium Acetate ([EMIM]OAc) and 1-ethyl-3-methylimidazolium Diethyl Phosphate ([EMIM]DEP) to dissolve the components of lignocellulosic biomass, which is the EFB through a process called pretreatment. The study was performed at temperatures below 100 °C and time, t = 6 hours and 10 hours. The analyses of the EFB were done by using Fourier Transform Infrared Spectroscopy and Thermogravimetric Analyzer.

Keywords – Lignocellulosic Biomass, Ionic Liquids, Empty Fruit Bunch, Cellulose

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

BF_4^-	Tetrafluoroborate
$CF_3CO_2^-$	Trifluoroacetate
$CF_3SO_3^-$	Triflate
$CH_3CO_2^-$	Acetate
PF_6^-	Hexafluorophospate
[BMIM]Cl	1-butyl-3-methylimidazolium Chloride
[EMIM]DEP	1-ethyl-3-methylimidazolium Diethyl Phosphate
[EMIM]OAc	1-ethyl-3-methylimidazolium Acetate
EFB	Empty Fruit Bunches
FT-IR	Fourier Transform Infrared
GHG	Green House Gases
HCl	Hydrochloric Acid
IL(s)	Ionic Liquid(s)
NaOH	Sodium Hydroxide
NMR	Nuclear Magnetic Resonance
OPF	Oil Palm Fronds
OPT	Oil Palm Trunks
TFA	Trifluoroacetic acid
TGA	Thermogravimetric Analyzer
USA	United States of America
$(CF_3SO_2^-)$2N-1	Bos(trifluoromethylsulfony)imide
H_3PO_4	Phosphoric Acid

H_2SO_4	Sulphuric Acid
Na_2CO_3	Disodium Carbonate
H_2O_2	Hydrogen Peroxide
NH_3	Nitric Acid
NO_3	Nitrate
CO_2	Carbon Dioxide
$Ca(OH)_2$	Calcium Hydroxide

NOMENCLATURES

%	Percentage
°C	Degree Celcius
β	Beta
π	Pi
μm	Micro meter
g	Gram
mL	Milimeter
h	Hour
cm^{-1}	Per centimeter
min^{-1}	Per minute
mg	Milligram

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The world nowadays is facing issues regarding the current energy consumption. The usage of energy in many countries has exploded at an unimaginable rate in the last century. This is shown by the great dependency of our current economy on fossil energy sources like oil, coal and natural gas where they are mainly used in fuel and electricity production (Sarkar et al., 2011).

However, the fossil fuel-based economy is encountering several crisis and challenges of its own, which involve high Carbon Dioxide (CO_2) emissions, reduction in fossil fuel reserves and the arising of energy prices (Holm & Lassi, 2011). Thus, in order to mitigate this problem, the world has gaining interest on replacing the fossil fuels with renewable sources, which are biofuels, due to their sustainability and the environmental benefits that they could provide.

Mott MacDonald (2012), a global multidisciplinary consultancy on biofuels defines the word 'biofuel' as liquid or gaseous fuel that are derived from fixed carbon, such as plant biomass, vegetable oils and treated wastes. The source for biofuels is biomass, which is defined by MacDonald as living or recently dead biological material than could be used as fuel or for industrial activity. There are many types of biomass exist in the environment.

Mousdale (2008) stated that in a conventional sense, biomass is from vegetation (such as woody plants and sun-dried grasses) and animals' excrement too. Among plants that could be used as biomass are including wood, straw, mischantus (elephant grass), hemp, corn (maize), poplar, willow and sugarcane. The carbon exist in these plants is absorbed from CO_2 present in the atmosphere by using energy from the sun, which makes biomass as the most abundant renewable resources available (Holm & Lassi, 2011). However, in Malaysia, most biomass is produced from agricultural residues such as rice straws, sugarcane bagasse and oil palm empty fruit bunches (EFB) (Ngoh et al., 2010).

The industry of oil palm in Malaysia has shown excellent performance in the recent years. Currently, this country accounts for 39% of world palm oil production and 44% of world exports (MPOC, 2012). One advantage of oil palm is that it is a multipurpose plantation (Basiron & Simeh, 2005 as cited in Lee, 2007). In a fresh fruit bunch, only 21% of the bunch is made of palm oil, 6-7% is palm kernel, 14-15% is fibre, 6-7% is shell and the other 23% is the EFB, which is left as biomass waste (Umikalsom et al., 1997 as cited in Lee, 2007). Studies on usage of EFB have been done and still ongoing.

The utilisation of EFB to become a source for renewable energy is somehow a wise option in Malaysia. According to Syed Abdullah et al. (2009), the annual generation of EFB biomass waste from palm oil mills in Malaysia is approximately 15 million tonnes. Considered as a lignocellulosic biomass plant due to the presence of cellulose, hemicelluloses and lignin in its structure, EFB has high potential in producing high value-added products besides having the advantage of zero-waste strategy that could create additional profits for palm oil industry. Lignocellulosic biomass, which is the EFB is likely recognized to be a low-cost renewable source of mixed sugar in fermentation process to produce biofuel (Bayer et al., 2010).

1.2 Problem Statement

Lignocellulosic biomass has wide potential as a renewable energy source due to the variety and availability of the plant biomass in our surrounding. Through the fermentation of the plant biomass, fuel could be obtained. However, the complex structure of cellulose, hemicelluloses and lignin in lignocellulosic biomass has cause resistance for the biomass to most chemicals and hydrolysis process.

According to Viikari et al., (2011), the reason for the resistance of the biomass crystalline cellulose to hydrolysis is due to the strong intramolecular and intermolecular hydrogen bonds of the biomass itself. This structure has made it hard for the cellulose structure in the biomass to be hydrolysed. Biomass should undergo pretreatment processes to disrupt the lignocelluloses structure and enable enzymes to have access to the cell wall polysaccharides (Mosier et al., 2005; Wyman et al., 2005; Galbe and Zacchi, 2007; Brunecky et al., 2009 as cited in Blaschek et al., 2010). The structure of the lignocellulosic biomass needs to be altered so that the structure is more accessible to enzymes/chemicals (Holm & Lassi, 2011).

1.3 Objectives

The main objective of this research study is to identify the ability of three types of Ionic Liquids (ILs) which are 1-butyl-3-methylimidazolium Chloride ([BMIM]Cl), 1-ethyl-3-methylimidazolium Acetate ([EMIM]OAc) and 1-ethyl-3-methylimidazolium Diethyl Phosphate ([EMIM]DEP) to dissolve lignocellulosic components of palm oil Empty Fruit Bunch (EFB) at different reaction times, t = 6 hours and t = 10 hours and at various temperatures of T = 70 °C, 80 °C, 90 °C, 95 °C by using Ionic Liquids as solvents. Another objective of this project if to identify the best IL that could dissolve the lignocellulosic components (cellulose) of EFB at mentioned time and temperature in order to obtain optimum result.

1.4 Methodology

In order to accomplish the objectives of this research study, a proper methodology has been developed. The stages of the methodology that is going to be implemented are presented as below:

Stage 1: Literature Review

To start the research study, Literature Review is done. Information is gathered and collected from previous studies. The collection of this information is important to widen the knowledge regarding the lignocellulosic biomass and its structures, earlier pretreatments that have been conducted, types of ILs that have been developed for the purpose of pretreatment and information on EFB.

Stage 2: Experimental Design

After gathering all the necessaries information, the experimental procedures will be designed in order to ensure that the experiments could be conducted in a correct manner. The designs of the experimental procedures are based on several previous studies that have been carried out.

Stage 3: Conducting the Pretreatment

At this stage, experimental work is initialized. The raw material, which is the EFB is obtained and prepared. Subsequently, the EFB is pretreated with the ILs and heated according to the parameters that have been set. After heating, the mixtures of EFB and ILs would be filtered. EFB residues would be separated before being washed and dried.

Stage 4: Analysis by using Analytical Equipments

The next stage of the methodology is the analysis. The EFB residues obtained from the pretreatment is analyzed by using two analytical equipments namely, Fourier Transform Infrared (FT-IR) Spectroscopy and Thermogravimteric Analyzer (TGA). FT-IR Spectroscopy is used to detect the presence of lignocellulosic structures in the EFB. Meanwhile, TGA is used to analyze the amount of these structures, especially the cellulose, in order to know how much cellulose that has been dissolved by the ILs. From there, comparison could be made among the ILs to identify which IL has the best effect on the EFB at each parameter that has been set.

The schedule of this research study is illustrated in Gantt Chart attached in **Appendix A.**

1.5 Expected Outcome

The expected outcome from this research study is the amount of cellulose remained in the EFB. From there, the amount of cellulose that has been dissolved through the pretreatment could be determined.

1.6 Summary

This chapter generally describes the background of the research study. As a good source in producing biofuel that could replace fossil-fuel based industry, lignocellulosic biomass is getting more popular among a few other renewable sources. However, the structure of lignocellulosic biomass is rather complex and pretreatment is required in order to achieve maximum efficiency during the conversion of biomass into biofuel. The chapter also emphasized on the problem statement arisen that brings into the deployment of this project and the objectives that will be achieved at the end of the research study.