UNIVERSITI PUTRA MALAYSIA

BIO-OIL PRODUCTION VIA SOLVOLYSIS OF OIL PALM EMPTY FRUIT BUNCH USING ZN-SUPPORTED ZEOLITE CATALYST

RACHEL TANG DUO YAO

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By

RACHEL TANG DUO YAO

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

May 2017

DEDICATION

This thesis is dedicated to my family, especially to my beloved aunt, Madam Lim Chiew Neo for her love and support, my siblings and last but not least, my beloved grandmother. Thank you very much.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Master of Science

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Chairman : Professor Taufiq-Yap Yun Hin, PhD
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Biomass is one of the renewable energy that has been revealing its potential as a substituent for natural fossil fuels recently. Nowadays, converting biomass via liquefaction technology appears to be another alternative to obtain valuable high energy products such as biofuel, gas and char. In this study, oil palm empty fruit bunch (EFB) has been chosen as the source of biomass for biomass-to-biofuel conversion. The main focus of the study was on the presence of different composition of Zn supported on zeolite ZSM-5 as solid acid catalyst to enhance the production of bio-oil from the biomass. The prepared catalysts were characterized using X-ray diffraction (XRD), *Brunauer–Emmett–Teller (*BET), field-emission scanning electron microscope with energy-dispersive X-Ray spectroscopy (FE-SEM/EDX) and temperature-programmed desorption (TPD)–NH_3. Gas chromatography mass spectroscopy (GC-MS) was employed for bio-oil analysis. Conversion of EFB to liquid products was carried out by using an autoclave. The production of bio-oil from EFB was subjected to a series of optimization tests: reaction temperature, reaction time, catalyst loading and catalyst composition. The optimum condition for the conversion of EFB to liquid products was achieved at 180°C for 90 min with 0.5wt% of 15% Zn supported on ZSM-5. Without the presence of the catalyst, there are many compounds found in the bio-oil such as aromatics compounds, phenols and others. In contrast, high selectivity towards the production of furfural (approximate 83% of total compounds in the bio-oil) was reported under optimum condition with the presence of catalyst. Phenols were also found to be the second highest compound obtained after furfural (~8.2%). This value-added product obtained in this study is a very useful chemical feedstock especially in adhesive industry.

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

PENGHASILAN BIO-MINYAK MELALUI SOLVOLISIS KELAPA SAWIT TANDAN BUAH KOSONG DENGAN MENGGUNAKAN PEMANGKIN Zn BERPENYOKONG ZEOLIT

Oleh

RACHEL TANG DUO YAO

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Biojisim adalah salah satu tenaga boleh diperbaharui yang telah mendedahkan potensinya sebagai gantian bahan api fosil semula jadi baru-baru ini. Pada masa kini, penukaran biojisim melalui teknologi pencairan telah menjadi salah satu alternatif untuk mendapatkan produk tenaga tinggi yang berharga seperti bahan api bio, gas dan arang. Dalam kajian ini, kelapa sawit tandan buah kosong (EFB) telah dipilih sebagai sumber biojisim untuk penukaran biojisim ke bahan api bio. Fokus utama kajian ini adalah untuk mengenai kesan komposisi zink yang berbeza disokong pada pemangkin zeolite ZSM-5 bagi meningkatkan pengeluaran minyak bio daripada biojisim. Ciri-ciri pemangkin yang telah disediakan telah dianalisi oleh pembelauan sinar-X (XRD), analysis luas permukaan Brunauer-Emmett-Teller (S_{BET}), mikroskop imbasan elektron pancaran medan yang dilengkapi dengan tenaga serakan spektroskopi sinar-X (FE-SEM/EDX) dan penyahjerapan suhu terancang-NH_3 (TPD-NH_3). Gas kromatografi yang dilengkapi dengan spektroskopi jisim (GC-MS) telah digunakan untuk analisis bio-minyak. Penukaran EFB kepada produk cecair telah dilakukan dengan menggunakan autoklaf. Penghasilan bio-minyak daripada EFB telah dikaji melalui sesiri ujian optimasi: suhu reaksi, masa reaksi, muatan pemangkin dan komposisi pemangkin. Keadaan optimum bagi penukaran EFB ke produk cecair telah dicapai pada suhu 180°C selama 90 min dengan 0.5 peratusan jisim daripada 15% Zn disokong pada ZSM-5. Tanpa pemangkin, sebatian-sebatian yang dapat dikesan dalam bio-minyak yang dihasilkan adalah seperti kompaun aromatik, fenol dan lain-lain. Sebaliknya, pemilihan yang tinggi terhadap penghasilan fufural (anggaran 83% daripada jumlah sebatian bio-minyak) dicapai di bawah keadaan optimum dengan kehadiran pemangkin. Fenol juga dikenali sebagai sebatian kedua tinggi yang diperolehi selepas furfural (~8.2%). Produk nilai tambah yang diperolehi dalam kajian ini adalah bahan mentah kimia yang sangat berguna terutamanya dalam industri pelekat.

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

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LIST OF ABBREVIATIONS

DEG	Diethylene glycol
DES	Diethyl Ether Soluble
E_a	Activation energy
EC	Ethylene carbonate
EFB	Empty Fruit Bunch
EG	Ethylene glycol
FE-SEM	Field Emission Scanning Electron Microscopy
GC-MS	Gas Chromatography Mass Spectrometry
JCPDS	Joint Committee of Powder Diffraction Standards
LPY	Liquid Product Yield
MFI	Mordenite Framework Inverted
PG	Propylene glycol
RES	Renewable Energy Sources
S_{BET}	*Brunauer-Emmett-Teller* Surface Area Measurement
TPD-NH_3	Temperature Programmed Desorption of Ammonia
WS	Water Soluble
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence Spectroscopy
ZC	Calcined Zeolite ZSM-5
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 Background and definitions

1.1.1 Worldwide Energy Consumption and Consequences

Energy is economically and socially required to improve and enhance the quality of human life. Energy could be found in many forms, such as electrical, thermal, chemical, gravitational, mechanical, nuclear, motion and sound. Generally, energy resources that are available in this world have been categorized natural fossils fuels, renewable resources and nuclear resources (Demirbas A, 2000).

In older days, natural fossil fuels such as coal, petroleum and natural gas have been the main source of energy to supply worldwide energy needs. Energy is needed for almost all kind of operations and activities such as economic developments, agriculture, industrialization, transportation and others. **Fig. 1.1** shows the world total primary energy supply from 1971 to 2013 by fuel. The demand for energy from natural fossil fuels such as coal, oil and natural gas is in an almost steady ascending trend from year 1971 to 2013.

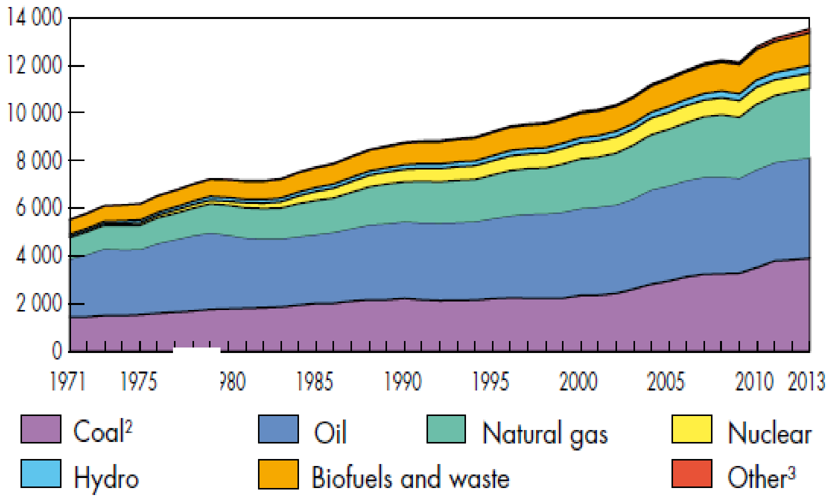

Figure 1.1 : World total primary energy supply from 1971 to 2013 by fuel (Mtoe)
(Key World Energy Statistics, OECD/IEA, 2015)

The role of natural fossil fuel as energy supply is still very important even until today. However, rapid increment in world's population and economic developments increases the demand for energy supply. Furthermore, the large dependence on the usage of fossil fuels to sustain the need of energy supply leads to the occurrence of global environmental issues. Some of the common environmental issues resulting from the utilization of fossil fuel include global warming, ozone depletion, acid rain and greenhouse effect. Due to the negative effects given by fossil fuels, this have stirred up the attention of finding alternatives or substituents to restore the energy source structure and promote greater efficiency of energy, as well as to satisfy the existing energy consumption in this world.

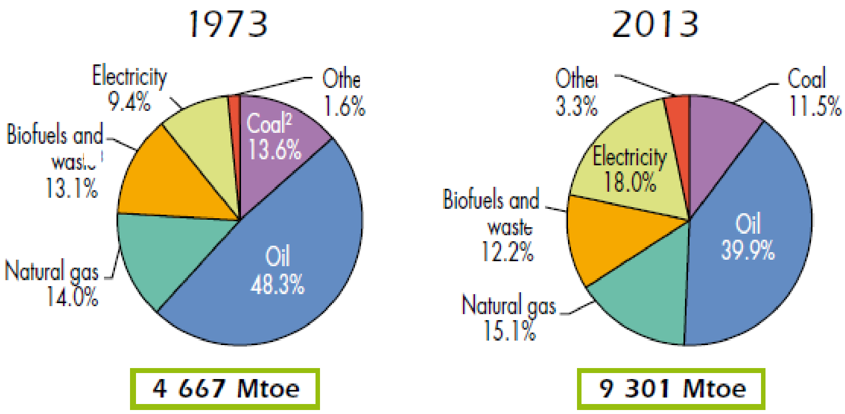

Figure 1.2 : 1971 and 2013 fuel shares of total final consumption
(Key World Energy Statistics, OECD/IEA, 2015)

The fuel shares of total final consumption for 1973 and 2013 are shown in **Fig. 1.2**.According to the statistics above, the total final consumption by fuel increased almost up to 50% in 4 decades time from 1973. This has come to pin point to the importance of the renewable energy as energy supply source in coming decades.

1.1.2 Biomass: The Promising Renewable Energy Source and Its Advantages

Due to the depletion of the natural energy source, renewable energy sources (RES) have been revealing their potential as a substituent for natural fossil fuel as these renewable energy sources offer some advantages over energy produced from fossil fuel. Common RES that are in use include wind, solar, biomass and geothermal (Shuit *et al.*, 2009). Among all the existing renewable energy sources, biomass has attracted a lot of interests as the promising substituent for fossil fuel. The abundancy of biomass all around the world has increased its utilization in many aspects, thus replacing crude-based non-renewable energy resources. It is highly remarked that biomass has an important role in future energy supply.

Biomass mainly consists of carbon, hydrogen and oxygen, and is an organic substance from living which mainly includes agricultural crops, forestry residues and sea products. It provides significant environmental advantages and at the same time appears to be the best solution for the substitution of fossil resources in many applications such as heat production, power and fuels for transportation. Apart from being a source of energy supply, chemical and biomaterials production from the biomass is also getting more and more common. In other words, biomass can help to control environmental issues that are related to fossil fuels despite its main function as the source of energy supply.

The source of biomass includes agricultural crops, forestry residues, municipal and solid wastes and others. All these wastes could be converted and are very useful in various applications such as transportation fuels, value-added chemicals, fertilizers and agro-chemicals (Demirbas, 2001; Chan *et al.*, 2014). In Malaysia, biomass produced from different industries in shown in **Fig. 1.3**.

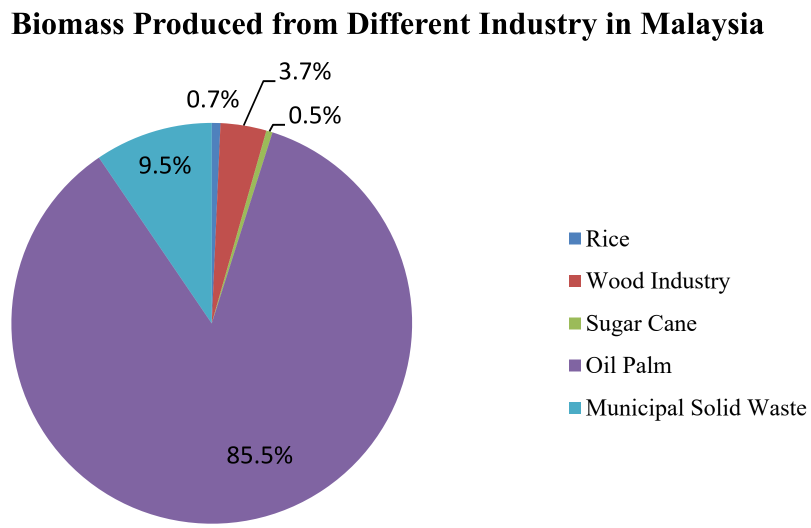

Figure 1.3 : Biomass produced from different industry in Malaysia
(Shuit *et al.*, 2009)

Malaysia is one of the major producers of palm oil in the world. Hence, as shown in the chart above, the biomass produced from oil palm industry has the highest percentage among all the industries in Malaysia, summing up to approximately 85.5% of the total biomass produced. It was reported that as in 2010, Malaysia contributed an incredible amount of oil palm biomass waste, approximately 86.9Mt/year (Ng *et al.*, 2012). As such, the abundance of oil palm biomass waste can be served as feedstock for biomass to biofuel conversion. Looking deep into the biomass produced from oil palm industry, types of biomass produced includes oil palm empty fruit bunch (EFB), trunks, fronds, fiber, shell, wet shell and palm kernel (Shuit *et al.*, 2009). As a result of that, oil palm empty fruit bunch (EFB) has become a great option to be used as the feedstock of biomass-to-biofuel conversion.

The conversion of biomass into fuel products could be done either biologically or thermochemically. Fermentation and anaerobic digestion are two of the examples of biological conversion of biomass. Meanwhile, examples for thermochemical conversion are gasification, liquefaction and pyrolysis (Pan *et al.*, 2010; Mohan *et al.*, 2006; Demirbaş, 2001; Collard and Blin, 2014). Among these two routes of methods, thermochemically-converted biomass appears to be more promising in obtaining products in three phases: low molecular weight liquid, gas fuel and solid residue (Yaman, 2004).

Biomass could be converted into valuable high energy products effectively such as biofuels, gas and char (Mohan *et al.,* 2006). It is remarked that the liquid fuel from biomass has an important role in future energy supply. There are several advantages offered by biofuel as energy product. Biofuels produced from biomass are environmentally friendly as they do not produce toxic gases such as SO_x and NO_x. Apart from that, these biofuels are renewable, bio-degradable and able to reduce greenhouse effect (Puppan, 2002; Sensöz and Kaynar, 2006; Iliopoulou *et al.,* 2007).

The thermochemically-generated liquid product produced from biomass is called bio-oil. Bio-oil appears to be a dark brown organic liquid with distinctive smoky odor. Another typical property of bio-oil is that bio-oil generated from biomass consists of different size of molecules (Peacoke *et al.,* 1994). One of the biggest advantages offered by bio-oil is the ability to function as liquid fossil fuel substituent (Abdullah and Gerhauser, 2008; Sulaiman *et al.,* 2011). In addition, bio-oil contains valuable chemicals and chemicals extracted from bio-oil are used as food flavorings, resins, adhesives, agrichemicals, and fertilizers (Liu and Zhang, 2008; Yip *et al.,* 2009). Not only that, bio-oil is also used for power generation for diesel engines and turbines.

1.1.3 Catalyst

Catalyst is any substance that accelerates the rate of chemical reaction by lowering activation energy of a specific reaction without itself participating or being consumed in the reaction. The function of a catalyst is best described in **Fig. 1.3**. A catalyst works by providing an alternative pathway with lower activation energy (E_a) compared to non-catalyzed system (Farnetti *et al*., 2009).

Thermodynamically, reactant must obtain energy that is greater than the activation energy in order for reactants to be able to react and become products. Otherwise, reactants with energy lower than E_a will remain unreacted and unable to go through transition state to react and become products. In this case, the function of the catalyst is magnified as catalyst provides an alternative pathway with lower activation energy that helps reactant to overcome the energy barrier and able to transform into products successfully. The difference of the activation energy between catalyzed and uncatalyzed reaction is clearly shown in **Fig. 1.4**.

There are two categories of catalyst: homogeneous and heterogeneous catalyst. Homogeneous catalyst can be distinguished from heterogeneous catalyst by the difference of phases in a particular reaction. In homogenous catalyst, the catalyst has the same phase with the reactant or sample feedstock. Meanwhile in heterogeneous catalyst, the reactants and catalyst are not of the same phase.

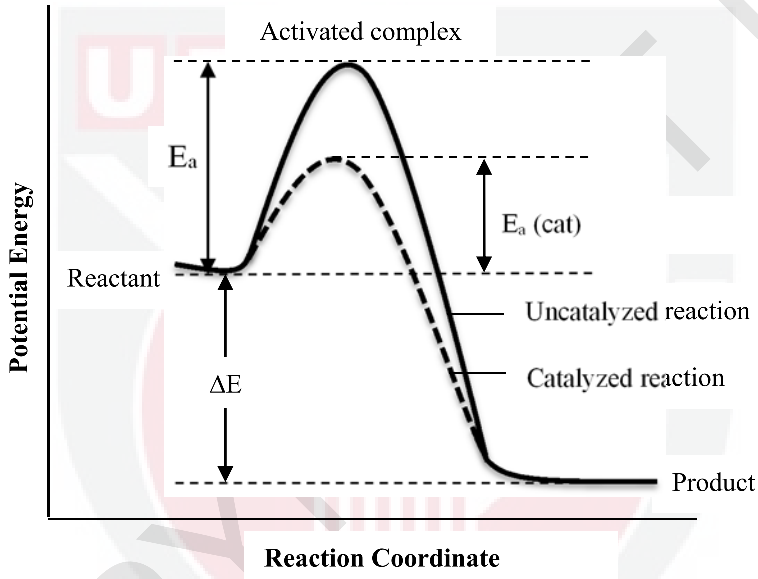

Figure 1.4 : Comparison of activation energy between catalyzed and uncatalyzed reaction (Clark, 2012)

1.2 Problem Statement

In the past two decades, pyrolysis has always been selected as the thermochemical method for the production of bio-oil. Although pyrolysis technology is a promising way to give high yield product, it has become less favorable as reaction time needed is long and temperature needed for this method is high. High operating temperature of pyrolysis gives forth to a very big problem: cross-linking and re-combination reaction between hydrocarbons and aromatics. This may further lead to tar and char formation which eventually causes difficulty in decomposition.

In addition, pyrolysis requires dry biomass in basis prior every treatment and this will lead to substantial energy consumption due to high heat of water vaporization. Moreover, the reaction time for pyrolysis is longer. It is therefore unfeasible from the view of economy. To overcome these matters, solvolysis was used in this research, a method which does not have the disadvantages resulting from pyrolysis.

In most of the biomass conversion, homogeneous catalysts were used instead of heterogeneous catalyst. Effect of heterogeneous catalyst on the yield of the liquid product and chemical components derived from the biomass via liquefaction on the other hand is not common. There are limited studies reporting on the biomass-to-bio-oil conversion via liquefaction.

In this work, zinc (in oxide form) supported on zeolite solid acid catalysts was introduced to enhance the production of the bio-oil production. It was reported that zeolite ZSM-5 provides many advantages such as shape selectivity, limited coke deactivation and high thermal activity. Zinc oxide on the other hand has found to be a mild catalyst and the use of zinc oxide as a catalyst has testified to have insignificant effect on the water-insoluble fraction. Zn-supported zeolite catalyst is used to ease the separation of liquid product and the catalyst, in which with the application of heterogeneous catalyst in this study, the problem arising from homogeneous catalyst is overcame.

Conversion of biomass into bio-oil via catalytic solvolysis is dependent on many factors, which includes the choice of biomass, solvent, catalyst, reaction parameters etc. Sources of biomass to be used are such as rice straw, wood, oil palm biomass and municipal solid waste. While different feedstock may vary the final product of the bio-oil, empty fruit bunch has been chosen to be used to convert biomass into bio-oil is due to its main advantage: abundance availability of this feedstock. However the utilization of EFB for biomass-to-biofuel conversion is not very common especially with the enhancement of solid acid catalyst although it has been reported that EFB that has been generated is able to be used as biofuel. It is therefore one of the interest in this study to further expand the utilization of EFB in biomass-to-biofuel conversion.

1.3 Objectives

Generally, there are three objectives in this study:

1. To synthesize a suitable catalyst for the bio-oil production via catalytic solvolysis of oil palm empty fruit bunch fiber.
2. To produce bio-oil from oil palm empty fruit bunch (EFB) fiber via catalytic solvolysis.
3. To optimize the yield of bio-oil by manipulating various parameters, such as temperature, amount of catalyst and reaction time.

1.4 Scope of study

There were two highlights of this study: (1) to prepare Zn/ZSM-5 in an appropriate composition of zinc deposited on zeolite ZSM-5 successfully via wet impregnation method; (2) to produce and optimize the bio-oil produced from EFB fiber with the enhancement of the catalyst synthesized by varying parameters such as temperature, reaction time etc. Characterization tests such as XRD analysis, FE-SEM/EDX, TPD-NH_3 and BET were employed to further analyze the synthesized catalyst, while the chemical composition on the bio-oil produced was determined by GC-MS analysis.

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