PRODUCTION OF ETHYL LEVULINATE FROM OIL PALM FRONDS USING HETEROPOLY ACID AS CATALYST

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To my beloved parents, siblings, family and friends
for their Love, Prayer and Support

ABSTRACT

Ethyl levulinate is a versatile chemical with numerous industrial applications. The production of ethyl levulinate from glucose and oil palm fronds (OPF) were investigated. The optimization of the effects of parameters was conducted by response surface methodology (RSM), and the data obtained was performed the regression analysis. In this study, three different heteropoly acids (HPAs) were screened and tested for glucose conversion to ethyl levulinate. The heteropoly acids; phosphomolybdic acid ($H_3PMo_{12}O_{40}$), silicotungstic acid ($H_4SiW_{12}O_{40}$) and phosphotungstic acid ($H_3PW_{12}O_{40}$) were tested and the experimental results shown that phosphotungstic acid produced highest ethyl levulinate yield. Optimization of ethyl levulinate was conducted using the potential heteropoly acid catalyst meanwhile glucose was used as model compound. The conducted experiment for glucose conversion to ethyl levulinate produced 19.01% ethyl levulinate yield at 183 °C in 200 min and 5.66 wt% of reaction temperature, time and catalyst loading, respectively. The optimization of the OPF for producing ethyl levulinate at the optimum conditions at 198 °C in 166 min and 1.44 wt% of reaction temperature, time and catalyst loading, respectively, was established wherein 4.65% of ethyl levulinate yield was produced from OPF. Additionally, the high acidity of phosphotungstic acid was significantly can increase the ethyl levulinate yield with increase the amount of catalyst load and reduce the reaction temperature for the OPF conversion into ethyl levulinate. This study demonstrated that the heteropoly acid has potential to be applied in biomass conversion to ethyl levulinate under adequate process conditions.

ABSTRAK

Etil levulinat adalah bahan kimia yang serba boleh dengan pelbagai aplikasi industri. Penghasilan etil levulinat dari glukosa dan pelepah kelapa sawit (OPF) telah dikaji. Pengoptimuman kesan parameter telah dijalankan oleh metodologi permukaan sambutan (RSM), dan data yang diperolehi telah dijalankan analisis regresi. Dalam kajian ini, tiga asid heteropoly berbeza (HPAs) telah diperiksa dan diuji untuk penukaran glukosa kepada etil levulinat. Asid heteropoli; asid fosfomolibdik ($H_3PMo_{12}O_{40}$), asid silikotungstik ($H_4SiW_{12}O_{40}$) dan asid fosfotungstik ($H_3PW_{12}O_{40}$) telah diuji dan keputusan eksperimen menunjukkan bahawa asid fosfotungstik menghasilkan etil levulinat yang terbanyak. Pengoptimuman etil levulinat telah dijalankan menggunakan asid heteropoli yang berpotensi sebagai pemangkin. Glukosa telah digunakan sebagai model bahan di dalam eksperimen. Eksperimen yang dijalankan untuk penukaran glukosa kepada etil levulinat menghasilkan 19.01% hasil etil levulinate pada suhu 183 °C dengan masa 200 min dan sebanyak 5.66 wt%. Pengoptimuman OPF untuk menghasilkan etil levulinat pada keadaan optimum iaitu pada suhu tindak balas 198°C dengan masa tindak balas 166 min dan jumlah pemangkin yang digunakan sebanyak 1.44 wt%, telah menghasilkan 4.65% hasil etil levulinat daripada OPF. Selain itu, asid fosfotungstik yang mempunyai keasidan yang tinggi ketara boleh meningkatkan hasil etil levulinate dengan meningkatkan jumlah pemangkin dan mengurangkan suhu tindak balas bagi penukaran OPF ke etil levulinat. Kajian ini menunjukkan bahawa asid heteropoli mempunyai potensi untuk digunakan dalam penukaran biojisim kepada etil levulinat di bawah keadaan proses yang optimum.

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LIST OF SYMBOLS

Δ	-	Step change
%	-	Percent
°	-	Degree
°C	-	Temperature
g	-	Gram
h	-	Hour
k_i	-	Rate constant
K	-	Kelvin
m	-	Meter
mm	-	Milimeter
mL	-	Mililiter
min	-	Minutes
nm	-	Nanometer
pKa	-	Dissociation constants
rpm	-	Rotation per minute
t	-	Time
wt	-	Weight
wt%	-	Weight percent
α	-	Alpha
β	-	Beta
γ	-	Gamma
θ	-	Angle
λ	-	Wave number

LIST OF ABBREVIATIONS

$(CH_3)_2CO$	-	Acetone
3D	-	Three-dimensional
Al_2O_3	-	Aluminium oxide
ANOVA	-	Analysis of variance
BET	-	Brunauer-Emmett-Teller
C_2H_5OH	-	Ethanol
CCD	-	Central composite design
CH_3CN	-	Acetonitrile
Df	-	Degree of freedom
DOE	-	Design of experiment
EFB	-	Empty fruit bunch
EL	-	Ethyl levulinate
FAME	-	Fatty acid methyl ester
FID	-	Flame ionization detector
GC-MS	-	Gas chromatography – mass spectrometry
H_2SO_4	-	Sulfuric acid
$H_3PMo_{12}O_{40}$	-	Phosphomolybdic acid
$H_3PW_{12}O_{40}$	-	Phosphotungstic acid
$H_4SiW_{12}O_{40}$	-	Silicotungstic acid
HCW	-	Hot compressed water
HF	-	Hierarchy factor
HMF	-	5-hydroxymethylfurfural
HOAc	-	Acetic acid
HPA	-	Heteropolyacid
LAP	-	Laboratory analytical procedures

MPOB	-	Malaysia Palm Oil Board
MS	-	Mean square
NREL	-	National Renewable Energy Laboratory
OPF	-	Oil palm fronds
R^2	-	Coefficient of determination
RSM	-	Response surface methodology
sc	-	Supercritical
scMeOH	-	Supercritical methanol
sctBuOH	-	Supercritical butanol
SiO_2	-	Silicon dioxide
SS	-	Sum of square
TGA	-	Thermal gravimetric analysis
TiO_2	-	Titanium oxide
ZrO_2	-	Zirconium oxide

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The conversions of biomass as raw material into basic chemicals have been studied over past decades. The earliest work conducted to postulate the reaction pathways of biomass conversion was dated back in 1970s. Moreover, in these recent years, the world is highly affected by serious environmental and economic issues. These problems are related to rapid consumptions and dependence on fossil fuels, economic development, population growth, and also resulting global warming (Yuan *et al.,* 2011). Concerns towards energy demand have led to the discovery of alternatives for fossil resources to supply chemicals and energy in the future (Zhang *et al.,* 2011). Due to the availability of the biomass feedstock as it is not compete with the food chain, a lot of studies have been carried out to identify its potential in integrating into biofuel and bio-based chemical products.

The potential of oil palm frond can be enhanced for producing chemical products by develop a new industrial uses of it. The acid catalyzed reaction of oil palm frond to produce ethyl levulinate can be a good alternative method for these plentiful and readily available biomass feedstocks in Malaysia. Lignocellulosic biomass such as oil palm fronds, have complex structures which consist of cellulose and hemicellulose polymers that are bound together by lignin. Both cellulose and hemicellulose structures involve in most biomass including oil palm fronds (OPF) conversion to produce ethyl levulinate as depicted in Figure 1.1 (Peng *et al.*, 2010). The presence of insoluble humin (carbonaceous residue), one of the side products in the reaction process might increase the complexity of the reaction network (Fang and Hanna, 2002).

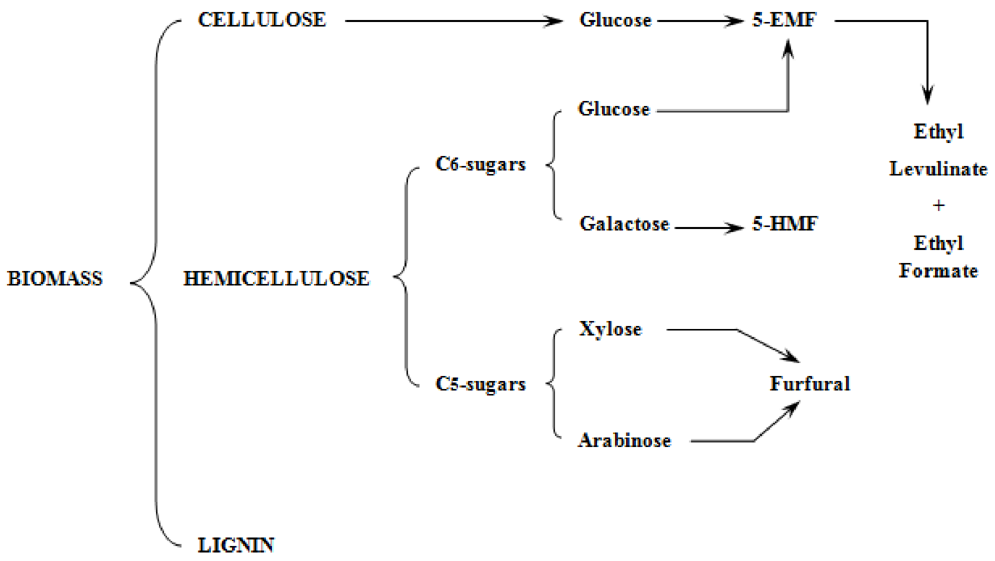

Figure 1.1 Reaction scheme for the conversion of the biomass to ethyl levulinate (Fang and Hanna, 2002 and Peng *et al.*, 2011)

Biomass has been converted into new bio-based chemicals with various applications such as pharmaceutical compound, biofuels, fragrance, flavouring, coating material and resin (Werpy *et al.*, 2004; Chang *et al.*, 2009). There are many catalysts produced and been used in converting biomass into bio-based chemicals.

Ethyl levulinate; a levulinic acid ester is a useful compound that can be used as fuel additives, also in flavouring and fragrance. Commonly, ethyl levulinate and other levulinic acid esters can be produced by esterification reaction with acid catalyst such as *p*-toluenesulfonic, sulphuric and polyphosphoric acid which are in homogeneous medium (Ayoub, 2005; Bacler and Kontowicz, 1953; Olah and Welch, 1974). However, homogeneous catalysts (mineral acids) are well known to cause serious pollution, due to their corrosive and toxic nature. These problems have been overcome nowadays as the use of solid acid (heterogeneous) catalysts is getting more important (Corma and Garcia, 2003; Ledneczki *et al.*, 2005). Heteropoly acids (HPAs) are an example of solid acid that have potential of a low cost resources reward and green benefits (Kozhevnikov, 2007). This study will demonstrate the combination of economic resources with a new technology approach that can establish the bio refinery development activities.

1.2 Problem Statement

In these few years, there are a lot of studies had been conducted in production of chemicals or fuels from renewable biomass resources (Mascal and Nikitin, 2010; Chang *et al.*, 2012; Zhou *et al.*, 2011; Torre *et al.*, 2010). It has been a worldwide demand as the increasing of dependency on fossil resources. The developments of sustainable and clean technologies that can replace the depleting of fossil fuels can be achieved by utilizing the renewable feedstock through tremendously researches (Alonso *et al.*, 2010; Chun *et al.*, 2011; Hayes and Hayes, 2009). A polysaccharide type, cellulose can be a source of sugar and sugar-based molecules (Klemm *et al.*, 2005). This component is the most abundant source of biomass in production of various chemicals and other products.

In the petrochemical industry, ethyl levulinate can be produced via two routes; direct conversion from biomass by acid hydrolysis reaction and by esterification of levulinic acid (Bozell and Petersen, 2010). These conversion routes are more complex than the acid catalyzed reaction of biomass.

There are many researches in production of fine chemicals and its other products in various conditions have been successfully conducted. The direct production of ethyl levulinate from lignocellulosic biomass has been reported by some researchers, but none of them have used oil palm fronds as biomass feedstock (Saravanamurugan and Riisager, 2012; Pasquale *et al.*, 2012; Peng *et al.*, 2011; Chang *et al.*, 2012). The direct formation of ethyl levulinate from lignocellulosic biomass by solid acid catalyst in ethanol media provides a very simple step reaction as shown in Figure 1.2.

$$\text{Biomass} \xrightarrow[\text{Ethanol}]{\text{HPA}} \text{5-ethoxymethyl furfural} \longrightarrow \text{ethyl levulinate + ethyl formate}$$

Figure 1.2 Direct formation of ethyl levulinate from lignocellulosic biomass (Peng *et al.*, 2011)

The production of ethyl levulinate either from model compound or biomass, there are a lot of researches that have widely used hazardous catalyst such as sulphuric acid (H_2SO_4) (Chang et al., 2012a; Peng et al., 2011; Chang et al., 2012b; Garves, 1988). This kind of catalyst is promise in causing a serious pollution especially to the environment due to their high corrosivity properties and toxic nature. In this research, heteropoly acid (HPA) that has the same acidity condition with sulphuric acid was used. HPAs are well-known environmental friendly acid catalyst is promising to produce ethyl levulinate yield from model compound and biomass itself.

1.3 Objectives

The objectives of this research are:

i. To screen a series of heteropoly acids (HPA) catalysts for catalytic performance of glucose conversion to ethyl levulinate.

ii. To study the effect of parameters (i.e reaction temperature, reaction time, and catalyst loading) of ethyl levulinate production.

iii. To optimize process conditions for glucose and oil palm fronds conversion to ethyl levulinate using Response Surface Methodology (RSM) using screened HPA catalyst at optimum conditions.

1.4 Research Scopes

The generalized scopes involved in this research are:

i. Heteropoly acid catalysts used were phosphotungstic acid, phosphomolybdic acid, and silicotungstic acid.

ii. Model compound of glucose was utilized for catalyst testing, screening and optimization process.

iii. HPAs testing and screening for glucose conversion to ethyl levulinate.

iv. Optimization process for glucose conversion to ethyl levulinate by using screened catalyst.

v. Optimization of oil palm frond for ethyl levulinate production by using screened catalyst.

vi. Parameters optimized were reaction temperatures, reaction time, and catalyst loading.

vii. The concentration of final product was analyzed by a gas chromatography with a flame ionization detector (FID).

viii. In addition, the Response Surface Methodology (RSM) was used for optimization of acid catalyzed reaction process.

1.5 Thesis Outline

This thesis is divided into 5 main chapters. Introduction to this research has been explained in Chapter 1. This chapter consists of research background, recent problem statements, objectives, and scopes of this research. Literature reviews are given in Chapter 2 which explain in detailed the previous researches that is related to the biomass conversion into ethyl levulinate and other high value chemical products by using various methods as well as researches concerned in this area. Chapter 3 has been described the experimental procedures such as catalyst screening, optimization of the production of ethyl levulinate from glucose as well as production of ethyl levulinate from biomass, and analytical procedures involved to evaluate the efficiency of the method in this study. Chapter 4 is the main part of this research whereby Chapter 4 explains in detail the results and discussions for the optimization processes and utilization of lignocellulosic biomass. Finally, Chapter 5 concludes the findings and significance of this study. Recommendations for the future works are also suggested in assurance the positive outlook of this research area.

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