

HYDROLYSIS OF BIOMASS TO LEVULINIC ACID OVER HY-ZEOLITE
SUPPORTED IONIC LIQUID CATALYST

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SUPPORTED IONIC LIQUID CATALYST

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ABSTRACT

Levulinic acid has received significant attention as a platform chemical for synthesizing a broad range of bio-based fuels. In this study, a series of hydrogen form of Y zeolite (HY-zeolite) supported ionic liquid (HY-IL) catalysts: HY-IL-1, HY-IL-2 and HY-IL-3 were synthesized, characterized and explored for catalytic conversion of glucose to levulinic acid. The synthesized ionic liquid, 1,4-methylsulfonic acid imidazolium tetrachloroaluminate was characterized using elemental analysis. Meanwhile, the HY-IL catalysts and the parent HY zeolite were characterized using x-ray diffraction, field emission scanning electron microscopy, nitrogen physisorption, Fourier-transform infrared, thermogravimetric analysis, ammonia temperature-programmed desorption and infrared pyridine to determine the catalyst properties. The experimental result revealed that HY-IL-2 exhibited the highest catalytic performance with 62.2 % of levulinic acid yield from reaction conducted at 180 °C for 6 h using 0.4 g of catalyst and 0.5 wt% of glucose concentration. High surface area, high concentration of acid sites and low Brønsted to Lewis acid ratio of HY-IL-2 were the reason for the high levulinic acid production from glucose. The optimization study of levulinic acid production from glucose and cellulose was conducted using response surface methodology with Box-Behnken design. At optimum condition, 60.6% and 27.2% of levulinic acid yields were obtained from glucose and cellulose, respectively. Meanwhile, when the testing was done on the biomass, oil palm frond (OPF) and empty fruit bunch (EFB), 21.0% and 22.4% of levulinic acid yield were obtained respectively at reaction temperature of 170 °C, reaction time of 4 h, 0.6 g of HY-IL-2 and 0.4 wt% of feedstock concentration. The process efficiency for OPF and EFB for levulinic acid production was 65.4% and 77.0%, respectively. Kinetic study of glucose conversion to levulinic acid was derived using the first-order model pseudo-homogeneous. The study was done at various temperature and time ranges of 120–200 °C and 1–6 h, respectively. The kinetic model consists of 4 key steps: 1) glucose dehydration to 5-hydroxymethylfurfural (5-HMF), 2) glucose degradation to produce humin, 3) 5-HMF rehydration to produce levulinic acid, and 4) 5-HMF degradation to form humin. The kinetic study revealed that the reaction rate for every step increased with the increase of the temperature. The activation energy for glucose conversion to 5-HMF and 5-HMF conversion to levulinic acid was 36.1 and 26.1 kJ/mol, respectively. The activation energy obtained was lower and comparable with the previous catalysts employed for glucose conversion to levulinic acid. The finding of this study demonstrated the potential of zeolite-supported ionic liquid as a catalyst for biomass transformation to platform chemicals under mild process conditions.

ABSTRAK

Asid levulinik telah menjadi perhatian utama sebagai bahan kimia platform untuk sintesis pelbagai bahan api berasaskan bio. Dalam kajian ini, satu siri mangkin zeolit Y bentuk H (HY) yang disokong oleh cecair ionik (HY-IL): HY-IL-1, HY-IL-2 dan HY-IL-3 disintesis, diciri dan dikaji untuk mangkin penukaran glukosa kepada asid levulinik. Cecair ionik, 1,4 metilsulfonik imidazolium tetrakloroaluminat yang telah disintesis dicirikan dengan menggunakan analisis unsur. Sementara itu, mangkin HY-IL dan zeolit HY asal dicirikan dengan menggunakan belauan sinar-x, pancaran medan mikroskopi imbasan elektron, penjerapan fizik nitrogen, inframerah transformasi Fourier, analisis termogravimetri, penyaherapan berprogram suhu ammonia dan inframerah piridina untuk menentukan sifat mangkin. Keputusan eksperimen mendedahkan bahawa HY-IL-2 mempamerkan prestasi tertinggi mangkin dengan 62.2% hasil asid levulinik daripada tindak balas yang dijalankan pada suhu 180 °C selama 6 j menggunakan 0.4 g mangkin dan 0.5 wt% kepekatan glukosa. Penghasilan asid levulinik yang tinggi daripada glukosa disebabkan oleh luas permukaan yang besar, kepekatan yang tinggi bagi tapak asid dan nisbah rendah asid Brønsted kepada Lewis dari mangkin HY-IL-2. Kajian pengoptimuman terhadap penghasilan asid levulinik daripada glukosa dan selulosa telah dijalankan dengan menggunakan kaedah sambutan permukaan dengan reka bentuk Box-Behnken. Pada keadaan optimum, 60.6% and 27.2% hasil asid levulinik masing-masing telah diperolehi daripada glukosa dan selulosa. Manakala, apabila ujian dilakukan terhadap biojisim, pelepah sawit (OPF) and tandan buah kosong (EFB), 21.0% dan 22.4 % hasil asid levulinik masing-masing diperolehi pada suhu tindak balas 170 °C, masa tindak balas 4 j, 0.6 g HY-IL-2 dan 0.4 wt% kepekatan stok suapan. Kecekapan proses untuk penukaran OPF and EFB kepada asid levulinik masing-masing adalah 65.4% dan 77.0%. Kajian kinetik penukaran glukosa kepada asid levulinik diterbitkan dengan menggunakan model tertib pertama pseudo-homogen. Kajian ini dilakukan pada pelbagai suhu dan masa masing-masing dengan julat 120–200 °C dan 1–6 jam. Model kinetik ini terdiri daripada 4 langkah utama: 1) penyahhidratan glukosa kepada 5-hidroksimetilfurfural (5-HMF), 2) penurunan glukosa untuk menghasilkan humin, 3) penghidratan semula 5-HMF untuk menghasilkan asid levulinik, dan 4) penurunan 5-HMF untuk membentuk humin. Kajian kinetik mendedahkan bahawa kadar tindak balas bagi setiap langkah meningkat dengan peningkatan suhu. Tenaga pengaktifan bagi penukaran glukosa kepada 5-HMF dan penukaran 5-HMF kepada asid levulinik adalah masing-masing 36.1 dan 26.1 kJ/mol. Tenaga pengaktifan yang diperolehi adalah lebih rendah dan setanding dengan mangkin sebelumnya yang digunakan untuk penukaran glukosa kepada asid levulinik. Kajian ini menunjukkan potensi zeolit yang disokong cecair ionik sebagai mangkin untuk transformasi biojisim kepada bahan kimia platform di bawah keadaan proses sederhana.

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LIST OF ABBREVIATIONS

3D	-	Three dimensional
5-HMF	-	5-Hydroxymethylfurfural
Al	-	Aluminium
AlCl ₃	-	Aluminium (III) chloride
ANOVA	-	Analysis of variance
AZ25	-	zeolite treated with alkaline (0.25 M NaOH)
[BMIM][BF ₄]	-	1-butyl-2,3-dimethylimidazolium tetrafluoroborate
[BMIM]Br	-	1-butyl-3-methylimidazolium bromide
[BMIM][Cl]	-	1-butyl-3-methylimidazolium chloride
[BMIM]HSO ₄	-	1-butyl-3-methylimidazolium hydrogen sulfate
BET	-	Brunauer Emmet Teller
[C ₃ SO ₃ HMIM]HSO ₄	-	1-methyl-3-(3-sulfopropyl)imidazolium hydrogen sulfate
[C ₄ SO ₃ HPhim][Cl]	-	1-butyl sulfonic acid-2-phenylimidazoline chloride
CH ₂ Cl ₂	-	Dichloromethane
CH ₃ SO ₃ H	-	Methanesulfonic acid
Cu/NbP	-	Copper doped niobium phosphate
Df	-	Degree of freedom
DNS	-	3,5- dinitrosalicylic acid
EFB	-	Empty fruit bunch
[EMIM][HSO ₄]	-	1-ethyl-3-methylimidazolium hydrogen sulfate
Fe-NbP	-	Ferum doped niobium phosphate
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier Transform Infrared spectroscopy
H ₂ SO ₄	-	Sulfuric acid
HMOR-34	-	Hydrogen form of mordenite zeolite (Si/Al = 34)
HPLC	-	High-pressure liquid chromatography
HSO ₃ Cl	-	Chlorosulfonic acid
HY-IL	-	HY-zeolite supported ionic liquid
IR-pyridine	-	Infrared pyridine
KBr	-	Potassium bromide

$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	-	potassium sodium tartrate tetrahydrate
MIBK	-	Methyl isobutyl ketone
$\text{MIO}/\text{SO}_4^{2-}$ B-BSAC	-	sulfated magnetic iron oxide biomass-based solid acid
MnCl_2	-	Manganese (II) chloride
MPOB	-	Malaysian Palm Oil Board
NaCl	-	Sodium chloride
NaOH	-	Sodium hydroxide
Na_2SO_3	-	sodium sulfite
Nb- β zeolites	-	niobium-modified Beta-zeolites
OPF	-	Oil palm frond
RSM	-	Response surface methodology
SAPO-18	-	Silicoaluminophosphate (Si/Al=18)
Si	-	Silica
[SMIM]AlCl ₄	-	1-sulfonic acid-3-methyl imidazolium tetrachloroaluminate chloride
[SMIM]Cl	-	1-sulfonic acid-3-methyl imidazolium chloride
SnCl_4	-	Tin tetrachloride
Sn-MMT/ SO_4^{2-}	-	sulfated Tin-loaded montmorillonite
SO_3HCl	-	Chloro sulfonic acid
TEM	-	Transmission Electron Microscope
TGA	-	Thermal gravity analysis
TOF	-	Turn over frequency
XRD	-	X-ray diffraction
ZSM-5	-	Zeolite Socony Mobil-5

LIST OF SYMBOLS

°	-	Degree
°C	-	Degree Celcius
%	-	Percentage
A	-	Pre-exponential factor
g	-	gram
h	-	hour
k	-	Reaction rate constant
Ea	-	Activation energy
k	-	Reaction rate constant
K	-	Kelvin
J	-	joule
wt%	-	Weight percent
min	-	Minutes
mL	-	Millilitre
mAU	-	Mili Absorbance Unit

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CHAPTER 1

INTRODUCTION

1.1 Background

The search for alternative resources for chemical and fuel production is progressing because petroleum or fossil resources are estimated to deplete in the near future. Apart from that, the increase in consumption and supply of petroleum resources also hikes the fuel price. According to (Satari *et al.*, 2019), fossil resources are often related to gas pollution issues due to greenhouse gas releases to the environment. Therefore, it is high time that research been done to find alternatives for petroleum resources replacement.

Among all the resources available, biomass utilization to produce chemical substances is preferable due to its sustainability, renewability, and natural carbon dioxide resources. These advantages caused the utilization of biomass to produce chemicals and fuel to receive significant attention among researchers and industry. Among the application of biomass, hydrolysis of biomass to produce levulinic acid has been extensively studied. Figure 1.1 shows the top building chemical blocks that can be derived from biomass as listed by the National Renewable Energy Laboratory. These building blocks were listed for their potential in the market, and levulinic acid is among the potential building blocks that can be prepared via acid hydrolysis of lignocellulosic biomass.

Several routes of levulinic acid to fuel additive have been investigated; for example, esterification of levulinic acid to levulinic ester (fuel additive) in the presence of alcohol (Lucas *et al.*, 2019). Condensation of levulinic acid with phenol could produce diphenolic acid (DPA), a chemical intermediate in lubricant (Mthembu *et al.*, 2021a). γ -valerolactone (GVL), a flavoring agent, and 2-methyl tetrahydrofuran (MTHF), a fuel additive, can be obtained from the hydrogenation of levulinic acid (Liu

et al., 2019; Roa and Garcia, 2021). Levulinic acid also can be converted to resin, solvent, polymer, and other chemical intermediates.

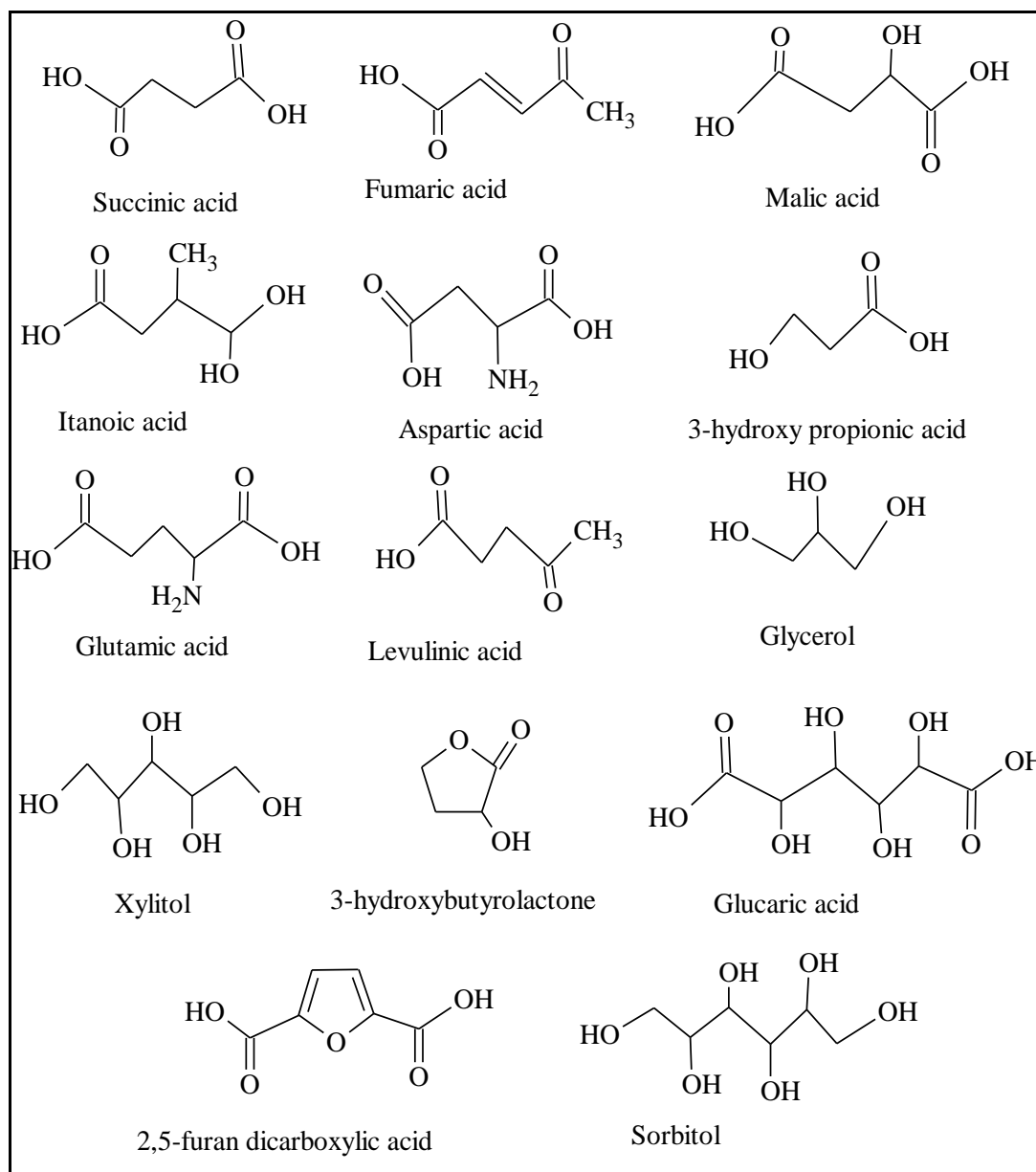


Figure 1.1 Potential biobased derived products from biomass feedstock (Werpy and Petersen, 2004)

The pathway of conversion lignocellulosic biomass to levulinic acid can be summarized as in Figure 1.2. Lignocellulosic biomass is composed of 3 major components, including cellulose, hemicellulose, and lignin. Production of levulinic acid can be divided into two routes which are cellulose and hemicellulose route. For the cellulose route, cellulose undergoes a hydrolysis process to become glucose. Then,

glucose dehydrates to 5-HMF and subsequently rehydrates to levulinic acid (Boonyakarn *et al.*, 2019). In the hemicellulose route, hemicellulose dehydrates to furfural, and the furfural will undergo hydrogenation to become furfuryl alcohol. Finally, furfuryl alcohol will hydrolyze to levulinic acid (Kang *et al.*, 2018).

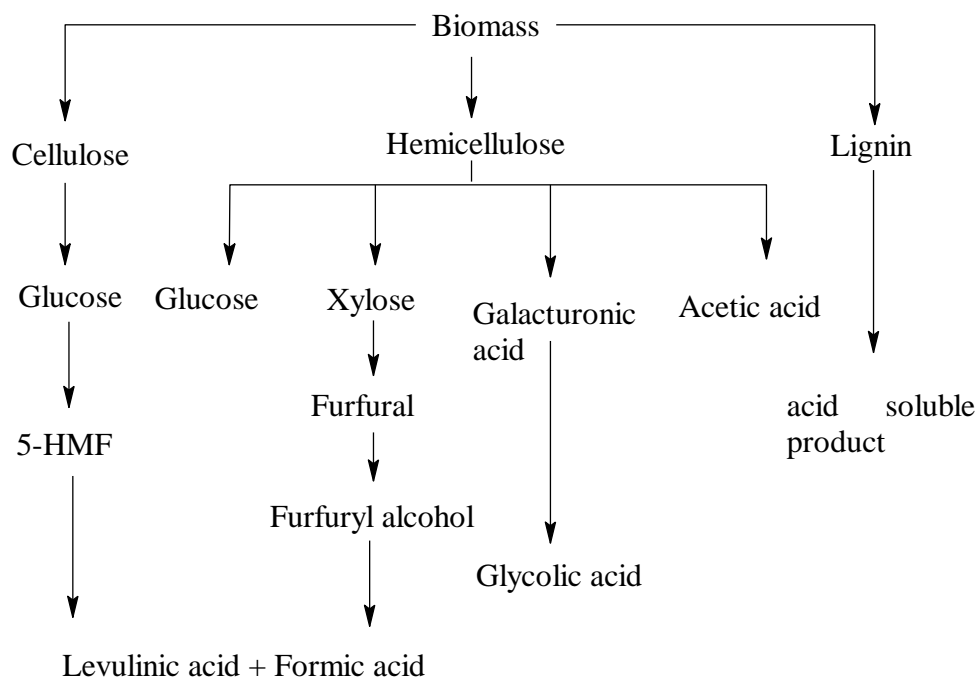


Figure 1.2 Pathway for the conversion of biomass to levulinic acid (Girisuta *et al.*, 2006b)

Several methods have been introduced for levulinic acid production. Acid-catalyzed dehydration and hydrolysis of biomass with acid were frequently used in levulinic acid production. Other methods have also been applied, such as oxidation of ketones, acid hydrolysis of furfuryl alcohol, and alkylation of nitroalkanes (Bozell *et al.*, 2000). However, these methods suffer drawbacks such as expensive feedstocks and the generation of large amounts of side products.

Conversion of biomass to levulinic acid has been carried out by various catalysts such as mineral acid (Sweygers *et al.*, 2018), zeolite (Li *et al.*, 2019), metal chloride (Di Fidio *et al.*, 2019; Wei and Wu, 2017), copper doped niobium phosphate (Fang *et al.*, 2019), mesoporous niobium catalyst (Liu *et al.*, 2017) and acidic ionic liquid (Liu *et al.*, 2019).

Among the catalysts used, ionic liquids received great attention due to their unique properties such as negligible volatility, high thermal stability, and easily separate from reaction (Tadesse and Luque, 2011). Various combinations of cation and anion in ionic liquids could be made to achieve different performances. For example, the addition of an acidic carboxylic group into ionic liquid was efficient for dehydration of carbohydrate to 5-HMF without the formation of by-products (Hu *et al.*, 2013b). Whereas, the sulfonic acid-functionalized ionic liquid was effective for the conversion of cellulose to levulinic acid (Ren *et al.*, 2013).

Despite the excellent activity of ionic liquids, their application is limited due to high cost, complex separation, and ionic liquid toxicity (Sidhpuria *et al.*, 2011). Therefore, to overcome these problems, the concept of supported ionic liquid catalysts (SILC) has been introduced. Generally, SILC requires a smaller amount of ionic liquid and consequently minimized the limitation related to ionic liquid in terms of economy, toxicity, and viscosity. SILC have been used as catalyst in various chemical reaction such as gas separation (Feng *et al.*, 2018), oxidation (Restrepo *et al.*, 2015), biodiesel production (Chang and Zhou, 2018), esterification (Han *et al.*, 2019) and condensation reaction (Hierro *et al.*, 2018). Few studies have reported the use of SILC for the conversion of carbohydrates to 5-HMF, an intermediate compound that undergoes ring cleavage to form levulinic acid and formic acid. Xu *et al.* applied ionic liquid-supported silica gel to synthesize 5-HMF from various substrates such as fructose, glucose, xylose, and sucrose (Xu *et al.*, 2015a). In terms of catalytic activity, SILC (IL-SO₃H-HSO₄/SiO₂) performed quite similarly to its ionic liquid (IL-SO₃H-HSO₄) for fructose dehydration to 5-HMF (Xu *et al.*, 2015a).

Zeolite has been extensively studied as catalyst or catalyst support for various dehydration reactions due to its uniform pore size, high surface area, and high thermal stability (Li *et al.*, 2019; Wang *et al.*, 2019; Wei and Wu, 2018). However, low levulinic acid yield has been reported by (Wei and Wu, 2018) using zeolite alone as the catalyst for biomass conversion reaction. This condition occurred due to its low acid sites of the catalyst that could influence biomass conversion. Therefore, HY zeolite modification to increase acid sites is required to improve the catalytic properties of HY-zeolite and enhance levulinic acid production at adequate process conditions.

1.2 Problem Statement

The utilization of biomass becomes important due to the production of second-generation biofuels. This biofuel can overcome the competition problem between food and fuel, associated with the first-generation biofuel problems. However, biomass utilization for biofuel production was very challenging due to its complex structure in cellulose and lignin. The complex structure involves a hydrogen bond between cellulose that forms the crystalline structure and covalent bonds between lignin and hemicellulose. Their complex structure can hinder the chemical reaction. Therefore, many studies have been done to improve the hydrolysis process, such as homogeneous acidic hydrolysis (Kumar *et al.*, 2018), hydrolysis in supercritical water (Jeong *et al.*, 2017b), and enzymatic hydrolysis (Chylenski *et al.*, 2017). Despite the improvement efforts, there are still drawbacks to the hydrolysis approach. The acidic hydrolysis could result in corrosion of equipment and high energy utilization involving separation, recycling, and treatment of the acid. Hydrolysis in supercritical water involves severe conditions such as high temperature (i.e., 380°C) and high pressure (22 MPa), while enzymatic hydrolysis involves a slow process, the high price of enzyme, and difficult recovery of enzyme.

Heterogeneous catalysts were used as an alternative to replacing homogenous catalysts. Among heterogeneous catalysts used, zeolite catalyst has received great interest from researchers due to its pore structure, thermal stability, and high surface area (Li *et al.*, 2019; Wei and Wu, 2018). However, due to low acid density and lack of Lewis acid sites, zeolite as catalyst exhibit poor performance for the conversion of biomass to levulinic acid. Therefore, several works modify zeolite to improve the catalytic performance of the zeolite (Velaga *et al.*, 2019; Wei and Wu, 2018). In this study, the zeolite was modified by adding an ionic liquid onto the zeolite. Taking the efficient performance shown by ionic liquid for levulinic acid production from various substrates, the addition of ionic liquid into HY-zeolite might promote LA production from biomass.

Levulinic acid production is influenced by the interaction between process variables during the reaction. The common manipulated process variables were reaction temperature, reaction time, catalyst dosage, and feedstock loading. The determination of the optimum process is important to give the best levulinic acid production. Moreover, with the optimization process, a more feasible process and better utilization of resources can be achieved. A conventional method can be costly and time-consuming since it evaluates the effect of a parameter one at a time. By applying the design of the experiment, multiple parameters can be evaluated within the same factorial experiment. As such, response surface methodology (RSM) can be used for optimizing the levulinic acid production process.

Besides, a kinetic study is important to provide a foundation for the understanding of any chemical reaction. In previous work, many kinetic studies have been conducted on the conversion of biomass to levulinic acid in various catalysts. Therefore, finding from the kinetic study can help in better understanding the glucose conversion to levulinic acid involving solid catalyst, especially for application in industrial processes.

1.3 Research Objective

The objectives of this research are:

- (a) To synthesize, characterize and screen a series of HY-ILs for glucose conversion to levulinic acid.
- (b) To optimize levulinic acid production from glucose and cellulose over selected HY-IL catalyst using RSM and apply the optimum condition on the OPF and EFB.
- (c) To perform kinetic studies for glucose conversion to levulinic acid over selected HY-IL catalyst.

1.4 Scope of Research

Several steps were required to achieve all the research objectives. The first step is to synthesize ionic liquids: [MSIM][Cl] and [MSIM][AlCl₄]. The synthesized ionic liquid was then characterized using elemental analysis. For the experiment, different ionic liquid to zeolite (HY) ratio (0.4, 0.5, and 0.6) was prepared and labeled as HY-IL-1, HY-IL-2, and HY-IL-3, respectively. The synthesized HY-ILs were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), nitrogen (N₂) physisorption, temperature-programmed desorption (NH₃-TPD), thermal gravimetric analysis (TGA), field-emission scanning electron microscopy with energy dispersive X-ray (FESEM-EDX), and IR pyridine to examine the physical and chemical properties of all catalysts. The HY-ILs and HY zeolite catalyst were screened for levulinic acid production from glucose under the same condition. The selected catalyst was tested under 4 parameters to find the optimum condition that could produce the highest levulinic acid yield.

The second research objective is to investigate optimum conditions for levulinic acid production from glucose and cellulose over selected catalysts using RSM. Four process variables selected for optimization studies were reaction temperature, reaction time, catalyst dosage, and feedstock concentration. These variables were selected based on their great influence on levulinic acid yield reported in previous works. The optimum condition obtained was then applied for OPF and EFB for the production of levulinic acid.

For the third objective, the kinetic study of glucose conversion to levulinic acid over selected HY-IL was investigated to determine reaction rate constant, activation energy and pre-exponential factor. The kinetic study was performed using the first-order kinetic model and Arrhenius plot equation.

1.5 Significances of the Research

This study investigates the potential of OPF and EFB as starting materials for levulinic acid production. OPF and EFB are among the common biomass used in Malaysia as starting materials to produce chemicals and fuel. They can become the alternative to replace petroleum resources as they are readily available, abundant supply, renewable, and environmentally friendly.

Modified zeolite is one of the methods that can be used to improve the catalytic performance of the zeolite. The catalyst was tested for a one-pot catalytic reaction, which can skip pretreatment, isomerization, dehydration, and rehydration process. Several biomasses and their derivatives were tested for levulinic acid production using this catalyst. Based on current work, the zeolite-supported ionic liquid catalyst has potential for future work on catalytic conversion of biomass to levulinic acid under mild conditions.

The main product, levulinic acid, has gained interest among researchers as a value-added chemical due to its potential utility to produce a wide range of chemicals and fuel. It can produce a flavoring agent, pharmaceutical, polymer, resin, and fuel additive.

1.6 Thesis Outline

This thesis consists of 7 chapters. Chapter 1 covers the introduction and research background, including several issues related to this research, research objectives, scopes, and significance.

Chapter 2 discussed the previous research related to levulinic acid production, including starting material, applied catalyst, applications and conditions that can influence levulinic acid production. The optimization and kinetic studies related to levulinic acid production are also discussed in this chapter.

Chapter 3 presents in detail the experimental procedure, such as catalyst synthesis, catalyst characterization, catalyst testing on biomasses, and measurement for the efficiency of the catalysts used in this study. It also covers the analysis of several products such as glucose, 5-HMF, and levulinic acid. Optimization and kinetic study were also discussed in this chapter.

Chapter 4 discusses more on the characterization of catalysts, the relationship between catalyst's chemical properties and product yield and testing of the catalyst toward several biomasses. It also discusses the proposed mechanism of the catalyst. Chapter 5 explains the optimization of levulinic acid production from several feedstocks over selected HY-IL catalysts using RSM. Two feedstocks applied in the experiment were glucose and cellulose. Then, the optimum condition obtained was used to testing the selected catalyst for the OPF and EPF conversion.

In Chapter 6, the kinetic studies of glucose conversion to levulinic acid were carried out using the selected HY-IL catalyst and were compared with the previous studies. Finally, Chapter 7 concludes the research and proposes the recommendation for future works in this research area.

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LIST OF PUBLICATION

Indexed journal

1. **Abu Zarin, M.**, Zainol, M., & Amin, N. (2020). Optimizing levulinic acid from cellulose catalyzed by HY-zeolite immobilized ionic liquid (HY-IL) using response surface methodology. *Malaysian Journal of Fundamental and Applied Sciences*.16(6), 625-629. <https://doi.org/10.11113/mjfas.v16n6.1970>.
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