

LEVULINIC ACID PRODUCTION FROM LIGNOCELLULOSIC BIOMASS  
USING HY ZEOLITE SUPPORTED CHROMIUM CATALYST IN IONIC  
LIQUID

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*To my beloved husband, mother and children  
for their Love, Prayer and Support*

***“So, verily, every difficulty, there is relief.  
Verily, with every difficulty, there is relief”  
(Al-Inshirah 94:5-6)***

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## ABSTRACT

Levulinic acid is a sugar-derived building block that can be produced from biomass feedstock as an alternative to the petrochemical resources. The purpose of this study was to investigate the performance of HY zeolite supported chromium catalysts in producing levulinic acid from glucose, cellulose and lignocellulosic biomass before it was further optimized using response surface methodology (RSM). The catalysts comprising of different weight ratios of  $\text{CrCl}_3$  and HY zeolite (1:1, 1:2 and 2:1) were synthesized using wetness impregnation method. Characterization of the catalysts using XRD, BET, FT-IR, TGA,  $\text{NH}_3$ -TPD and FT-IR of adsorbed pyridine demonstrated the catalytic reaction of the catalysts was predominantly influenced by type (Lewis acid), amount and strength of acid sites, surface area, hierarchical porous structures and shape selectivity of the catalysts. Experimental results showed that the  $\text{CrCl}_3/\text{HY}$ -1:1 catalyst exhibited the highest catalytic performance with 62% levulinic acid yield at reaction temperature, 160 °C and reaction time, 180 min. Optimization of levulinic acid was conducted using the potential  $\text{CrCl}_3/\text{HY}$ -1:1 catalyst and ionic liquid, [EMIM][Cl] was introduced as a solvent for the cellulose conversion to levulinic acid. At optimum process conditions, 55.2%, 46.0%, 15.5% and 15.0% of levulinic acid yields were produced from glucose, cellulose, empty fruit bunch (EFB) and kenaf. Meanwhile, in the presence of ionic liquid under the same process conditions, 20.0% and 17.0% of levulinic acid yields were produced from EFB and kenaf. In addition, the compositions of EFB and kenaf were determined to compute the highest theoretical levulinic acid yields in the samples feedstock and the efficiencies of the catalytic process. This study demonstrated that the combination of the proposed catalyst with ionic liquid has potential to be applied in biomass conversion to levulinic acid under adequate process conditions.

## ABSTRAK

Asid levulinik adalah blok binaan daripada gula yang boleh dihasilkan daripada biojisim sebagai satu alternatif kepada sumber petrokimia. Tujuan kajian ini adalah untuk menyiasat prestasi pemangkin zeolit HY disokong oleh kromium dalam menghasilkan asid levulinik daripada glukosa, selulosa dan lignoselulosa sebelum ia dioptimumkan menggunakan kaedah gerak balas permukaan (RSM). Pemangkin dengan nisbah berat  $\text{CrCl}_3$  dan zeolit HY yang berbeza (1:1, 1:2 dan 2:1) telah disintesis menggunakan kaedah impregnasi basah. Pencirian pemangkin menggunakan XRD, BET, FT-IR, TGA,  $\text{NH}_3$ -TPD dan FT-IR piridin terjerap menunjukkan tindakbalas oleh pemangkin dalam menghasilkan asid levulinik telah dipengaruhi oleh jenis asid (Lewis asid), jumlah kekuatan asid, luas permukaan pemangkin, struktur hirarki liang dan sifat pemilihan bentuk oleh pemangkin. Ujikaji menunjukkan pemangkin  $\text{CrCl}_3/\text{HY}-1:1$  telah menghasilkan asid levulinik tertinggi dengan hasil sebanyak 62% pada suhu tindak balas, 160 °C dan masa tindak balas, 180 min. Pengoptimuman hasil asid levulinik telah diuji menggunakan pemangkin yang berpotensi,  $\text{CrCl}_3/\text{HY}-1:1$  dan cecair ionik,  $[\text{EMIM}][\text{Cl}]$  telah diperkenalkan sebagai pelarut dalam penukaran selulosa kepada asid levulinik. Pada keadaan proses optimum, 55.2%, 46.0%, 15.5% dan 15.0% asid levulinik telah dihasilkan daripada glukosa, selulosa, tandan kosong (EFB) dan kenaf. Sementara itu, 20.0% dan 17.0% asid levulinik telah dihasilkan daripada EFB dan kenaf dalam keadaan proses yang sama dengan kehadiran cecair ionik. Disamping itu, komposisi EFB dan kenaf telah ditentukan untuk mengira penghasilan asid levulinik tertinggi secara teori daripada sampel biojisim dan menguji kecekapan proses pemangkin. Kajian ini menunjukkan bahawa kombinasi pemangkin yang disarankan dengan cecair ionik mempunyai potensi untuk diaplikasikan dalam penukaran biojisim kepada asid levulinik di bawah keadaan proses yang mencukupi.

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## LIST OF SYMBOLS

$\Delta$	-	Step change
$^{\circ}$	-	Degree
$^{\circ}\text{C}$	-	Temperature
A	-	Ampere
$\text{\AA}$	-	Armstrong
cP	-	Centipoise
g	-	Gram
h	-	Hour
J	-	Joules
K	-	Kelvin
min	-	Minutes
$pK_a$	-	Dissociation constants
rpm	-	Rotation per minute
V	-	Volt
w/v	-	Weight over volume
wt	-	Weight
$\alpha$	-	Alpha
$\beta$	-	Beta
$\gamma$	-	Gamma
$\theta$	-	Angle
$\lambda$	-	Wave number

## LIST OF ABBREVIATIONS

EFB	-	Empty fruit bunch
[EMIM][Cl]	-	1-ethyl-3-methyl-imidazolium-chloride
3D	-	Three-dimensional
Al	-	Aluminium
AlCl <sub>3</sub>	-	Aluminium (III) chloride
ANOVA	-	Analysis of variance
BET	-	Brunauer-Emmett-Teller
BJH	-	Barrett, Joyner & Halenda
CCD	-	Central composite design
CrCl <sub>2</sub>	-	Chromium (II) chloride
CrCl <sub>3</sub>	-	Chromium (III) chloride
CrCO <sub>3</sub>	-	Chromium (III) carbonate
CuCl <sub>3</sub>	-	Copper (III) chloride
DOE	-	Design of experiment
DTG	-	Differential thermal gravimetric
FeCl <sub>3</sub>	-	Iron (III) chloride
FTIR	-	Fourier transform infrared spectroscopy
H <sub>2</sub> SO <sub>4</sub>	-	Sulphuric acid
HBr	-	Hydrobromic acid
HCl	-	Hydrochloric acid
HF	-	Hierarchy factor
HMF	-	5-hydroxymethylfurfural
HPLC	-	High performance liquid chromatography
HY	-	Y-type faujasite zeolite
IL	-	Ionic liquid

IL-1	-	1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulphate ionic liquid
IR-Pyr	-	Infrared spectroscopy of adsorbed pyridine
LAP	-	Laboratory analytical procedures
LZY	-	Y-type faujasite zeolite
MnCl <sub>2</sub>	-	Manganese (II) chloride
NH <sub>3</sub>	-	Ammonia
NH <sub>3</sub> –TPD	-	Temperature programmed desorption of ammonia
$R^2$	-	Coefficient of determination
RSM	-	Response surface methodology
Si	-	Silica
TG	-	Thermal gravimetric
TGA	-	Thermal gravimetric analyzer
$t$ -plot	-	Statistical thickness
UV	-	Ultraviolet
XRD	-	X-ray diffraction
ZRP-X	-	Mordenite type zeolite

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Research Background**

Increasing of petroleum oil prices forces the chemical industry to find alternative raw materials for the basic chemicals production (Fang and Hanna, 2002). Biomass is the only renewable resource of fixed carbon, which is essential for the production of conventional hydrocarbon liquid transportation fuel and petrochemical products (Girisuta, 2007). Biomass resources are more preferable compared to others since the biomass feedstocks do not compete with the food chain (Rackemann and Doherty, 2011). A graphical representation of the top 30 building blocks derived from biomass feedstock (Figure 1.1) shows the potential of biomass for bio-based chemicals production as a replacement to the petrochemical resources. Among the screened building blocks, levulinic acid was the top twelve and it was ranked based on these criteria; suitability for the biorefinery, the value of the building block and its derivatives, the technical complexity of each part in the pathway transformation and the potential of the building blocks to produce groups with similar derivatives (Werpy and Petersen, 2004). Therefore, a lot of researches and technologies are carried out nowadays to identify the potential of integrating biomass feedstocks into biofuel and bio-based chemical products.

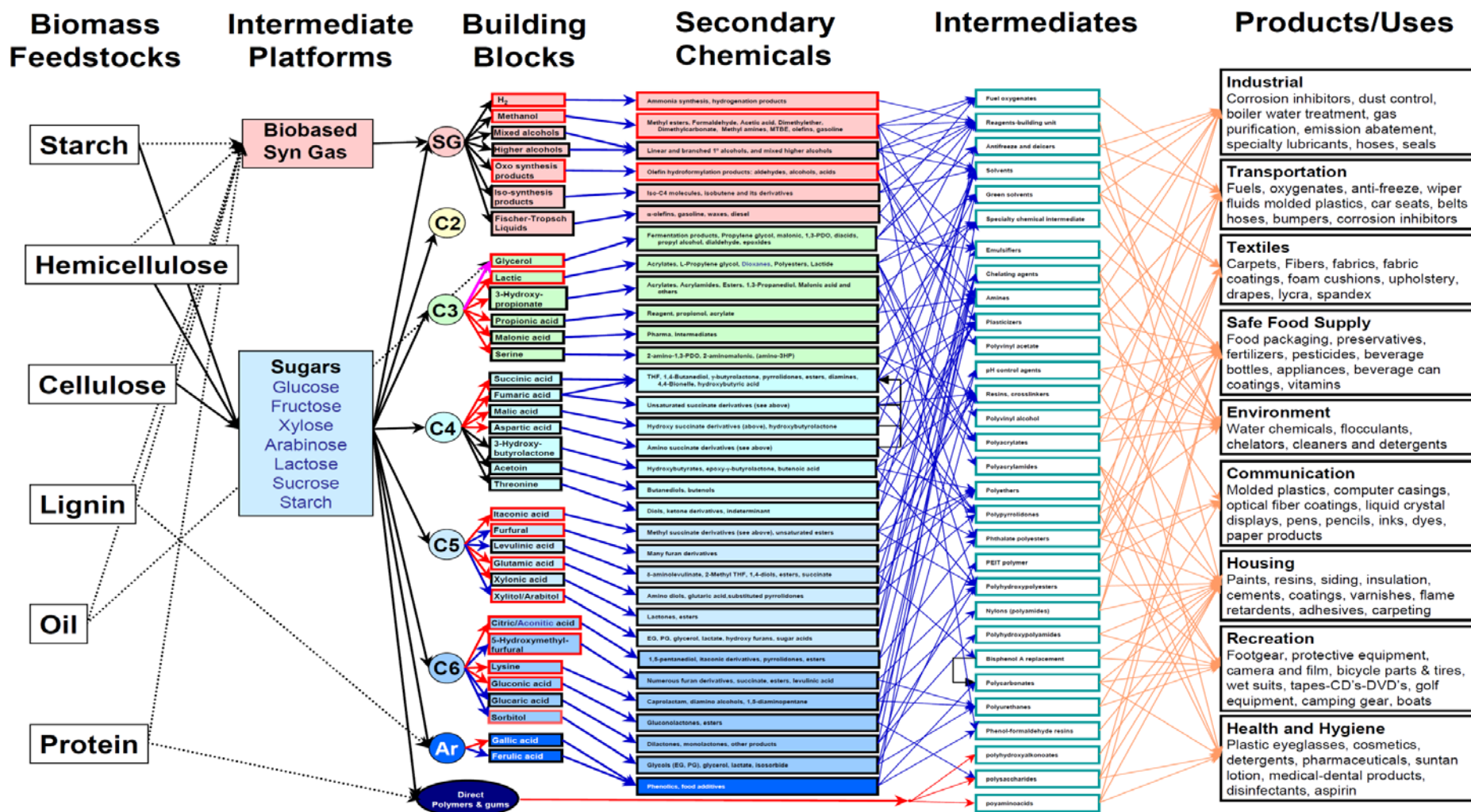
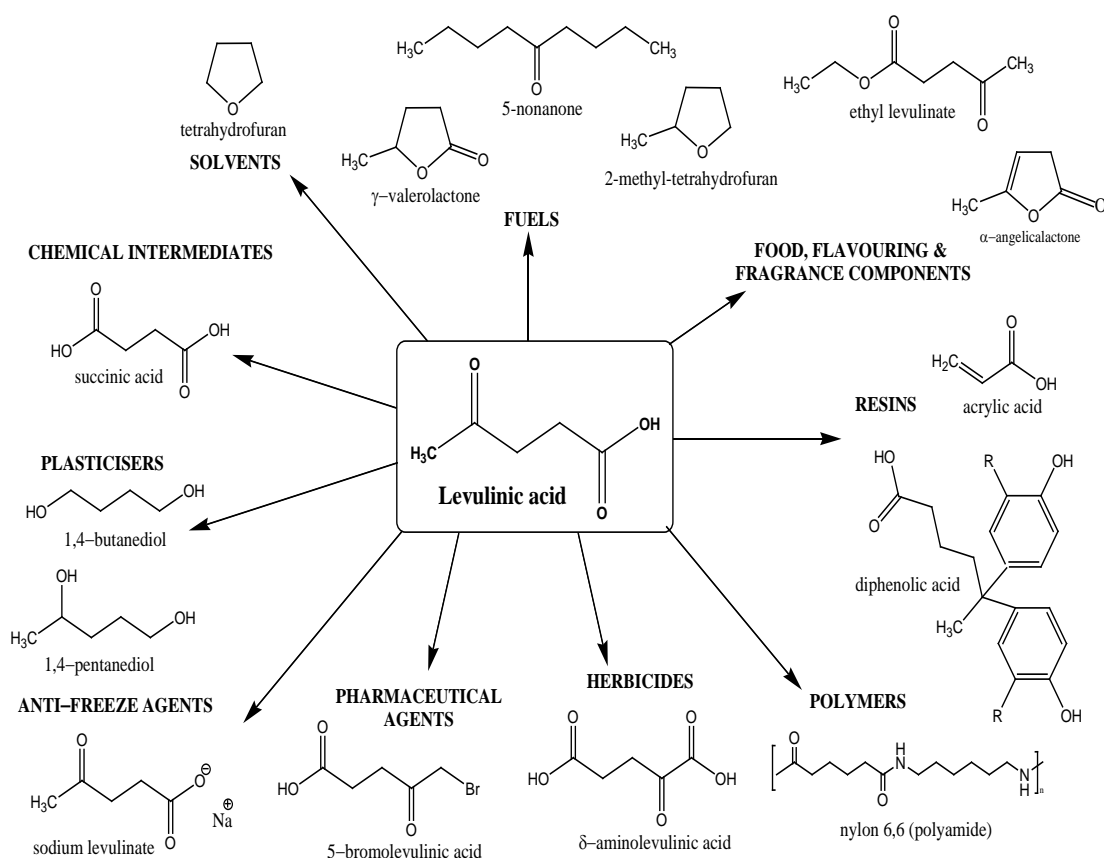


Figure 1.1 Potential bio-based derived products from biomass feedstocks (Werpy and Petersen, 2004)

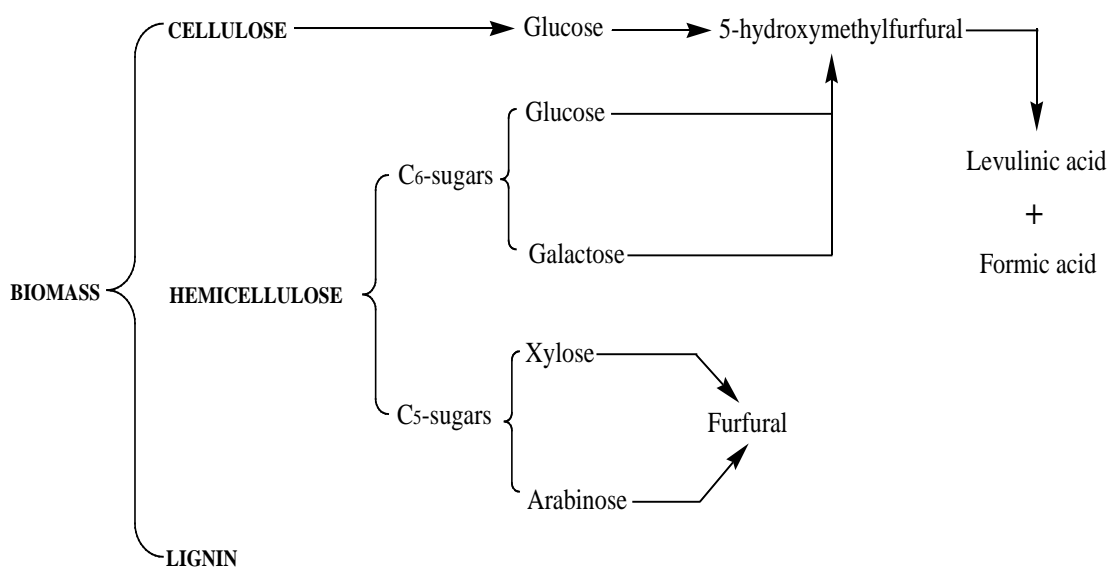
Levulinic acid is a short chain fatty acid having a ketone carbonyl group and a carboxylic acid group which makes this compound a versatile building block for various bulk chemicals (Hongzhang *et al.*, 2011). Levulinic acid was identified as one of the top 30 and amongst the top, it was the top twelve sugar-derived building blocks that can be produced from biomass as screened by National Renewable Energy Laboratory (Werpy and Petersen, 2004). It has been produced since 1870 and appeared to be an important basic chemical material with numerous potential uses (Figure 1.2). Levulinic acid can be used as textile dyes, antifreeze, animal feed, coating material, solvent, food flavoring agent, pharmaceutical compound and resin (Chang *et al.*, 2009). Recently, thermal de-oxygenation process is developed for converting levulinic acid to energy dense (low oxygen to carbon ratio) cyclic and aromatic products (Rackemann and Doherty, 2011). These products were produced for easily upgrading to the hydrocarbon fuels.



**Figure 1.2** Levulinic acid as a platform chemical for various potential uses of products (Rackemann and Doherty, 2011)



Lignocellulosic biomass such as empty fruit bunch (EFB) and kenaf are renewable, non-edible, cheap and widely abundant biomass resources. Based on the research findings regarding to their technical and commercial potential, EFB and kenaf have a potential in Malaysia's industrial crop (Abdul Khalil *et al.*, 2010; Goh *et al.*, 2010c). To enhance the potential of EFB and kenaf for producing chemical products, a new industrial uses of them need to be developed. The hydrolysis of EFB and kenaf to produce levulinic acid can be a good alternative method for these plentiful and readily available biomass feedstocks in Malaysia. Empty fruit bunch and kenaf plants have complex structures. They consist of cellulose and hemicellulose polymers that are bound together by lignin. Both cellulose and hemicellulose structures involve in EFB and kenaf conversion to produce levulinic acid as depicted in Figure 1.3. The presence of insoluble humin (carbonaceous residue), one of the side products in the reaction process might increase the complexity of the reaction network (Peng *et al.*, 2010; Fang and Hanna, 2002).



**Figure 1.3** Simplified reaction scheme for the conversion of the biomass to levulinic acid (Fang and Hanna, 2002)

A number of approaches have been reported for levulinic acid production. Acid-catalyzed dehydration and hydrolysis of biomass and carbohydrates with acid were widely used in levulinic acid production (Girisuta, 2007). Formic acid and

other byproducts also formed in this reaction (Chang *et al.*, 2007). Other approaches have also been applied such as hydrolysis of acetyl succinate ester, the acid hydrolysis of furfuryl alcohol, the oxidation of ketones, Pd-catalyzed carbonylation of ketones and by the alkylation of nitroalkanes (Bozell *et al.*, 2000). However, all these approaches require expensive feedstock and frequently formed large amounts of side products. The first commercial-scale plant for the levulinic acid production from lignocellulosic biomass was built in Caserta, Italy through a process developed by Biofine Renewables Corporation (Girisuta *et al.*, 2008). The Biofine process uses acid hydrolysis of tobacco bagasse for levulinic acid production in two reactor systems to minimize the side products (Hayes *et al.*, 2008).

A new pathway for biomass conversion to value-added products in a single process under mild conditions can be developed by catalytic hydrolysis in ionic liquid (Wang *et al.*, 2011a; Lee *et al.*, 2011). Ionic liquids are versatile green solvent where they can act as solvents, catalysts and they can be utilized in very different ways; homogenous, multiphase and heterogeneous for biomass transformations or in organo-catalysis (Olivier-Bourbigou *et al.*, 2010). Lately, most of the researchers are trying to build up the potential of ionic liquids as a reaction medium by combining with solid acid, metal halide or salts and mineral acid in biomass hydrolysis and dehydration processes to produce 5-hydroxymethylfurfural, HMF (Su *et al.*, 2009; Hu *et al.*, 2009; Li *et al.*, 2009; Zhang and Zhao, 2009). To date, a few literatures have been reported the potential use of these treatment methods for producing levulinic acid. Thus, this study intends to employ the combination of low cost sources of levulinic acid with this new technology wherein it can open up a new route opportunity for levulinic acid production.

## 1.2 Problem Statement

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). Lignocellulosic biomass feedstocks have seen to be the most suitable feedstock for an alternative to the petrochemical sources existing nowadays. The fractions of biomass can be converted into chemical products such as levulinic acid (Pike and Hertwig, 2008). In the petrochemical industry, levulinic acid can be produced from maleic anhydride and hydrolysis of furfuryl alcohol. These conversion routes are more complex than the acid hydrolysis of biomass and relatively higher market prices of levulinic acid (Rackemann and Doherty, 2011).

Traditionally, homogenous acid hydrolysis was used in the lab and industry scales in producing levulinic acid. Raw materials used for the levulinic acid production included simple sugars, starch, and cellulosic materials (Fang and Hanna, 2002). Extensive studies have been conducted by Chang *et al.* (2009), Girisuta (2007), Chang *et al.* (2007) and Girisuta *et al.* (2006) teams. They have reported the details about experimental and kinetic studies on the homogeneous acid-catalyzed hydrolysis of water hyacinth and wheat straw for levulinic acid production. Basically, production of levulinic acid requires high temperature (150–250 °C) and concentrated mineral acid. In terms of safety and environmental issues, this hydrolysis process is risky and hazardous. According to Chang *et al.* (2006), although high levulinic acid yield can be attained at low reaction temperature by applying diluted acid at a longer reaction time, the corrosion to equipment and the difficulty of acid recovery for further use caused this method inefficient to be implemented in industry. As an alternative, heterogeneous acid catalysts have been promoted since these catalysts can overcome the problems occurred in homogeneous acid catalysts (Hongzhang *et al.*, 2011).

Heterogeneous acid catalysts are feasible alternatives to homogenous acid catalysts and possibly will offer an environmental advantage due to their selective, recycle and regenerate abilities properties and easy to handle. These can reduce equipment corrosion problems and relatively low cost required if the catalyst can be easily separated and recycled. Due to their advantages compared to homogenous acid catalysts, a lot of studies have been conducted on the synthesis of levulinic acid using multiple solid acid catalysts and feedstock (Rackemann and Doherty, 2011). Low levulinic acid yields were produced in prolong reaction times as reported by Jow *et al.* (1987), Lourvanij and Rorrer (1993) and Zeng *et al.* (2010) Thus, further studies were conducted by Peng *et al.* (2010) and Hongzhang *et al.* (2011) by employing metal chlorides and solid superacid. They found that these methods have enhanced levulinic acid yields in shorter reaction times but higher reaction temperatures (200 °C) were required. Therefore, further studies are still necessary to comprehend the catalytic activities in the formation of levulinic acid by discovering more reactive catalysts. Exploration of heterogeneous acid catalysts through catalytic performance testing and physico-chemical properties is useful to enhance the levulinic acid yield and selectivity.

In present study, transition metal–modified HY zeolite is rarely utilized in biomass processing especially in levulinic acid production. HY zeolite supported transition metal catalysts have been used widely in the chemical processes especially for the synthesis of high quality fuel (Xiao and Mao, 1995). The catalysts were prepared by constituting the mixture of two or more components and the intention was to catalyze more than one reaction at once (Flores and Silva, 2008). Presently, HY zeolite (Brönsted type acid site) and  $\text{CrCl}_3$  (Lewis type acid site) showed high catalytic reactivity on glucose and cellulose conversion towards fructose production and simultaneously dehydrated to HMF before further rehydrated to levulinic acid and formic acid (Tan *et al.*, 2011; Peng *et al.*, 2010; Pidko *et al.*, 2010; Lourvanij and Rorrer, 1993). In addition, very low HMF yield was reported over zeolite and chromium catalysts alone in the reaction systems (Zhang and Zhao, 2009). The low levulinic acid yield could also be expected in these reaction systems since HMF is the intermediate compound before levulinic acid is formed. Therefore, modification of HY zeolite by introducing the  $\text{CrCl}_3$  is expected to improve the catalytic properties

and possibly enhance the levulinic acid yield and selectivity from glucose, cellulose and lignocellulosic biomass.

Moreover, the modified HY zeolite with  $\text{CrCl}_3$  catalyst assisted with ionic liquid allows the subsequent conversion of feedstock to levulinic acid in high yield and selectivity. Ionic liquid can act as solvent and catalyst for dissolving cellulose structures by disrupting the hydrogen bonds between the molecules (Zhang and Chan, 2010; Zhang and Zhao, 2009). The development of the catalytic activity in ionic liquid requires choosing the right catalyst and ionic liquid as different catalyst and ionic liquid will react with the different purpose. Thus, these limitations and challenges depend on the development of catalyst for the hydrolysis and dehydration processes of biomass feedstock to produce levulinic acid. The precision of catalyst would contribute to a sustainable and cost-effective process through greater utilization of the biomass feedstock. Besides, the catalyst can improve the conversion and enhance the levulinic acid yield and selectivity.

### **1.3 Research Objectives**

The objectives of the research are:

- i. To synthesize, characterize and screen  $\text{CrCl}_3$ /HY catalysts at different weight ratios for glucose conversion to levulinic acid.
- ii. To optimize levulinic acid yield from glucose using potential catalyst.
- iii. To optimize levulinic acid yield from cellulose using potential catalyst in an ionic liquid.

- iv. To utilize lignocellulosic biomass for levulinic acid production at optimum conditions.

#### **1.4 Scopes of Research**

The generalized scopes involved in this research are:

- i. Synthesis of catalysts with different weight ratios of  $\text{CrCl}_3$  and HY zeolite; 1:1, 1:2 and 2:1 via wetness impregnation method.
- ii. Characterizations of catalysts using x-ray diffraction (XRD), nitrogen adsorption Brunauer Emmett-Teller (BET), thermal gravimetric analyses (TGA), temperature programmed desorption ammonia ( $\text{NH}_3$ -TPD), Fourier transform infrared spectroscopy (FTIR) and infrared spectroscopy of adsorbed pyridine (IR-Pyr).
- iii. Model compounds of glucose and cellulose were utilized for the catalysts testing, screening and optimization process.
- iv. Catalysts testing and screening for glucose conversion to levulinic acid.
- v. Optimization process for glucose conversion to levulinic acid by using the potential catalyst.
- vi. Optimization process for cellulose conversion to levulinic acid by using the potential catalyst in an ionic liquid.
- vii. Determination of lignocellulosic biomass, EFB and kenaf compositions using a thermal gravimetric analyzer (TGA) and Laboratory analytical procedures (LAP).

- viii. Utilization of EFB) and kenaf for levulinic acid production at optimum process conditions.

## **1.5 Thesis Outline**

This thesis commences with an introduction to this research in Chapter 1. This chapter describes the research background, recent problems, objectives, scopes and significance of this research. The literatures in Chapter 2 review in detailed the previous researches related to the conversion of biomass and its constitution into valuable bio-based chemical products using various methods as well as researches concerned in this area. Chapter 3 elaborates the experimental procedures such as catalyst preparation, characterization, testing methods and the analytical procedures involved to evaluate the efficiency of the method in this study. The main parts of this research are Chapter 4 and 5 whereby Chapter 4 explains in detail the results and discussions for the characterizations and catalytic activities of the catalysts while Chapter 5 concerns the optimization processes and utilization of lignocellulosic biomass. Finally, Chapter 6 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.

## **1.6 Research Significance**

This research has developed catalysts with different weight ratios of metal halide ( $\text{CrCl}_3$ ) and HY zeolite. The catalysts have facilitated the steps of dehydration, isomerization and rehydration processes into one pot catalytic reaction.

The presence of ionic liquid could dissolve and cleave the glycosidic bonds in the cellulose structure into simple structure, glucose before further catalyzed into levulinic acid via potential catalyst. These methods were also tested to EFB and kenaf. The results revealed the potential of this study to be implemented in biomass conversion to levulinic acid under adequate process conditions.



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