



**UNIVERSITI PUTRA MALAYSIA**

**SYNTHESIS OF LEVULINIC ACID FROM OIL PALM MESOCARP  
FIBER BY ACID HYDROLYSIS**

**NOR AKHLISAH BINTI ZULKIPLI**

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**By**

**NOR AKHLISAH BINTI ZULKIPLI**

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

**November 2018**

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in  
fulfilment of the requirement for the degree of Master of Science

## **SYNTHESIS OF LEVULINIC ACID FROM OIL PALM MESOCARP FIBER BY ACID HYDROLYSIS**

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**NOR AKHLISAH BINTI ZULKIPLI**

**November 2018**

**Chair : Prof Robiah Yunus, PhD**  
**Faculty : Engineering**

Levulinic acid (LA) can be produced from both C6 and C5 carbohydrates via dehydration and hydrolysis processes of biomass. This study focuses on the production of LA from oil palm mesocarp fiber (OPMF). From proximate and thermogravimetric analysis (TGA), it was found that OPMF has 21.16 - 29.73% of cellulose, hemicellulose 21.81 – 27.61%, lignin 10.39 – 30.80%, ash 6.39% and extractive 25.23%. It is difficult to produce high yield of LA from the biomass due to generation of humins during hydrolysis reaction. Moreover, the high content of silica bodies on OPMF surface also causes lower sugar production which affects the formation of LA. Thus, pretreatment is needed to improve the yield of LA.

This study aimed to investigate the effect of several pretreatments on the synthesis of LA. Four pretreatments were conducted; acid pretreatment, ultrasonic-assisted acid pretreatment, alkali pretreatment and ultrasonic-assisted alkali pretreatment. Sulfuric acid ( $H_2SO_4$ ) and sodium hydroxide (NaOH) were used as catalysts in pretreatment. For acid and alkaline pretreatments, samples were pretreated with different temperatures (60 °C, 80 °C and 100 °C). The parameter for ultrasonic-assisted pretreatment was sonication power (40%, 60% and 80%). The highest content of HMF produced after pretreatment from all pretreatments was 1.71% pretreated by 6% (v/v) sulphuric acid pretreatment without ultrasonic at 100 °C. Direct hydrolysis of biomass was proposed after it was discovered that most of the sugars after pretreatment were present in the liquor. The maximum yield of LA was 20.54% obtained from direct acid hydrolysis of sample which was pretreated at 100 °C using 6% (v/v)  $H_2SO_4$  solution. The results on morphological structure of treated OPMF fiber after SEM analysis showed the evidence of silica bodies removal from the surface of OPMF fiber thus allowed for a direct exposure of acid pretreatment and acid

hydrolysis. FTIR analysis suggested that the formation of carbonyl groups indicates the formation of LA in hydrolysis samples. TGA results indicated that the sample which produced highest amount of levulinic acid had lowest activation energy in the reaction.

The second objective is to study the effect of process conditions on the hydrolysis of OPMF into LA using Response Surface Methodology (RSM). The pretreatment method chosen in this step was based on the results obtained from the first objective. The pretreated samples were hydrolyzed in an acid hydrolysis reactor. Three parameters were investigated; reaction time (2 – 4 hours), acid concentration (1 - 3% (v/v) H<sub>2</sub>SO<sub>4</sub>) and temperature of reaction (120 – 160 °C). The highest content of LA 17.88% was produced at the temperature 160 °C, using 3% sulphuric acid concentration for 4 hours. Since these are the highest conditions for each parameter, the optimized condition could not be determined due to the limitation of reactor specification for acid hydrolysis reaction.

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

## **SINTESIS ASID LEVULINIK DARIPADA SERAT MESOKARP KELAPA SAWIT MELALUI KAEDAH HIDROLISIS ASID**

Oleh

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Asid levulinik (LA) boleh diperolehi daripada kedua-dua C5 dan C6 karbohidrat melalui tindak balas dehidrasi dan hidrolisis. Kajian ini mengfokuskan kepada penghasilan asid levulinik daripada serat mesokarp kelapa sawit (OPMF). Melalui analisis penganggaran dan termogravimetri (TGA), OPMF mempunyai selulosa sebanyak 21.16 – 29.73%, hemiselulosa sebanyak 21.81 – 27.61%, lignin sebanyak 10.39 – 30.80 %, 6.39% abu dan 25.23% hasil ekstraktif. Didapati bahawa kandungan asid levulinik yang tinggi sukar diperolehi disebabkan oleh penghasilan humin semasa tindak balas hidrolisis. Tambahan pula, banyak jasad silika yang terdapat pada OPMF juga menyebabkan penghasilan gula menjadi rendah dan memberi kesan kepada penghasilan asid levulinik.

Kajian ini bertujuan untuk mengkaji kesan empat prarawatan ke atas penghasilan asid levulinik (LA) iaitu prarawatan asid, prarawatan asid dengan bantuan ultrasonik, prarawatan alkali, dan prarawatan alkali dengan bantuan ultrasonik. Asid sulfurik ( $H_2SO_4$ ) and natrium hidroksida (NaOH) telah digunakan sebagai pemangkin dalam prarawatan. Untuk prarawatan asid dan alkali, sampel diprarawat dengan menggunakan suhu yang berbeza (60 °C, 80 °C dan 100 °C). Parameter untuk prarawatan ultrasonik adalah kuasa ultrasonik (40%, 60% dan 80%). Kandungan HMF yang paling tinggi adalah 1.71% diprarawat menggunakan 6% asid sulfurik pada suhu 100 °C melalui kaedah prarawatan asid tanpa ultrasonik. Hidrolisis secara langsung ke atas biojisim telah disarankan selepas menemukan kebanyakan gula selepas prarawatan telah dialihkan ke dalam cairan prarawatan. Kadar kandungan maksimum asid levulinik yang dihasilkan adalah 20.54% diperolehi daripada hidrolisis asid secara langsung ke atas sampel yang diprarawat pada suhu 100 °C menggunakan 6% (v/v) asid sulfurik. Hasil pada struktur morfologi

terhadap serat OPMF selepas analisis SEM menunjukkan bukti bahawa jasad silica telah dibuang daripada permukaan serat OPMF dan membenarkan pendedahan langsung prarawatan dan hidrolisis asid. FTIR mengesahkan pembentukan asid levulinik dalam sampel hidrolisis melalui ikatan karbonil. Hasil TGA pula menunjukkan bahawa sampel yang menghasilkan asid levulinik yang tinggi mempunyai tenaga pengaktifan yang rendah dalam tindak balas.

Objektif kedua adalah untuk mengkaji kesan keadaan hidrolisis ke atas OPMF terhadap asid levulinik dengan menggunakan Response Surface Methodology (RSM). Kaedah prarawatan yang dipilih dalam langkah ini adalah berdasarkan hasil yang diperolehi daripada objektif pertama. Sampel yang telah diprarawat, dihidrolisis dalam reaktor hidrolisis asid. Tiga parameter telah dikaji; masa tindakbalas (2 – 4 jam), kepekatan asid (1 – 3% (v/v) H<sub>2</sub>SO<sub>4</sub>) dan suhu tindakbalas (120 – 160 °C). Kandungan asid levulinik tertinggi adalah 17.89% diperolehi pada suhu 160 °C menggunakan 3% kepekatan asid sulfurik selama 4 jam. Asid levulinik paling tinggi terhasil pada keadaan parameter yang paling ekstrem maka keadaan yang optimum tidak dapat ditentukan disebabkan oleh keterbatasan kebolehan reaktor yang digunakan untuk tindak balas hidrolisis asid.

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*“Rabbi Yassir Wa La Tuassir  
– O Allah, make it easy and do not make it difficult”*



This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment 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

ADL	Acid Detergent Lignin
ADF	Acid Detergent Fiber
ANOVA	Analysis of Variance
CCD	Central Composite Design
CNF	Cellulose Nanofiber
CrI	Crystallinity Index
DALA	Delta Aminolevulinic Acid
DPA	Diphenolic Acid
E <sub>a</sub>	Activation Energy
FAME	Fatty Acid Methyl Esters
FFB	Fresh Fruit Bunch
FTIR	Fourier Transform Infrared Spectroscopy
HBI	Hydrogen Bonding Index
HMF	Hydroxymethylfurfural
HPLC	High Performance Liquid Chromatography
ITMA	Institute of Advance Technology
LA	Levulinic Acid
LHW	Liquid Hot Water
LOI	Lateral Order Index
L/S	Liquid per Solid Ratio
M	Molar
MARDI	Malaysian Agriculture Research and Development Institute
MTHF	Methyl Tetrahydrofuran
NDF	Neutral Detergent Fiber
OPEFB	Oil Palm Empty Fruit Bunch
OPF	Oil Palm Frond
OPMF	Oil Palm Mesocarp Fiber
OPT	Oil Palm Trunk
PKS	Palm Kernel Shell
POME	Palm Oil Milling Effluent
PTSA	P-Toluenesulfonic Acid
RID	Refractive Index Detector
RSM	Response Surface Methodology
SEM	Scanning Electron Microscopy
TCI	Total Crystallinity Index
TGA	Thermogravimetric Analysis
TFA	2,2,2-Trifluoroacetic Acid
THF	Tetrahydrofuran
WDM	Wet Disk Milling
XOS	Xylo-Oligomers



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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background

##### 1.1.1 Energy Generation and Chemical Production from Biomass

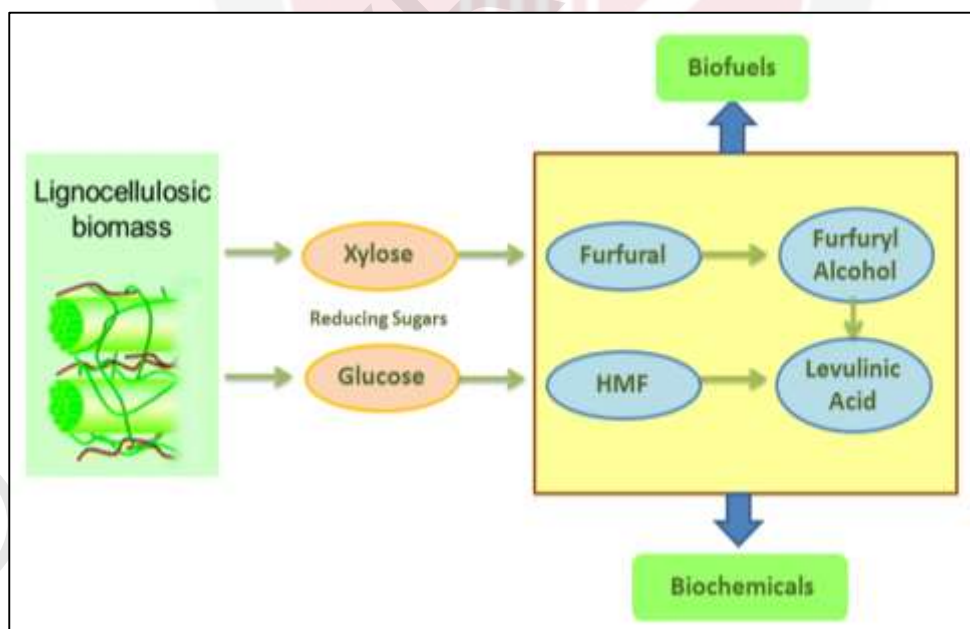
In the past years, unstable fuel price has affected the economy of many countries. Moreover, the use of fossil fuel which yields more carbon and sulphur leads to major environmental concerns including the global warming and acid rain (Hossain *et al.*, 2016). These two mentioned issues are considered as challenges and need to be resolved by developing new technologies especially the development of alternative fuel resources (Chiesa and Gnansounou, 2014). These concerns have escalated the development and application of alternative energies such as wind, biomass, hydro, and solar (Hossain *et al.*, 2016). Moreover, the research on the use of biomass as alternative energy sources has also increased lately due to its abundant supply. Generally, most of energy sources are used in two ways which are as a source of fuel or energy and second as raw materials in the production of chemicals.

Biomass, is one of the renewable resources which is widely available and can be considered as one of the promising affordable options for energy. Forestry, agriculture, waste and industry are known to be the sources of biomass (Sadhukhan *et al.*, 2018). They have their own potential to be converted into energy, chemical and other bio-products in various applications. Many types of waste biomass can be explored for examples; agricultural crops, food residuals, municipal solid wastes and animal waste. Agricultural wastes are by-products generated from agricultural industry. Embedded carbon released from combustion of biomass is seized during the growth of biomass thus alleviate the negative impact of using fossil fuels.

In addition, lignocellulosic biomass, a renewable source of carbon, has the potential to be converted into many chemicals such as levulinic acid (LA), furfural, ethanol and 5-hydroxymethylfurfural (HMF) (Alonso *et al.*, 2013b). Three main components of lignocellulosic biomass are cellulose, hemicellulose and lignin, which can be converted into monomer sugars such as glucose, fructose and xylose and then be converted into chemicals by process such as enzymatic or chemical hydrolysis (Alonso *et al.*, 2013b). Basically, biomass needs to be converted into reducing sugars at the first place before it is to be converted into bio-based chemicals and biofuels as shown in Figure 1.1 below. Levulinic acid (LA) is one of

chemicals produced from biomass. The simultaneous degradation of both hemicellulose and cellulose is one of the main challenges in utilizing lignocellulosic biomass. One of the most common thermochemical methods used to accomplish this process is acid hydrolysis (Sweygers *et al.*, 2017; Wettstein *et al.*, 2012). The process is carried out in the presence of acid catalyst. Routes for LA synthesis by acid hydrolysis are shown in Figure 1.2.

However, the presence of lignin slows down the reaction of acid hydrolysis. Thus, pretreatment was needed to improve the hydrolysis reaction. The examples of pretreatment are chemical pretreatment, physical pretreatment and biological pretreatment. Chemical pretreatments such as acid and alkali pretreatment are the most commonly applied techniques to remove lignin from lignocellulosic materials (Sun *et al.*, 2016). During both pretreatments, the ester linkages in lignin and hemicellulose are easily broken down under alkaline and acidic condition (Palamae *et al.*, 2014). Aqueous pretreatments such as dilute sulfuric acid and dilute alkali for example dilute sodium hydroxide have the advantages that they do not use organic solvents which can be expensive and can be carried out in batch reactors in laboratory studies (Bhagia *et al.*, 2016). Ultrasonic pretreatment is also widely used for biomass conversion. It should remove hemicellulose and disrupt the barrier of lignin (He *et al.*, 2017). Previous study found that ultrasonic waves can escalate the chemical reaction such as hydrolysis, resulted from the thermal effects, mechanical and cavitation of the ultrasound (Yu *et al.*, 2018).



**Figure 1.1: Flow of biomass conversion into biofuels and biochemicals** (Alonso *et al.*, 2013b).

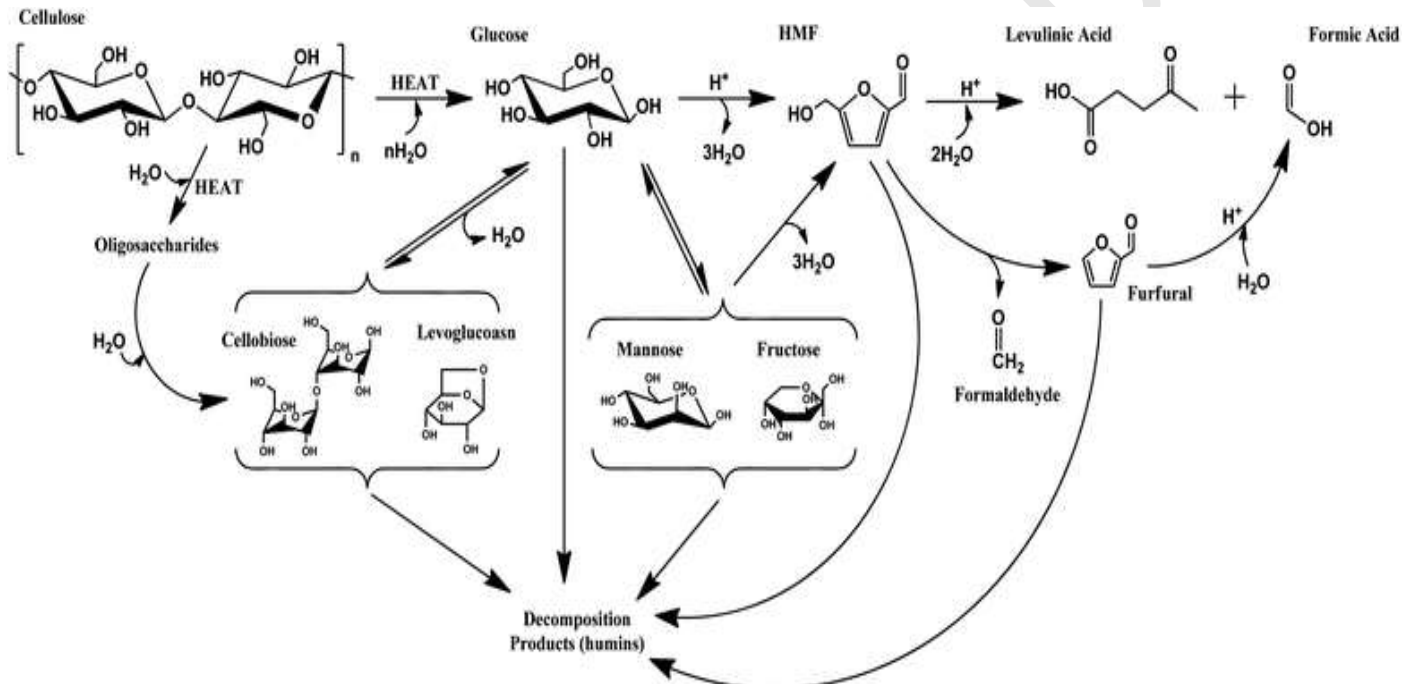


Figure 1.2: Acid hydrolysis reaction mechanism for LA synthesis. (Weingarten et al., 2012)



### 1.1.2 Oil Palm Biomass

Oil palm is known to be one of the potential sources of biomass. According to UI Islam *et al.* (2016), Malaysia is stated as one of the foremost trading countries for oil palm plantation as well as in industrial productions. In 2011, 5 million hectares of land in Malaysia was utilized for palm oil plantation (UI Islam *et al.*, 2016). Oil palm industry has significantly contributed to the Malaysia's economy especially in the plantation and manufacturing industry. Malaysia is also recognized as world's leading exporter of palm oil (Mumtaz *et al.*, 2010). Oil palm is often regarded as the most economic and productive oil crop (Ohimain and Izah, 2017). This is because oil palm can be extracted to produce edible oil known as palm oil and palm oil can be used as fuel via direct combustion (Nipattummakul *et al.*, 2012). Among 17 major oils traded in edible oil and fat market worldwide, palm oil is one of the main edible oils while palm kernel oil is used mainly in the oleo chemical industry (Zainudin *et al.*, 2009).

Palm oil is produced from the mesocarp (fiber) of the palm fruit while palm kernel oil is produced from the nut (kernel) of the fruit. In terms of chemical characteristics, palm oil contains mainly palmitic acid and oleic acid while lauric acid is the main fatty acid in palm kernel oil. Both palm oil and palm kernel oil can be utilized in many applications such as food, soaps, biodiesel and oleo chemicals either with or without any pretreatment.

Over the years, Malaysian palm oil industry has produced around 53 million tons of waste annually. However, a recent research shows a significant increase of oil palm solid residues at 80 million tons of dry residues in 2010, and estimated at 100 million by the year 2020 (Umar *et al.*, 2014). Oil palm biomass can be categorized into several types such as oil palm trunks, oil palm empty fruit bunches (OPEFB), oil palm fronds (OPF), oil palm leaves, palm kernel shells (PKS) and oil palm mesocarp fibers (OPMF) and palm oil milling effluent (POME) (Ahmad *et al.*, 2016; Mohammad *et al.*, 2012). Products and by products of oil palm is shown in Figure 1.3.

Basically, large quantities of oil palm biomass ended as wastes from the palm oil industry after oils (crude palm kernel oil and crude palm oil) were extracted from Fresh Fruit Bunch (FFB) as we can see in Figure 1.3. The production rates of the oil palm biomass with respect to the production rate of FFB are shown in Table 1.1. Recently, these biomasses present as readily available supply of raw materials for the production of green chemicals to curb the environmental issues.



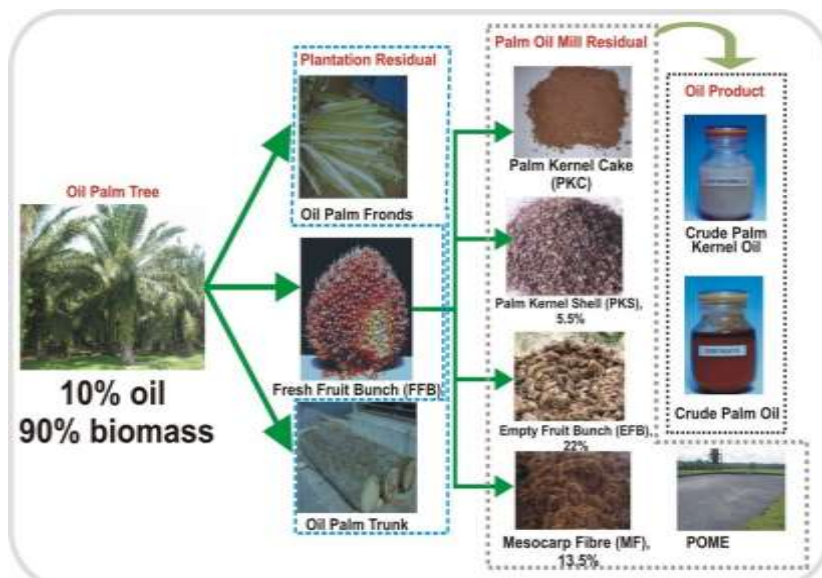


Figure 1.3: Products and by-products from oil palm biomass (Zafar, 2018)

Table 1.1: Production Rates of Oil Palm Biomass with Respect to FFB (Malaysia Energy Statistics Handbook, 2016).

Biomass available from Palm Oil Industry	% from FFB Quantity	Quantity million tonnes
OPEFB	23	21.24
OPMF	13	12.00
PKS	6	5.54
POME	60	55.40

## 1.2 Problem Statement

The commercially available LA is produced from carbohydrates and has limited success due to its high cost of raw materials for production. However, there are still many unexploited options of raw materials such as lignocellulosic biomass containing other carbohydrates and high starch that can be explored as an alternative raw material. Through many researches, they found that oil palm biomass including Oil Palm Mesocarp Fibre (OPMF) are considered as lignocellulosic biomass because their main components comprise of cellulose, hemicellulose and lignin. These lignocellulose biomasses can be converted into carbohydrates and be used to produce arrays of green chemicals including LA. The conversion of oil palm biomass from cellulose into levulinic acid can be seen in Figure 1.4 below. Unfortunately, most of OPMF are used as fuel in boilers and lack of research using OPMF available in literature for production of LA. This is because, previous research only utilized OPMF to produce sugars

such as glucose and xylose. It is expected that OPMF can produced high amount of levulinic acid via hydrolysis reaction.

OPMF is recalcitrant in nature due to the highly crystalline nature of the cellulose and the lignin content. The successful conversion of lignocellulosic biomass needs an effective pretreatment as an important step to optimize the process of conversion into reducing sugar before production of LA. Various pretreatment techniques have been explored to improve the efficiency of hydrolysis reaction and it was found that acid pretreatment and alkaline pretreatment are the common pretreatment applied. Ultrasonic pretreatment also has been proved to enhance the production of sugar. Lack of studies carried out the combination of acid or alkaline pretreatment with ultrasonic technology. Combination of pretreatment methods, for example, ultrasonic-assisted acid pretreatment and ultrasonic-assisted alkaline pretreatment would improve the efficiency of biomass conversion in the overall process.

Previous works have only reported on pretreatments of OPMF for production of sugars, not on the effect of pretreatment on the production of LA. Through pretreatment, OPMF is expected to produced high amount of sugars which can be attributed to high yield of HMF and LA. Characterization studies are important to establish the morphological and structural changes due to pretreatment methods and acid hydrolysis reaction. However, only limited studies are reported on characterization of OPMF after hydrolysis and related to the changes with respect to levulinic acid synthesis.

Furthermore, no attempt has been done to study the optimization of LA production from OPMF via acid hydrolysis reaction in order to improve LA content and productivity. If the parameters affecting acid hydrolysis reaction conditions are optimized, the production of LA by this reaction is expected to be more efficient and higher yield of LA can be obtained.

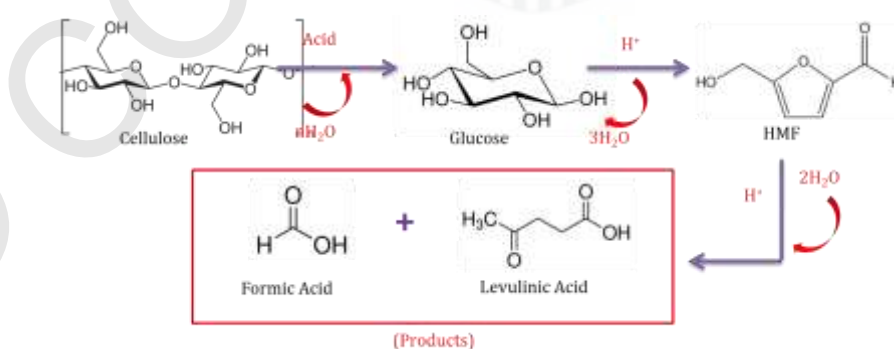


Figure 1.4: Chemical routes of biomass conversion into levulinic acid

### **1.3 Objectives**

The objectives of this research are as follows:

1. To evaluate the effects of different pretreatment methods on formation of levulinic acid (LA) via acid hydrolysis of oil palm mesocarp fiber (OPMF) and characterization of OPMF.
2. To study the effects of process conditions on conversion of OPMF into LA via acid hydrolysis using Response Surface Methodology (RSM).
- 3.

### **1.4 Scope of Work**

The scope of work for this research is primarily on the acid hydrolysis of OPMF for LA production. The research began by comparing several methods of pretreatment which were ultrasonic pretreatment, acid pretreatment and alkali pretreatment. For all pretreatments, effect of acid or alkali concentrations were investigated. Other parameter for ultrasonic pretreatments was on ultrasonic power while for acid and alkali pretreatments, both were investigated on effect of temperature. Effects of process conditions on conversion of LA were studied using Response Surface Methodology (RSM). Parameters involved in this study were effect of acid concentration, effect of temperature and effect of reaction time. The characterization of OPMF was also carried out. The properties investigated include moisture, lignin, cellulose and hemicellulose content.

### **1.5 Thesis Outline**

This reports comprises of five chapters. Chapter 1, the introductory chapter, provides the background of study, the problem statement, objectives and scope of work. Chapter 2 gives detailed analysis of literature review which includes review on lignocellulosic materials, application of oil palm biomass, various pretreatment methods used, LA production and parameters that affected the hydrolysis reaction. All materials and methods are discussed in Chapter 3. Chapter 4 comprises the results and discussions namely on characterization of OPMF using proximate analysis, moisture analysis, TGA analysis, FTIR analysis, effects of several pretreatments on acid hydrolysis and Response Surface Methodology study on effects of process conditions on LA contents. Finally, chapter 5 concludes the present research work and provides the recommendations for future works.

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## LIST OF PUBLICATIONS

- Zulkipli, N.A., Yunus, R., Abidin, Z.Z. and Lim, B.Y., 2019. Broide plot for the effect of acid pretreatments on hydrolysis of oil palm mesocarp fiber. Intern. J. of Current Resear. 1270-1274. <https://doi.org/10.24941/ijcr.34032.02.2019>.
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