



**SYNTHESIS OF SULFONATED CARBON METAL CATALYSTS AND
OPTIMIZATION OF LEVULINIC ACID PRODUCTION FROM OIL PALM
EMPTY FRUIT BUNCH CELLULOSE**

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 Doctor of Philosophy**

July 2024

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DEDICATION

*This thesis is dedicated to my late mother and my late brother whose presence I
dearly miss as this journey concludes*

*To family members and people around me
With love, respect and a bunch of memories*

*To myself
for self-love, sacrifices and emotionally-spiritually-mentally determination*



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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July 2024

Chairman : Professor Ir. Wan Azlina binti Wan Ab Karim Ghani, PhD
Faculty : Engineering

Levulinic acid (LA) is an important building block chemical that can be produced from both monosaccharides and polysaccharides via hydrolysis reactions. Nowadays, biomass waste including oil palm empty fruit bunches (OPEFB) is an attractive source of LA due to their high cellulose content. Therefore, this study focuses on the production of LA from OPEFB-based cellulose utilizing sulfonated carbon metal catalysts. In the first part, a sulfonated carbon metal catalyst was synthesized and evaluated for its performance to produce LA. Among different ratios of iron (Fe) and nickel (Ni)-based catalysts, Fe.75Ni which referred to 25% Fe and 75% Ni, exhibited the most promising activity for LA production and yielded 10.51 % from cellulose at 180 °C for 5 h using 0.15 g catalyst loading. Subsequent impregnation of different Fe.75Ni metal loadings into sulfonated carbon catalyst led to further improvement in LA synthesis. 15%FeNi/ACSO₃H (15% Fe.75Ni impregnated into ACSO₃H) catalyst achieved the highest LA which was 16.76%. based on theoretical yield from cellulose at 180 °C, 5 hours, and 0.15g catalyst loading. The synthesized catalyst can be reused

for four reaction cycles. In the second part, the catalyst characterization was performed using X-ray diffraction (XRD), temperature-programmed desorption of ammonia (TPD-NH₃), thermogravimetric analysis (TGA), N₂ adsorption-desorption, X-ray fluorescence (XRF), field emission scanning electron microscope (FESEM), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Characterization studies confirmed successful metal incorporation in the ACSO₃H catalyst. Furthermore, the 15%FeNi/ACSO₃H catalyst demonstrated favorable properties such as a good surface area, high acidity value and good thermal stability which are advantageous to the synthesis of LA. However, from the results obtained using cellulose, the LA yield was relatively low indicating the necessity for cellulose modification. Subsequently, the study focused on enhancing the LA yield from cellulose. Since the main goal of the study is to explore the use of cellulose from OPEFB, the initial step focused on cellulose isolation from OPEFB. Successful isolation of cellulose was achieved using the dewaxing technique, followed by the treatment with sodium hydroxide and sodium chlorite solution, yielding 8.98% LA based on theoretical yield at 160 °C, 2 hours and 0.10 g catalyst loading. Molten salt hydrates (MSHs) pretreatment, particularly with lithium bromide (LiBr), significantly improved cellulose accessibility and hydrolysis efficiency and resulted in the highest LA yield of 24.3% compared to other MSHs. The optimization study focused on identifying the optimal conditions for LA synthesis from LiBr-pretreated OPEFB-based cellulose using Response Surface Methodology (RSM) revealed that the highest LA production (78.12%) was achieved at 200 °C, 4.5 hours and 10% catalyst loading. The kinetics model accurately predicted first-order irreversible reaction kinetics by combining experimental work and mathematical modeling. Its accuracy was confirmed by its correlation with experimental product distribution profiles, revealing

important reaction parameters, such as the activation energy for the conversion into LA, which was 59.01 - 102.45 kJ/mol. In conclusion, the applied approach presents a novel technique for converting abundant and cost-effective cellulosic biomass into LA.

Keywords: Sulfonated carbon metal catalyst, Levulinic acid, Oil palm biomass, Cellulose, Molten salt hydrates

SDG: GOAL 12: Responsible Consumption and Production



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**SINTESIS PEMANGKIN-PEMANGKIN LOGAM KARBON
TERSULFONAT DAN PENGOPTIMUMAN PENGELUARAN ASID
LEVULINIK DARIPADA SELULOSA TANDAN KOSONG KELAPA SAWIT**

Oleh

NOR AKHLISAH BINTI ZULKIPLI

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Asid levulinik (LA) ialah sebatian kimia blok binaan penting yang boleh dihasilkan daripada monosakarida dan polisakarida melalui tindak balas hidrolisis. Pada masa kini, sisa biojisim termasuk tandan buah kosong kelapa sawit (OPEFB) adalah sumber LA yang menarik kerana kandungan selulosanya yang tinggi. Oleh itu, kajian ini memberi tumpuan kepada pengeluaran LA daripada selulosa berasaskan OPEFB menggunakan pemangkin logam karbon tersulfonat. Pada bahagian pertama, pemangkin logam karbon tersulfonat telah disintesis dan dinilai prestasinya untuk menghasilkan LA. Antara nisbah pemangkin berasaskan besi (Fe) dan nikel (Ni) yang berbeza, Fe₇₅Ni yang merujuk kepada 25% Fe dan 75% Ni, menunjukkan aktiviti paling bagus untuk pengeluaran LA dan menghasilkan 10.51% daripada selulosa pada 180 °C selama 5 jam menggunakan 0.15 g pemangkin. Impregnasi seterusnya dengan pemuatan logam Fe₇₅Ni yang berbeza ke dalam pemangkin karbon tersulfonat membawa kepada peningkatan selanjutnya dalam sintesis LA. Pemangkin 15%FeNi/ACSO₃H (15% Fe₇₅Ni diimpregnasikan ke dalam ACSO₃H) mencapai LA

tertinggi iaitu 16.76%, berdasarkan hasil teori dari selulosa pada 180 °C, 5 jam, dan 0.15 g pemangkin. Pemangkin yang disintesis boleh digunakan semula untuk empat kitaran tindak balas. Pada bahagian kedua, pencirian pemangkin telah dilakukan menggunakan pembelauan sinar-X (XRD), penyahserapan ammonia yang diprogramkan suhu (TPD-NH₃), analisis termogravimetrik (TGA), penjerapan-penyahjerapan N₂, pendarfluor sinar-X (XRF), mikroskop elektron imbasan pancaran medan (FESEM), spektroskopi inframerah transformasi Fourier (FTIR) dan spektroskopi fotoelektron sinar-X (XPS). Kajian pencirian mengesahkan kejayaan penggabungan logam dalam pemangkin ACSO₃H. Selain itu, pemangkin 15%FeNi/ACSO₃H menunjukkan sifat yang baik seperti kawasan permukaan yang baik, nilai keasidan tinggi dan kestabilan terma yang baik yang memberi manfaat kepada sintesis LA. Walau bagaimanapun, daripada hasil yang diperoleh menggunakan selulosa, hasil LA adalah agak rendah menunjukkan keperluan untuk pengubahsuaian selulosa. Oleh itu, kajian ini memberi tumpuan kepada meningkatkan hasil LA daripada selulosa. Memandangkan matlamat utama kajian ini adalah untuk meneroka penggunaan selulosa daripada OPEFB, langkah awal memberi tumpuan kepada pengasingan selulosa daripada OPEFB. Pengasingan selulosa yang berjaya dicapai menggunakan teknik penyahwax, diikuti dengan rawatan dengan natrium hidroksida dan larutan natrium klorit, menghasilkan 8.98% LA berdasarkan hasil teori pada 160 °C, 2 jam dan 0.10 g pemangkin. Pra-rawatan garam cair terhidrat (MSHs), khususnya dengan litium bromida (LiBr), secara signifikan meningkatkan kebolehcapaian selulosa dan kecekapan hidrolisis dan menghasilkan hasil LA tertinggi iaitu 24.3% berbanding MSHs lain. Kajian pengoptimuman yang memberi tumpuan kepada mengenal pasti keadaan optimum untuk sintesis LA daripada selulosa berasaskan OPEFB yang di-rawat LiBr menggunakan Metodologi Permukaan

Respons (RSM) mendedahkan bahawa pengeluaran LA tertinggi (78.12%) dicapai pada 200 °C, 4.5 jam dan 10% pemangkin. Model kinetik dengan tepat meramalkan kinetik tindak balas tidak boleh balik tertib pertama dengan menggabungkan kerja eksperimen dan pemodelan matematik. Ketepatannya disahkan oleh hubungannya dengan profil pengagihan produk eksperimen, mendedahkan parameter tindak balas penting, seperti tenaga pengaktifan untuk penukaran kepada LA, iaitu 59.01 - 102.45 kJ/mol. Kesimpulannya, pendekatan yang diterapkan menunjukkan teknik novel untuk menukar biojisim selulosa yang melimpah dan kos efektif kepada LA.

Kata Kunci: Pemangkin logam karbon tersulfonat, Asid levulinik, Biojisim kelapa sawit, Selulosa, Hidrat garam cair

SDG: MATLAMAT 12: Penggunaan dan Pengeluaran Bertanggungjawab

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

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LIST OF ABBREVIATIONS

AC	Activated carbon
ACSO ₃ H	Sulfonated carbon
ADF	Acid detergent fiber
ADL	And acid detergent lignin
ANOVA	Analysis of variance
BET	Branauer emmett teller
BJH	Barrett–joyner–halenda
CCD	Central composite design
CI	Confidence interval
CrI	Crystallinity index
DoE	Design of experiments
DTG	Derivative thermogravimetric
EDX	Elemental dispersive spectroscopy
FA	Formic acid
Fe ₂ O ₃	Iron (II) oxide
FeCl ₃	Iron (III) chlroride
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared
GVL	γ-valerolactone
H ₂ SO ₄	Sulfuric acid
HCl	Hydrochloric acid
HMF	Hydroxymethylfurfural
HPLC	High performance liquid chromatography

ICDD	International Centre for Diffraction Data
ICP-OES	Inductively coupled plasma-organic element sampler
INTROP	Institute of Tropical Forestry and Forest Products
JCPDS	Joint Committee on powder Diffraction Standard
LA	Levulinic acid
LiBr	Lithium bromide
LiCl	Lithium chloride
MARDI	Malaysian Agriculture Research and Development Institute
MCC	Microcrystalline cellulose
MSHs	Molten salt hydrates
NaClO ₂	Sodium chlorite
NaOH	Sodium hydroxide
NDF	Neutral detergent fiber
Ni(NO ₃) ₂	Nickel nitrate
NiO	Nickel oxide
OPEFB	Oil palm empty fruit bunches
OPF	Oil palm frond
OPMF	Oil palm mesocarp fiber
OPS	Oil palm shell
OPT	Oil palm trunk
OVAT	One variable at a time
PI	Prediction interval
POME	Palm oil mill effluent
R ²	Coefficient of determination
RMSE	Root mean square error

RSM	Response surface methodology
SE	Standard error
SEM	Scanning electron microscopy
SO ₃ H	Sulfonic acid
SSE	Sum square errors
TGA	Thermogravimetric analysis
TPD-NH ₃	Ammonia-temperature programmed desorption
UPM	Universiti putra malaysia
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence Spectroscopy
ZnBr ₂	Zinc bromide
ZrC	Zirconium carbonate
ZnCl ₂	Zinc chloride
ZrO ₂	Zirconia

CHAPTER 1

INTRODUCTION

1.1 Background of study

The world is heavily reliant on fossil fuels for daily operations such as residential, industrial, transportation and commercial activity. In recent years, the utilization of fossil fuels for energy generation in industrial applications has been widely acknowledged as a significant contributor to global warming and environmental pollution thus garnering unfavorable attention (Lee *et al.*, 2022). By burning fossil fuels, hazardous chemicals such as volatile organic compounds, carbon dioxide, carbon monoxide and nitrogen dioxide are released into the atmosphere (Hossain *et al.*, 2016). This has prompted researchers to explore alternative resources that can be transformed into various products including biofuel, bioethanol and fine chemicals (Chin *et al.*, 2015). Concerns about these issues have prompted developments in renewable energy that can supply industrial items with sustainable energy (Tan *et al.*, 2017).

The utilization of biomass as a renewable energy source to produce biofuels and chemicals is gaining popularity due to the ability to maintain a carbon-neutral cycle, abundant availability and its lack of toxicity (Ji *et al.*, 2019). Biomass energy comes from plants, animals, and people. In the present context, lignocellulosic biomass is seen as a naturally occurring and renewable resource that has potential for the

production of second-generation bioenergy products, biofuels and chemicals (David *et al.*, 2018). Furthermore, lignocellulosic biomass is widely recognized as one of the most abundant and economically viable resources globally (Wei and Wu, 2017).

The primary crystalline structure in lignocellulosic materials is mostly attributed to the presence of cellulose which is known for its ordered arrangement and high stability. On the other hand, the amorphous area in lignocellulosic materials is mainly influenced by the presence of the highly branched lignin and hemicellulose (Abdul *et al.*, 2016). Both cellulose and hemicellulose can undergo conversion into monomeric sugars such as glucose and xylose. These monomer sugars can then be utilized for the production of valuable compounds, including levulinic acid (LA), ethanol and hydroxymethylfurfural (HMF) as shown in Figure 1.1.

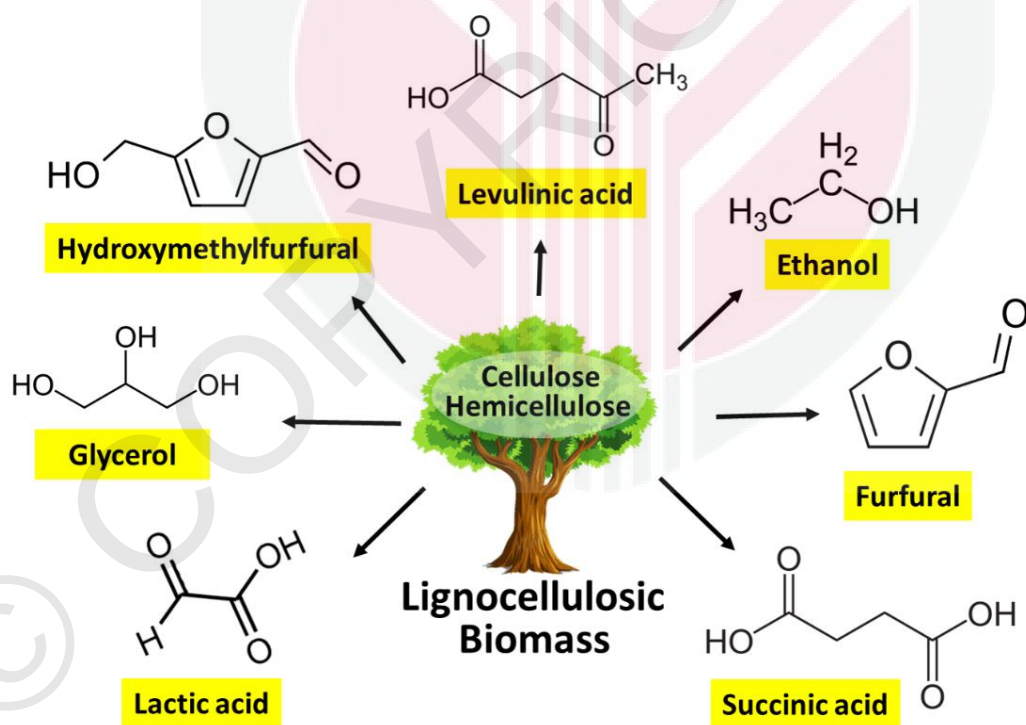


Figure 1.1: Chemicals derived from lignocellulosic biomass

The palm oil industry, which has grown significantly in tandem with the nation's economic expansion, dominates Malaysia's agricultural sector (Ahmad Farid *et al.*, 2020). Hence, a large quantity of oil palm biomass leftovers can be generated annually as a by-product in Malaysia's thriving oil palm sector. The biomass derived from palm oil plantations is commonly reused or recycled for many alternative purposes. The production of 1 kilogram of palm oil results in the generation of around 4 kilograms of dry biomass, with one-third of this biomass consisting of OPEFB (Chin *et al.*, 2015). In order to maintain economic growth, it is essential to establish the future driver for development in Malaysia, as palm oil production reaches a state of maturity. This entails exploring the conversion of oil palm biomass into more valuable commodities, specifically fine chemicals. LA, a value-added building block chemical has garnered significant attention as a highly promising platform molecule that can be derived from biomass sources (Mikola *et al.*, 2019). Cellulose as a major polymeric carbohydrate that exists in lignocellulosic biomass including oil palm biomass holds significant value as a primary source material for the production of LA.

Conventional methods to enhance LA conversion from biomass often involve the use of homogenous acid catalysts or mineral acids (Tiong *et al.*, 2018). Sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) are typically utilized for the synthesis of LA from a wide variety of biomass feedstock due to their low cost and strong catalytic activity for sequential hydrolysis and dehydration reactions. In certain applications, heterogeneous acid catalysts are preferred over homogeneous acid catalysts due to the fact that homogeneous acid catalysts are difficult to recycle properly after the reaction (Zhao *et al.*, 2021). A variety of heterogeneous catalysts have been developed, including solid acid catalysts such as Amberlyst 36 (Chen *et al.*, 2017), zeolite

(Pratama et al., 2020), niobium-based solid acids (Ding et al., 2014) and Sibunit carbon catalysts (Gromov et al., 2018). Incorporating carbon compounds containing $\text{-SO}_3\text{H}$ functional groups as heterogeneous acid catalysts has attracted attention in many recent studies. It has been reported that sulfonated carbons exhibited greater effectiveness in acid-catalyzed processes for utilization of biomass. These carbons possess notable attributes such as favorable mechanical and thermal stability, chemical inertness and low cost of materials (Zhang and Chen, 2016).

1.2 Problem statements

LA has received significant attention for its potential use in various industrial sectors such as biofuels, cosmetics, lubricants, chemical solvents, and plasticizers (Azlan *et al.*, 2022a). Mineral acids and metal salts are typically utilized as catalysts for the synthesis of LA. The main limitations of homogeneous acid catalysts are equipment corrosion and environmental pollution since they cannot be reused or recycled, hence posing challenges in cost reduction within industrial contexts (Shao *et al.*, 2021). Homogeneous alkaline catalysts such as sodium hydroxide are also not recommended since the hexose conversion process typically involves acid catalysts. Furthermore, acids would be required to neutralize the alkaline catalysts dissolved in the fructose or glucose solution (Kang *et al.*, 2018). As a result, much effort has been expended in creating heterogeneous and cost-effective catalysts for the conversion of biomass-derived feedstock into LA, particularly on solid acid catalysts. For LA production, the use of catalysts with high total acidity and excellent thermal stability properties is a primary concern for achieving high efficiency in the conversion reaction. In this study, metal catalysts were introduced onto a sulfonated carbon catalyst to assess its potential

on LA production and their properties. To date, there aren't much research that combines metals with sulfonated carbon catalysts to synthesize LA. As an innovative method for LA production, a number of metal modified carbon catalysts were synthesized to demonstrate their catalytic activity as a novel strategy for LA synthesis.

The commercialization of LA has encountered significant challenges, primarily stemming from the bottlenecks related to the cost of raw materials. Techno-economic analysis of LA production performed by many researchers has demonstrated that the consumption of low cost raw materials is essential for ensuring its sustainability, as the cost of raw feedstock constitutes the biggest percentages (59-75%) of the total operating cost (Maiti et al., 2018). Traditionally, LA is produced through the petrochemical process involving the hydrolysis and hydrogenation of furfuryl alcohol or maleic anhydride. However, this method is complex and cost-intensive, resulting in a high market price of LA, approximately US\$10/kg (Mthembu et al., 2023). There are still many sources of lignocellulosic biomass rich in cellulose which is low cost that remain unexplored as a potential raw material source to produce LA. The palm oil industry in Malaysia produces an annual average of 95.3 million tons of biomass waste and due to inappropriate waste management practices, these wastes contribute to harmful effects on the environment (Parthasarathy et al., 2024). Numerous studies have demonstrated that oil palm biomass, such as OPEFB is classified as lignocellulosic biomass due to its predominant composition of cellulose, which is believed to have a significant potential as a raw material for LA synthesis. Hence, in this study OPEFB is utilized to obtain cellulose (called OPEFB-based cellulose) for the production of LA.

A complex network of intra- and inter-chain hydrogen bonds exists between cellulose chains, making cellulose tough to breakdown (Deng *et al.*, 2015). Since there is only a small available contact area in the solid acid catalyst for an effective hydrolysis of cellulose, the reaction has a weak catalytic effect. Hence, the dissolution of cellulose is an essential pretreatment step that must take place in order to maximize the functionality of cellulose and expand its utilization scope for biomass conversion. Several molten salt hydrates (MSHs) such as lithium bromide (LiBr), lithium chloride (LiCl) and zinc chloride (ZnCl_2) were chosen in this research to dissolve the cellulose as these MSHs exhibited a remarkable ability to solubilize cellulose according to the recent findings. The mechanisms of cellulose dissolution in MSHs involve defibrillation, deconstruction and depolymerization (Huang *et al.*, 2022). However, high-temperature dissolution above 100 °C is needed for protonic acid to effectively attack the glycosidic linkages of cellulose macromolecular chains during cellulose depolymerization which would increase the cost of operation. The discovery of an efficient pretreatment method that excludes the depolymerization of cellulose would provide more benefits. Besides, there is no study on the non-dissolving pretreatment of OPEFB-based cellulose using MSHs at room temperature. Therefore, a novel strategy was developed by applying a non-dissolving pretreatment of OPEFB-based cellulose in MSHs at room temperature.

Furthermore, no attempt has been made to study the optimization of LA production from OPEFB-based cellulose via acid hydrolysis reaction using sulfonated carbon metal catalyst in order to improve LA content and productivity. Optimization of the factors that influence the condition of the acid hydrolysis process is predicted to increase the efficiency and yield of LA synthesis. To date, there are limited reports on

the kinetics study of the acid hydrolysis reaction for the synthesis of LA from cellulose using a heterogeneous catalyst. Hence, very little information is available to understand the reaction pathways for this reaction. The information from the kinetics study will provide insights on the mechanism of OPEFB-based cellulose conversion to LA using sulfonated carbon metal catalyst.

1.3 Objectives

The overall objective of this study is to synthesize LA from OPEFB-based cellulose by using the best sulfonated carbon metal catalyst with a focus on enhancing the hydrolysis process and its behavior. Specific objectives are listed as follows:

1. To examine the performance of sulfonated carbon metal catalysts for production of LA from cellulose.
2. To evaluate the physical and chemical properties of the sulfonated carbon metal catalysts for hydrolysis reactions.
3. To assess the optimum process parameters in the catalytic hydrolysis of cellulose from OPEFB using selected sulfonated carbon metal catalyst.
4. To develop a kinetics model for the hydrolysis of OPEFB-based cellulose into LA using selected sulfonated carbon metal catalyst.

1.4 Significance of research

This research utilized sulfonated carbon metal catalyst (iron and nickel) as benign catalyst for the production of LA from OPEFB-based cellulose. The production of this catalyst as a new carbon-based catalyst is an alternative to homogenous acid catalysts such as H_2SO_4 in the hydrolysis reaction. Sulfonated carbon metal catalysts with good

catalytic properties such as high acidity and high surface area were successfully produced to enhance the reaction towards high production of LA. The optimum synthesis parameters obtained from the Response Surface Methodology (RSM) study on the acid hydrolysis reaction can be used to produce LA more efficiently. This study is also particularly useful as baseline research when using cellulose from other oil palm biomass wastes and for upscaling processes. In addition, the kinetics and thermodynamic parameters obtained from this study can be used to describe the mechanism of acid hydrolysis for LA production under the influence of different reaction temperatures. Based on the overall results, the selected sulfonated carbon metal catalyst has high potential as a super acid carbon-based catalyst in the synthesis of LA.

1.5 Scope of work

The scopes of work in the study on the hydrolysis of cellulose from OPEFB for LA production using a sulfonated carbon metal catalyst are as follows.

- The preparation of sulfonated carbon metal catalysts followed by several steps which are calcination, sulfonation and hydrothermal processes. The ideal ratio of iron (Fe) to nickel (Ni) was investigated by analyzing different loadings of these elements, ranging from 25 wt.% to 100 wt.%. Subsequently, different loadings of the Fe-Ni catalyst (5 wt.% to 20 wt.%) were impregnated into sulfonated carbon catalysts using the selected ratio of Fe and Ni. These catalysts were evaluated based on the yield of LA.
- For physical and chemical tests on catalysts, several characterization techniques such as surface area and porosity (BET), phase and chemical composition (XRD, XRF, ICP-OES), acid site properties (TPD-NH₃), surface morphology (FESEM-EDX), surface analysis of elemental composition and chemical state (XPS), thermal behaviour (TGA) and the existence of functional groups (FTIR) were carried out.
- Preparation of cellulose from OPEFB as raw material for production of LA was done. The process started with the preparation of OPEFB waste by washing,

drying and mechanical treatment such as grinding and sieving. The steps were followed by dewaxing and delignification to extract cellulose from this biomass. Several MSHs were used for non-dissolving pretreatment of cellulose to maximize the functionality of cellulose for the synthesis of LA.

- Effects of process conditions on conversion of cellulose into LA were studied using Response Surface Methodology (RSM). Parameters involved in this study were effect of catalyst amount, effect of temperature and effect of reaction time. In all reactions, the selected sulfonated carbon catalyst was used.
- Kinetics of a hydrolysis reaction under optimized operating conditions was carried out to investigate the order and rate of reaction. The temperature effect from the Arrhenius equation was also determined. The models were validated using the linear plot of the kinetic models and the parity plot of the predicted data and actual data.

1.6 Thesis outline

Chapter 1 is the introductory chapter which provides the background of the study focusing on the significance of energy generation, chemical production and oil palm biomass waste. This chapter also introduces the background, problem statement, research objectives, scope, and significance of the study. It also outlines the organization of the thesis. Chapter 2 presents the literature review of a wide process overview, synthesis and analysis as accounted by previous authors related to previous works. This chapter provides a review of relevant literature related to lignocellulosic biomass, LA production, catalysts for hydrolysis, characterization techniques and kinetic modeling. All materials and methods are discussed in Chapter 3. This chapter also details the catalyst preparation and characterization, biomass pretreatment, product analysis, experimental design and kinetic study procedures used in this research. Chapter 4 presents and discusses the key results obtained from the LA production, catalyst characterization, process optimization, and kinetic modeling experiments. Finally, Chapter 5 summarizes the major conclusions from this work,

highlights the significance and limitations, and provides recommendations for future research. The thesis also contains a complete list of references and supporting appendices. In summary, Chapter 1 introduces the research and orientations the reader, Chapter 2 reviews background knowledge, Chapter 3 explains the methodology, Chapter 4 analyzes and discusses the results, and Chapter 5 concludes the thesis and suggests future work. The organization provides a logical flow to guide the reader through the thesis.



CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter covers literature reviews on LA, the potential of oil palm biomass as raw materials and the roles of heterogeneous catalysts. In addition, the techniques of producing cellulose from OPEFB for the production of LA are also discussed. The discussion also includes the topic of optimization by studying several parameters, as well as kinetic and thermodynamic studies.

2.2 Levulinic Acid (LA)

LA is a C5 chemical and also known as γ -keto-valeric acid, 4-oxopentanoic acid, α -ketovaleric acid and β -acetylpropionic acid (Ya'aini *et al.*, 2012). LA is a colorless liquid with a crystalline structure that can dissolve in organic or inorganic solvents such as water, esters, acetaldehyde and ethanol (Pereira Santana *et al.*, 2022). Table 2.1 shows the physical properties of LA. LA has α -hydrogen and two highly reactive carbonyl and carboxyl groups as shown in Figure 2.1, which make it very attractive towards the chemical transformations and reagents (Badgujar *et al.*, 2019). These reactive characteristics make LA among the most promising novel platform chemicals that serves as an intermediate for the production of plasticizers, pharmaceuticals, additives, synthetic rubbers and bioenergy (Bounoukta *et al.*, 2022). LA can perform

a wide range of reactions such as redox, hydrolysis, chiral synthesis, esterification, polymerization, substitution, and solvent extraction (Zhang *et al.*, 2022).

Table 2.1: Physical properties of LA

Physical properties item	Values
Color	White
Molecular Weight	116.2 g/mol
pKa	4.59
Solubility (water and polar organic solvents)	Soluble
Density	1.14 kg/m ³
Boiling point	246 °C
Melting point	57 °C
Surface tension (25 1C)	39.7 dyn cm ⁻¹
Refractive index (20 1C)	1.447
Heat of formation	-2417 kJ mol ⁻¹
Heat of fusion	79.8 kJ mol ⁻¹
Heat of vaporization	74.4 kJ mol ⁻¹

(Source: Antonetti *et al.*, 2016)

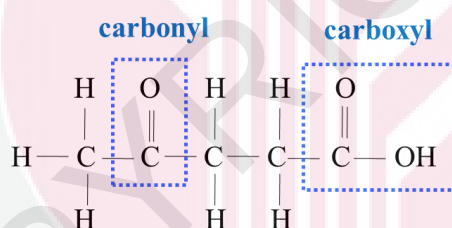


Figure 2.1: Molecular structure of LA (C₅H₈O₃)

2.2.1 General mechanism

Previous studies have reported three techniques for producing LA. Traditionally, LA is produced using the petrochemical method of hydrolysis and hydrogenation of furfuryl alcohol or maleic anhydride (Mthembu *et al.*, 2023). Nevertheless, this traditional approach is laborious and expensive, resulting in a slightly expensive market price of US\$10/kg for LA. Techno-economic assessments indicate that raw

materials represent the major components of the production cost (Rackemann and Doherty, 2011), hence, it is costly to employ the process that uses maleic anhydride or furfuryl alcohol as a raw material.

Alternatively, the potential of using furfuryl alcohol from cheaper sources, such as biomass can also be explored. Two main components of biomass residues that can be converted into LA are cellulose and hemicellulose as shown in Figure 2.2. Furfural, which is derived from hemicellulose, can be converted to furfuryl alcohol which is then converted into LA. However, production of furfuryl alcohol involved hydrogenation of furfural, so a different catalyst is needed for this route (Yadav *et al.*, 2017). However, the catalytic depolymerization of furfuryl alcohol has strong reactivity but leads to a relatively low selectivity of LA due to the presence of undesirable byproducts (Lopes *et al.*, 2020b).

The third approach addressing several reaction mechanisms such as conversion from cellulose into sugars, followed by dehydration into hydroxymethylfurfural (HMF) and lastly, rehydration to produce LA (Kang and Yu, 2018). The conversion of renewable biomass into LA has gained significant attention both in academic research and from the industry. Hence, this study only focused on the production of LA from cellulose which is the third approach.

Cellulose can be converted into hexose sugars such as glucose and fructose. According to Huber *et al.* (2006), during the initial phase of cellulose hydrolysis, it is necessary to break the glucoside bonds between α -D-glucose units. The cleavage mechanism of the C-O-C bond in cellulose involves the protonation of glucoside bonds. The proton

has the option to either target the cyclic oxygen or the oxygen bond connecting two glucose molecules. In acidic conditions, glucose hydrates to hydroxymethylfurfural (HMF), and subsequently it rehydrates to LA as shown in Figure 2.2 (Pradipta *et al.*, 2019). Hexose sugar is converted to LA by hydrolyzing HMF to yield equal amounts of formic acid (FA) and LA (Rackemann and Doherty, 2013). LA has so far been synthesized utilizing a chemical process catalyzed by acid (H^+), unlike other high-value biomass derivatives that are derived through biological pathways such as fermentation (Kumar *et al.*, 2021).

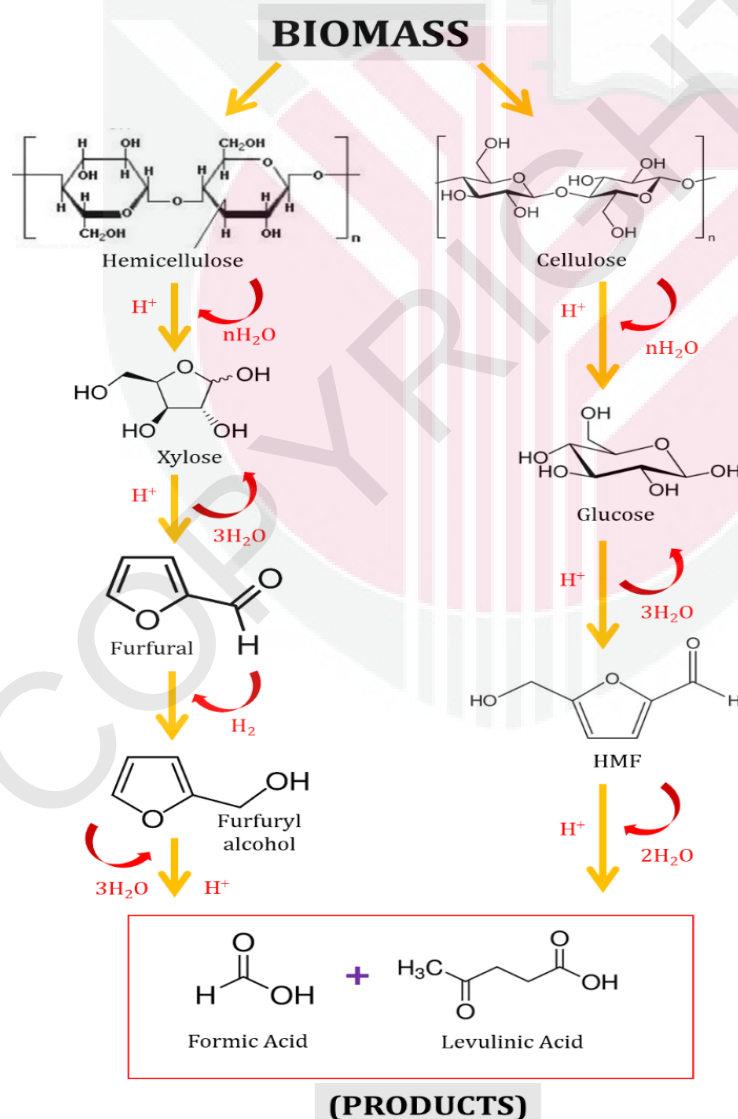


Figure 2.2: Mechanism for LA production from biomass

2.3 Raw materials for LA production

Prior researches suggest that the production of LA are influenced by the type of raw materials used (Leal Silva *et al.*, 2018). LA can be produced through the synthesis of several raw materials, including polysaccharides, monosaccharides and precursors like HMF and furfural. Besides, LA can also be produced from renewable resources such as starch-rich waste and lignocellulosic biomass (Morone *et al.*, 2015). The production of LA using these materials from previous studies will be discussed below.

2.3.1 LA from renewable resources

The biomass utilization specifically lignocellulosic or second-generation biomass as a renewable and environmentally friendly source of fuels and valuable chemical production has been a significant focus among the researchers (Taghavi *et al.*, 2022a). Lignocellulosic biomass sources commonly include agricultural crops, cellulosic mass, wood, food processing waste and garden residues (Akram *et al.*, 2023). The main components of lignocellulosic biomass are cellulose and hemicellulose as primary polysaccharides. The composition of these major components and biomass structure varies depending on the nature of the biomass for example, the type of biomass, part of the plant harvesting time and growth conditions (Sidana and Yadav, 2022). These materials can be converted into monosaccharides or sugars and consequently into high value-added products as shown in Figure 2.3 such as LA, FA, levulinate esters, acetic acid and ferulic acid (Junior *et al.*, 2021).

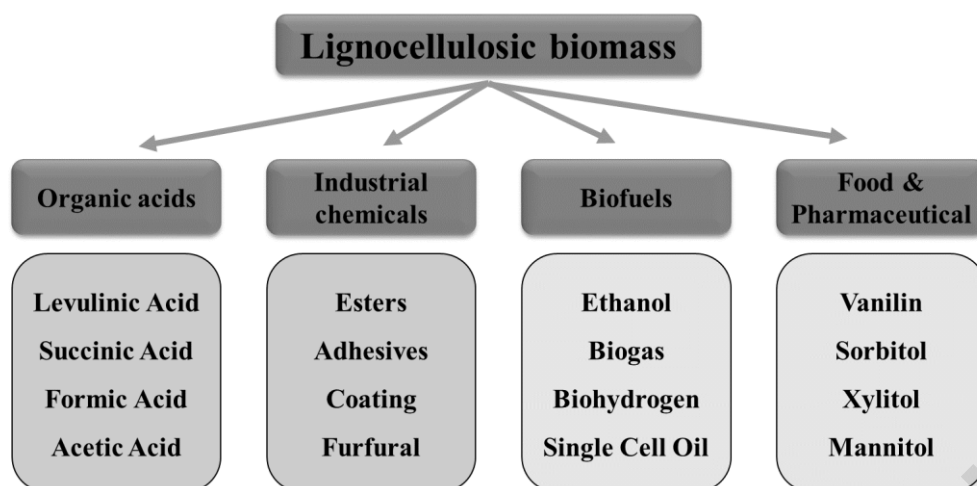


Figure 2.3: High value-added products produced from lignocellulosic biomass

Renewable feedstock is emerging as the current raw material for LA production, primarily because of its plentiful availability and eco-friendly characteristics (Morone *et al.*, 2015). There were several studies conducted to evaluate the performance of biomasses as raw materials in the production of LA, as shown in Table 2.2. The study conducted by Galletti *et al.* (2012) demonstrated two experiments that involved different types of biomass but were performed under identical reaction conditions. The results showed a 9% variation in the yield of LA, indicating that the choice of raw materials significantly influences the LA production. Yan *et al.* (2008) also utilized different biomasses in their research and the result showed 1% variation in LA yield even though the conditions are similar. This discrepancy in yield could potentially be attributed to variations in the cellulose content of the different biomass samples.

Table 2.2: Production of LA from biomass

Reference	Biomass	Catalyst	Temp. (°C)	Times (min)	LA yield	
					Based on Weight%	Based on theoretical yield%
Galletti <i>et al.</i> (2012)	Olive tree pruning	37% HCl	200	60	20.0	-
Galletti <i>et al.</i> (2012)	Poplar sawdust	37% HCl	200	60	29.0	-
Girisuta <i>et al.</i> (2013)	Sugarcane bagasse	H ₂ SO ₄ (0.55 M)	150	8 h	63.0	-
Girisuta <i>et al.</i> (2008)	Water hyacinth	1 M H ₂ SO ₄	175	30	53.0	-
Hartono <i>et al.</i> (2016)	Corn cob	Acid modified zeolites	200	60	0.01	-
Kang and Yu (2015)	Eucalyptus wood chips	H ₂ SO ₄	180	90	57.0	-
Khan <i>et al.</i> (2018)	Bamboo	[C ₄ (MIM) ₄] [(2H ₂ SO ₄)(H ₂ SO ₄) ₄]	110	1	13.6	28.6
Liu <i>et al.</i> (2018)	Straw	[C ₃ SO ₃ HMIM][HSO ₄]	180	1.5	5.30	24.6
Ya'Aini <i>et al.</i> (2013)	Kenaf	CrCl ₃ /HY	177	2.3	17.0	22.7
Yan <i>et al.</i> (2008)	Bagasse	4.45 wt% HCl	220	45	23.0	-
Yan <i>et al.</i> (2008)	Paddy straw	4.45 wt% HCl	220	45	23.0	-
Zhi <i>et al.</i> (2015)	Corn stalk	FeCl ₃	230	10	49.0	-
Zheng <i>et al.</i> (2017)	Corn stalk	FeCl ₃	180	40	48.9	-

Note: " " = not available

Establishing a sustainable method for producing LA from biomass is crucial. One of the benefits of one-pot synthesis is its ability to minimize energy and time required to synthesize LA, hence reducing the overall cost of the process. However, a limitation is that the lignin and hemicellulose components are not separated for individual utilization, despite the fact that the combined solids are assessed for their potential as a fuel source through combustion (Schmidt *et al.*, 2017). Hence, this study focused on the extraction of cellulose from biomass first before being introduced into a one-pot synthesis reaction.

2.3.2 LA from oil palm biomass waste

The palm oil sector in Malaysia produces approximately 80 million dry tons of lignocellulosic biomass annually (Sharip *et al.*, 2016). OPEFB, oil palm mesocarp fiber (OPMF), oil palm frond (OPF), oil palm trunk (OPT), oil palm shell (OPS) and palm oil mill effluent (POME) are the six types of biomass generated from the oil palm industry. The main biomass waste from the palm oil industry is OPEFB fiber, which is produced after the palm oil fruitlets are stripped from fruit bunches and represents about 20% of the weight of fresh fruit (Fatriasari *et al.*, 2017). The subsequent processes to produce crude palm oil generate other oil palm wastes, comprised of 6% of OPS and 15% of OPMF (Liew *et al.*, 2018). Indonesia and Malaysia annually generate 25.9 and 19.8 million tons of OPEFB respectively (Tan *et al.*, 2016).

The primary components of the oil palm biomass consist mostly of cellulose, hemicellulose and lignin, as shown in Table 2.3. These biomass wastes have gained massive attention as feedstocks to generate high value added chemicals due to their

lignocellulosic contents. As shown in Table 2.3, OPEFB contains a high amount of cellulose, followed by the oil palm frond. These OPEFB typically consist of approximately 39.9 to 55.8% cellulose by weight. Cellulose has high potential for conversion into sugars such as glucose and fructose. These sugars then be served as the precursors for the production of high added-value chemicals such as LA and FA. Oil palm biomasses reveal promising potential for production of LA due to their substantial cellulose content.

Table 2.3: Primary components in oil palm biomass

Biomass	Composition (%)			References
	Cellulose	Hemicellulose	Lignin	
OPEFB	39.9-55.8	13.3-29.8	21.4-28.9	Ajayi <i>et al.</i> (2023); Harahap <i>et al.</i> (2020a); Hidayah and Wusko, (2020); Masran <i>et al.</i> (2020); Risanto <i>et al.</i> (2023); Saengsen <i>et al.</i> (2022); Zarin <i>et al.</i> (2022)
OPMF	12-42.8	17.7-31.8	16.7-30.0	Azlan <i>et al.</i> (2022b); Henrique <i>et al.</i> (2020a); Jafri <i>et al.</i> (2021); Saepoo <i>et al.</i> (2023); Shrivastava <i>et al.</i> (2020);
OPS	20.8-37.9	11.5-23.8	38.2-50.7	Alfatah <i>et al.</i> (2022); Budiman <i>et al.</i> (2019); Ma <i>et al.</i> (2018); Ameen <i>et al.</i> (2022); Shrivastava <i>et al.</i> (2020)
OPT	26.6-46.8	17.8-41.6	12.9-35.9	Shrivastava <i>et al.</i> (2020); Thamsee <i>et al.</i> (2018); Pulingam <i>et al.</i> (2022); Wilaitup <i>et al.</i> (2022); Terry <i>et al.</i> (2023); Qureshi <i>et al.</i> (2021)
OPF	20.6-54.4	17.1-25.6	8.96-62.3	Zarin <i>et al.</i> (2022); Ajayi <i>et al.</i> (2022); Shrivastava <i>et al.</i> (2020); Ameen <i>et al.</i> (2022); Ong <i>et al.</i> (2021); Tnah <i>et al.</i> (2022)

In the past few years, LA has been studied extensively and mostly derived from oil palm biomasses by acid hydrolysis as shown in Table 2.4. Studies by Ramli and Amin (2014), Tiong *et al.* (2019) and Zarin *et al.* (2022) compared the yield of LA under the same condition by using different types of oil palm biomasses. In the research by Tiong *et al.* (2019), OPEFB yielded 9.3 wt% LA, which is higher than OPMF (7.3 wt.%).

Meanwhile, a comparison between OPF and OPEFB was conducted by Ramli and Amin (2014) and the outcome showed OPF produced a slightly higher amount of LA (11.1 wt.%) compared to OPEFB (9.3 wt.%). However, only a 2% variation in the yield of LA from both raw materials. Furthermore, a study by Zarin *et al.* (2022) demonstrated a similar yield of LA from both OPF and OPEFB (15.0 wt.%). Based on the high yield of LA produced by OPEFB in the previous studies, OPEFB was selected as the raw material for producing LA in this study.

The yields of LA from oil palm biomass wastes based on previous studies were generally very low when used heterogeneous catalysts as shown in Table 2.4. The highest LA yield was produced from oil palm biomass waste using a heterogeneous catalyst at only 19.6 wt.%, reported by Ramli and Amin (2015a), even with optimized process conditions. A study by Ramli and Amin (2017) and Tiong *et al.* (2018) managed to obtain a high yield of LA when using heterogeneous catalysts because their studies were performed in ionic liquids (ILs) medium. ILs have been recognized for their remarkable function as reaction solvents, particularly in the dissolution of polysaccharides (Yin *et al.*, 2021). Furthermore, it is commonly linked to that the presence of lignin in the biomass which acts as a “glue” that connects cellulose and hemicellulose, hence restricting the production of LA (Rezania *et al.*, 2020). Several pretreatments were performed to improve the yield of products by removing lignin from the biomass (Muranaka *et al.*, 2014). The application of pretreatments significantly decreased the resistance of the biomass after delignification (Chen *et al.*, 2017). Therefore, this study also conducted several treatment methods to remove lignin and assessed its effect on LA yield. The review and discussion on pretreatments is discussed in Section 2.6.

Table 2.4: Production of LA from oil palm biomass by acid hydrolysis

Reference	Biomass	Catalyst	Temp. (°C)	Reaction time (h)	LA yield	
					Based on weight %	Based on theoretical yield %
Chin <i>et al.</i> (2015)	OPEFB	0.57N H ₂ SO ₄	185.9	3.3	53.9	-
Gozan <i>et al.</i> (2018)	OPEFB	1M H ₂ SO ₄	170.0	1.5	52.1	-
Noparat <i>et al.</i> (2015)	OPT	3% H ₂ SO ₄	180.0	0.6	2.5	-
Ramli <i>et al.</i> (2014)	OPEFB	8.1% H ₂ SO ₄	165.5	0.7	31.6	-
Ramli and Amin (2017)	OPF	7.2g [SMIM][FeCl ₄]	154.4	3.7	24.8	-
Ramli and Amin (2015a)	OPF	1.13g Fe/HY zeolite	181.7	7.7	19.6	-
Ramli and Amin (2014)	OPEFB	FeCl ₃ /HY zeolite	120.0	6.0	9.3	27.1
Ramli and Amin (2014)	OPF	FeCl ₃ /HY zeolite	120.0	6.0	11.1	32.1
Tiong <i>et al.</i> (2018)	OPMF	Bronsted-Lewis acidic ILs	175.0	4.5	85.0	-
Tiong <i>et al.</i> (2019)	OPMF	InCl ₃ -[HMIM][HSO ₄]	180.0	6.0	7.3	-
Tiong <i>et al.</i> (2019)	OPEFB	InCl ₃ -[HMIM][HSO ₄]	180.0	6.0	9.3	-
Zarin <i>et al.</i> (2022)	OPF	Zeolite immobilized ionic liquid	180.0	6.0	15.0	-
Zarin <i>et al.</i> (2022)	OPEFB	Zeolite immobilized ionic liquid	180.0	6.0	15.0	-

Note: "-" = not available

2.3.3 LA from cellulose

Most of the literature on cellulose focused on the synthesis of a specific platform chemical from a particular type of lignocellulosic biomass. However, a major challenge in the effective utilization of lignocellulosic biomass is the simultaneous conversion of both cellulose and hemicellulose (Sweygers *et al.*, 2018b). Furthermore, there has been a growing scientific interest in the direct conversion of cellulose into HMF and LA in recent years (Mukherjee *et al.*, 2015). Hence, many previous studies were focused only on the production of LA from cellulose. Cellulose can also be extracted from biomass before subjected to the reaction for LA production as executed by Chen *et al.*, (2022).

The mechanism for conversion of cellulose into LA can be seen in Figure 2.4 which involves several steps: (1) the process of breaking down cellulose as polysaccharides into glucose with the presence of an acid; (2) the conversion of glucose into HMF by dehydration with the assistance of an acid; and (3) the conversion of HMF back into LA through rehydration, facilitated by an acid.

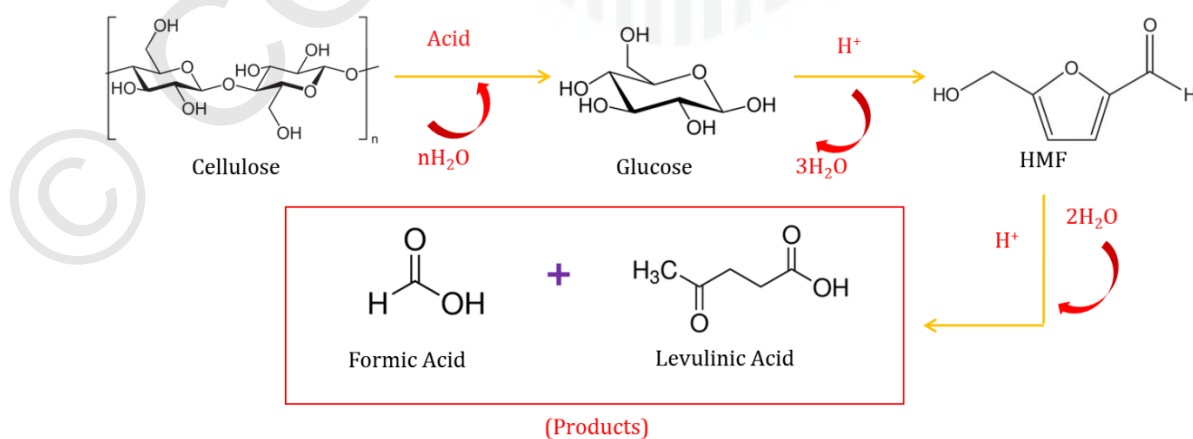


Figure 2.4: Mechanism of LA production from cellulose

Table 2.5 shows the yield of LA from the conversion of cellulose using commercial cellulose. Higher LA yields were generated compared to the amount of LA from biomass or oil palm biomass as discussed before. The research conducted by Bond *et al.* (2014) discovered that the most significant amount of LA was yielded through the hydrolysis of cellulose using H₂SO₄ as a homogenous catalyst at a temperature of 200 °C for a duration of 45 minutes. This process resulted in a LA yield that accounted for 75.5% of the maximum theoretical content of LA. Li *et al.* (2020) managed to obtain 70% LA based on theoretical yield from cellulose by using Brønsted acid phosphotungstic acid as heterogeneous catalyst. The theoretical yield is the maximum amount of LA that could be produced from the given amounts of raw materials. Some researchers also reported the yield of LA based on weight percentage. The results based on percentage by weight show that the highest LA yield was collected from the study by Shi *et al.* (2021b) which was 66.5 wt.% LA.

The list of various catalysts and reaction conditions that are applied in the synthesis of LA also can be seen in Table 2.5. The differences and comparison are elaborated in the section of "Factors Influencing LA Synthesis" which covers the crucial elements that influence the yield of LA and evaluate the performance of the catalyst such as the reaction duration and temperature, solid-liquid ratio and the dosage of catalyst. The type of catalysts applied to generate LA also is reviewed.

Table 2.5: Production of LA from commercial cellulose

Raw material	Catalyst	Tem p. (°C)	Reaction time	LA yield		Reference
				Based on Weight %	Based on Theoretical yield %	
Cellulose	CrCl ₃	200	5 min	40.0	-	Boonyakarn <i>et al.</i> (2019)
Cellulose	Sulfonated catalyst (PLSA4-550)	180	3 h	42.3	-	Chen <i>et al.</i> (2022)
Cellulose	Sulfonated catalyst (PLSA4-550)	190	3 h	55.0	-	Chen <i>et al.</i> (2022)
Cellulose	HCl	180	3 h	50.8	-	Ma <i>et al.</i> (2021)
Cellulose	CrCl ₃	180	2 h	33.0	-	Peng <i>et al.</i> (2010)
Cellulose	Phosphoric acid	200	2 h	0.53	0.82	Muranaka <i>et al.</i> (2014)
Cellulose	Brønsted acid phosphotungstic acid	195	2 h	-	70.7	Li <i>et al.</i> (2020)
Cellulose	NbOPO ₄ /HZSM-5	175	1 h	-	57.0	Wang <i>et al.</i> (2020)
Cellulose	[BSim]Br	180	10 min	66.5	-	Shi <i>et al.</i> (2021b)
Cellulose	H ₂ SO ₄	150	2 h	-	60.0	Girisuta <i>et al.</i> (2007)
Cellulose	H ₂ SO ₄	160	1 h	-	60.0	Morales-de-la-Rosa <i>et al.</i> (2014)
Cellulose	[HO ₃ S-(CH ₂) ₃ -py]Cl-FeCl ₃	180	10 h	-	49.1	Cheng <i>et al.</i> (2022)
Cellulose	H ₂ SO ₄	200	45 min	-	75.5	Bond <i>et al.</i> (2014)
Cellulose	Lignin-based solid acid catalyst	185	2 h	48.5	-	Han <i>et al.</i> (2019)

Note: '-' = not available

2.4 Factor affecting LA synthesis

The performance of the reaction for the production of LA is affected by several factors including temperature, reaction time, solid-liquid ratio, type of catalysts and catalyst dosage. These factors are reviewed in this section except the type of catalyst which is discussed in the other section (Section 2.5). The main focus was on selecting the most favorable reaction conditions to optimize the production of LA.

2.4.1 Effect of temperature

Extensive research has been carried out to evaluate the impact of reaction temperature on the production of LA utilizing various types of feedstock. Peng *et al.* (2010) conducted studies to examine the impact of reaction temperature on the conversion of cellulose into LA. The experiments were carried out within the temperature range of 180-220 °C. The temperature imposes a substantial influence on the yield of LA. Upon increasing the reaction temperature beyond 200 °C, the LA yield declined and the presence of intermediates such as glucose and HMF became undetectable. Higher temperatures can accelerate the speed of chemical processes. However, concurrent unwanted side reactions such as the generation of humins also appear. Consequently, elevated temperatures are detrimental to the progress of the reaction and temperatures hinder the rate of reaction. Similar findings about the optimal temperature have been published by Szabolcs *et al.* (2013) (for cellobiose) and Shen and Wyman (2012) (for cellulose).

According to Jeong *et al.* (2018), the LA concentration increased progressively from 150 °C until it finally reached a maximum at 190 °C, resulting in a yield of 4.62 g/100 g biomass. They discovered that the LA concentration was greater than prior studies conducted at a lower temperature (170 °C) due to various factors, including the catalyst's effectiveness in terms of acid site quantity. Their investigation additionally discovered that the LA concentration was reduced to 3.93 g/100 g biomass at a temperature of 210 °C as a result of an excessive hydrolysis reaction and the generation of humins. In a study conducted by Liu *et al.* (2019), it was observed that when the temperature reached 180 °C, the glucose and HMF yields decreased from 12.74% to 10.85% and from 1.47% to 0%, respectively, while LA yield increased from 51.0% to 67.51%. However, the conversion of glucose to isomers and the transformation of HMF to LA may be restricted when the operating temperature exceeds the optimal level. This is because, at higher temperatures, there is a greater tendency for cross-polymerization to occur, resulting in the formation of by-products such as humins instead of the desired glucose and HMF conversions. Zhi *et al.* (2015) discovered that elevated temperatures can decrease the reaction time in the conversion of corn stalks catalyzed by FeCl₃. However, the maximum yield of LA (achieved with a 0.5 mol/L FeCl₃ solution) remained constant regardless of temperature. This suggests that increasing the temperature speeds up the rate of reaction without impacting the chemical equilibrium.

In conclusion, high temperatures can increase the reaction rate and reduce the activation energy gap. Furthermore, elevated temperature may improve the solubility of biomass or cellulose and enhance the availability of dissolved cellulose to the catalytic active sites (Zuo *et al.*, 2014). Simultaneously, excessively elevated

temperature could cause subsequent reactions, leading to the formation of side products such as humin, and reduced yield of the main product, LA. Therefore, it is necessary to maintain the optimal temperature. Typically, the production of LA from biomass is enhanced when temperatures increase within the range of 170°–230 °C. Numerous investigations have identified an optimal temperature of 200°–220 °C (Rackemann and Doherty, 2011). Hence, in this study, the effect of temperature was examined within the suggested range to improve the yield of LA and find the optimal temperature.

2.4.2 Effect of reaction time

The conversion of biomass into LA is also significantly influenced by reaction time. Yuan *et al.*, (2016) discovered that the duration of hydrolysis is a crucial factor in the acid-catalyzed conversion process of *Pennisetum alopecuroides* for the synthesis of LA and the amount of LA obtained grows in a linear manner during the initial phase of the reaction as the reaction time extends. Comparable findings were also noted in the conversion of *Gelidium amansii* into LA by Jeong and Park (2010). Yan *et al.* (2008) investigated the impact of time on LA production using biomass and found that a short reaction time of 15 minutes did not initiate the hydrolysis process. Additionally, they observed variations in the reaction kinetics, which could be attributed to differences in content of cellulose and intrinsic composition structure. Furthermore, it was noted from their research that a reaction duration of 45 minutes resulted in the occurrence of side reactions, as the extended reaction time and elevated temperature caused the degradation of products. Meanwhile, Li *et al.* (2014) discovered that extending the reaction time beyond 1 hour resulted in the involvement of lignin

degradation. A study conducted by Ya'aini *et al.* (2012) also showed that reaction time significantly influenced the conversion of glucose and formation of LA when optimized using Response Surface Methodology, however, humin as a carbonaceous residue, may be produced as a side product when high temperatures and prolonged reaction times were utilized in the process operations.

Long reaction times and harsher reaction conditions are needed to generate good yields when solid feedstocks such as cellulose or biomass are utilized (Alonso *et al.*, 2013). A study by Alonso *et al.* (2013) demonstrates that the production of the primary reaction products, LA and FA, progressively increases as the reaction period extends, reaching its peak at 6 hours. Boonyakarn *et al.* (2019) clearly illustrated the impact of reaction time on cellulose conversion. Within the temperature range of 160 to 200 °C, the production of glucose and HMF initially rose over time, but eventually began to reduce at a certain time. Meanwhile, LA consistently grew over time, indicating that glucose was easily transformed into HMF, and then turned into LA as the reaction progressed.

The LA yield in the research by Chen *et al.* (2022) displayed an initial increase from 42.1% to 50.1%, followed by a subsequent fall to 40.1%. The yield of residue such as humins steadily rose as the duration was extended beyond 3 hours. Similar to Ma *et al.* (2021), the conversion of cellulose and the yield of LA increased from 72.04 and 37.56% to 83.54 and 50.40%, respectively, as the reaction period extended from 2 to 3 hours. Subsequently, the production of LA began to decrease progressively as the duration of the reaction exceeded 3 hours. At a reaction period of 4 hours, the yield of LA decreased to 39.48% while the conversion of cellulose increased to 99.01%. It was

assumed that prolonged response time can induce the polymerization of the products, hence causing a decrease in the yield of the LA products. Additionally, humins can be generated from cellulose when the reaction time exceeds a certain duration. Cheng *et al.* (2022) found that the maximum yield of LA was achieved when the reaction duration reached 10 hours and the conversion of cellulose into intermediates such as glucose and HMF was found to be 71.4%. Nevertheless, when the duration extended to 10 hours, the production of LA declined to 39.0%, while the conversion of cellulose rose to 73.5%. Extending the reaction time beyond a certain point does not significantly enhance the yield of LA or the conversion of cellulose. Therefore, this study aimed to investigate the impact of the reaction on the conversion of cellulose into LA and the literature suggests that the reaction can last up to 4-10 hours.

2.4.3 Effect of solid liquid ratio (SLR)

The proportion of solids and liquids in the feed ratio is a crucial component that impacts the formation of LA. In theory, a decreased ratio of solid to liquid should lead to a greater production of LA. It has been discovered, meanwhile, that a large carbohydrate loading negatively impacted the reaction in the production of LA (Ahlkvist, 2013). Generally, low cellulose concentration led to an increase in LA production. In order to produce each LA molecule, two molecules of water are required and failure to provide the necessary water molecules may result in the conversion of HMF into humins (Girisuta *et al.*, 2006). These findings align with previous research on the production of LA, where the presence of low amounts of the substances resulted in higher yields of LA.

Many literature studies have recommended a low substrate loading, often between 1.5% and 3.0% (Liu *et al.*, 2019; Peng *et al.*, 2010; Zhou *et al.*, 2013) which could produce high LA yields from 60% to 70%. Jeong *et al.* (2017) and Wang *et al.* (2019) found that the LA yield consistently fell to 19% when the substrate loading reached 15%. This phenomenon arises due to the collision of reactive chemicals, such as glucose, fructose, and HMF, under conditions of high substrate loading. These collisions result in the creation of undesired cross-polymerization and humins (Ramli and Amin, 2017).

It is possible to draw the following conclusions: (i) As not all catalytic active sites will be completely utilized for catalytic transformation, insufficient feedstock loading may result in a reduced yield of the desired product and impact process economics. (ii) Overloading the feedstock can result in the production of undesirable by-products through secondary reactions. (e.g., increased levels of sugar loading result in the creation of humin and reduce the production of LA), (iii) High feedstock loading may lead to insufficient catalytic sites, hence reducing the reaction rate. Therefore, this work employed substrate loadings of no more than 10% in all experiments.

2.4.4 Effect of catalyst amount

The optimal catalyst loading varies among different catalysts and plays a crucial role in achieving the highest LA yield. Increasing the amount of catalyst used enhances the amount of active sites, hence enhancing the catalyst's effectiveness which resulted in a substantial yield of LA (Azlan *et al.*, 2022a). Compared to the bifunctional catalytic system, the catalyst loading in the single acidic system was incomparable. Based on

the findings by Jeong *et al.* (2017) and Liu *et al.* (2019), in the acidic system, the presence of strong mineral acids like HCl and H₂SO₄ resulted in the production of LA that ranged from 22% to 45% when the acid concentrations were between 1% and 6%. However, the LA yield started to decline when the acid concentration reached 7%, which was comparable to 0.9 M HCl and 1.3 M H₂SO₄.

Similar to a study by Wei and Wu (2017), their study shows that the impact of a higher catalyst loading can be seen in the increased production of LA, as a result of the greater availability of acidity for the further degradation of sugar products. For example, the yield increased dramatically from 12.1 to 38.3 mol% when the loading of the SO₂/TiO₂ catalyst was increased from 0.15 to 0.30 g (50 wt% from feed). Nevertheless, the yield of HMF experienced a slight decline at the highest catalyst loading. This outcome can be attributed to the surplus of active sites present at the highest catalyst loading, which enhances the rehydration of HMF into LA, FA or humins. A study conducted by Li *et al.* (2020) confirmed that increasing the amount of catalyst beyond the optimal amount did not result in an improvement in LA formation which can be attributed to the fact that an excess of catalyst actually promoted undesired side reactions. As a conclusion, the optimal amount of catalyst was discovered in this study to enhance the performance of LA production.

2.5 Catalyst for levulinic acid

LA can be obtained by hydrolysis of biomass or cellulose which is determined by the chosen catalyst. Various catalysts have been explored for the purpose of producing LA such as homogeneous acid catalysts, solid acid catalysts and solid base catalysts.

Homogeneous catalysts are usually in a liquid state and exist in the same phase as the reactants, whereas heterogeneous catalysts are commonly solid catalysts in a different phase than the reactants which are in liquid or gas phase reactions (Mandari and Devarai, 2022). Homogeneous mineral acids such as H_3PO_4 (Jung *et al.*, 2021), H_2SO_4 (Jeong *et al.*, 2017; Su *et al.*, 2017; Dutta *et al.*, 2020) and HCl (Garcés *et al.*, 2017; Pulidindi and Kim, 2018) have been utilized to convert biomass or cellulose into LA. However, these techniques are not environmentally friendly since homogeneous catalysts or strong acids catalysts are not recyclable (Horikoshi *et al.*, 2017). Furthermore, the application of homogeneous catalysts results in the corrosion of reactors (Taghavi *et al.*, 2022b). For these reasons, recent literature highlights the preference for heterogeneous catalysts such as zeolites, ion exchange resins, heteropoly acids (HPAs) and carbon-based solid acids. This alternative offers numerous notable benefits such as less toxicity, less corrosion and reducing environmental problems (Hidayat *et al.*, 2015). Interestingly, the efficiency of heterogeneous systems by facilitating the recycling of the catalyst and separation of the product makes the one-pot conversion to LA more practical (Azlan *et al.*, 2022a).

Heterogeneous catalysts or solid catalysts can exhibit either basic or acidic properties. Exploration of solid base catalysts for the production of LA has been limited, with only zirconium carbonate (ZrC) or zirconia (ZrO_2) being reported (Son *et al.*, 2014; Lin *et al.*, 2012). Although these catalysts were found effective in LA production, these catalysts are only selective for isomerization of glucose into fructose, hence, a solid acid catalyst is required to assist the conversion of fructose into LA in further reaction (Azlan *et al.*, 2022a). Due to the weaknesses of basic catalysts, more research focused on the utilization of heterogeneous acid catalysts to synthesize LA. Furthermore, the

mechanism of LA production from cellulose required acid (H^+) in the reaction as discussed in Section 2.2.1.

There are two types of solid acid catalysts; Brønsted-Lowry acids or Lewis acids. Based on previous studies, Brønsted-Lowry acids used in the synthesis of LA were carbonaceous catalysts (Gromov *et al.*, 2018; Deng *et al.*, 2022), aluminosilicates such as zeolites (Sobuś and Czekaj, 2022; Bisen *et al.*, 2021), ion exchange resins such as Amberlyst (Hu *et al.*, 2013; Tang and Yu, 2014) and solid phosphates (Liu *et al.*, 2017). The selection of these solid acid catalysts was based on their cost-effectiveness, large pore volumes, high acidity and large surface areas which facilitate the efficient diffusion of biomass for LA production. In contrast, Lewis acids utilize metal salts (Di Fidio *et al.*, 2019), metal triflates (Fu *et al.*, 2015) and metal oxides (Pratama *et al.*, 2020) to produce LA. In the following section, a more detailed discussion is provided on metal catalysts (Lewis acid) and sulfonated carbon catalysts (Bronsted-Lowry acid), as well as the synergistic between these two type of catalysts for biomass or cellulose conversion and LA production.

2.5.1 Metal catalysts

Metal salts such as metal oxides, metal chlorides, and metal triflates are commonly used as Lewis acids catalysts. The metal chlorides such as $FeCl_3$, $SnCl_4$, $CuCl_2$, $CrCl_3$ and $AlCl_3$, demonstrated notably higher rates of both cellulose and glucose conversion (>60%) in comparison to Zn^{2+} , Mn^{2+} and Co^{2+} (Azlan *et al.*, 2022a). The acidity of a reaction can be increased through the formation of a Lewis acid from metal cations like Fe^{3+} , Cr^{3+} and Al^{3+} when they oxidize with water molecules. The presence of

halide anions such as I^- , Br^- , and Cl^- to form the Lewis acid/base pair catalyzed the sequential dehydration processes that convert sugars into HMF or furfural (Marcotullio and De Jong, 2010).

A study by Cai *et al.* (2014) compared the performance of five promising metal salt acid catalysts, $FeCl_3$, $CuCl_2$, $CrCl_3$, $ZrOCl_2$ and $AlCl_3$ for the conversion of sugars and the production of HMF and LA. Their study found that all metal salts yielded high selectivity of HMF compared to sulfuric acid (21.0% of theoretical) with $FeCl_3$, $CuCl_3$ and $AlCl_3$ metals performing best (41.0%, 22.0% and 33.0% based on theoretical yield, respectively). The performance of $FeCl_3$ was superior to that of $CuCl_2$ and $AlCl_3$ in terms of HMF production (yielding 42% for corn stover and 41% for maple wood), furfural production (yielding 97% for both maple wood and maize stover) and solubilization of biomass. However, the yield of LA for all metal salts was lower than sulfuric acid. Hence, the reaction of HMF conversion into LA using these salts should be investigated further. Boonyakarn *et al.* (2019) found that, $FeCl_3$ has high acidity ($\sim pH$ 2.5) which contributed to catalytic activity for cellulose conversion to glucose. Metal chlorides with low acidity, such as $MnCl_2$, $CdCl_2$ and $CoCl_2$ (with a pH of around 7) do not exhibit catalytic activity in converting cellulose to glucose. Consequently, the yields of HMF and LA were low.

Metal oxide catalysts have recently been developed to produce LA. Wang *et al.* (2020) converted cellulose into LA using metal oxide by impregnating this type of metal into Zr-MOF material. The result from their study showed that the amount of acid in the medium-strong acid region enhanced with the catalyst loaded with metal oxide (CeO_2). A study by Wang *et al.* (2015) found that a combination of metal oxide (10% Nb/Al

oxide catalyst) used in their study presented the highest selectivity for LA production, thus producing a comparatively higher yield of LA from raw material. The most notable of the many advantageous characteristics of mesoporous metal oxides is their high catalytic efficiency. Mesoporous metal oxides possess distinct structural characteristics, including a large surface area, the capacity to modify pore size and improved resistance to high temperatures (Babu *et al.*, 2023). Nevertheless, it has been demonstrated that attaining both a high level of mesoporous order and highly crystalline pore walls is not always feasible for the same materials. Subjecting the material to elevated temperatures during heat treatment enhances the degree of crystallization in the walls of the pores. However, this process also causes the mesoporous structure to collapse. Mesoporous metal oxides have exceptional catalytic efficiencies, which will make their research important. The presence of mesopores in the oxides allows reactants to reach more active acid sites (Guo *et al.*, 2012). Therefore, it is necessary to construct the mesoporous structure in order to enhance the surface area and improve the accessibility of reactants. Various metal oxides possess Lewis acid sites that facilitate the isomerization of sugars into highly reactive molecules (Pattnaik *et al.*, 2021). These compounds can subsequently undergo diverse processes to generate platform chemicals.

To the best of our knowledge, there was no research using nickel (Ni) as a metal catalyst for LA production. Based on the previous studies, Ni can promote the hydrolysis of cellulose (Zhang *et al.*, 2011). Research by Collard *et al.* (2015) found that Ni can assist in the destruction of the crystalline cellulose structure which is important in the cellulose hydrolysis reaction. Hence, the synthesis of catalysts by incorporating Ni with other metals for LA production should be further studied.

Considering the excellence performance of Fe metal as a catalyst in previous studies, Fe was selected in this study and precipitated with Ni to form a mixed metal catalyst for the production of LA.

2.5.2 Sulfonated carbon catalysts

Research has been done on heterogeneous catalysts, including activated carbon, for the breakdown of biomass, cellulose or sugars. According to Onda *et al.* (2008), a promising sulfonated carbon catalyst has been found that efficiently transforms cellulose into glucose, yielding a noteworthy 41%. Many studies have already been carried out to assess the cellulose hydrolysis process using sulfonated carbon catalysts. Table 2.6 shows the performance of activated carbon and sulfonated carbon to produce HMF or LA.

In a recent development, carbon-based catalysts derived from activated carbon (AC) or graphene oxide have been sulfonated with sulfuric acid to form SO_3H functionalized carbon catalysts for the biomass or cellulose conversion. A study by Bounoukta *et al.* (2022) compared the performance of AC and ACSO_3H catalysts in the production of LA. Their study revealed that the sulfonation of AC by sulfuric acid enhanced LA yields from 1.0% to 4.0%. Chen *et al.* (2022) managed to obtain 67.9% of LA from cellulose at 190 °C for 150 minutes but their study was carried out in a biphasic system. Although Gromov *et al.* (2018) were unsuccessful in generating LA when utilizing both AC and sulfonated AC in their research, they were able to achieve a yield of 19.7% HMF using sulfonated AC and 6.0% HMF using AC at 190 °C for 7 hours. Lawagon *et al.* (2021) collected a high yield of 61.2 mol% of LA from sugars by

conducting the reaction at a temperature of 160 °C for a duration of 1 hour. The sulfonated AC catalyst in the research carried out by Ozel *et al.* (2019) has shown greater activity than the commercial Amberlyst 15 catalyst under the optimum reaction conditions. As a result, 403.7 ppm of HMF (16.2 mg HMF per gram of biomass) and 1624.8 ppm of LA (65.6 mg LA per gram of biomass) were collected from corn straw biomass in water within 1 hour at a temperature of 200 °C. The results from previous studies show that a sulfonated carbon catalyst has a good potential to produce LA from biomass or cellulose.

A comparison study for methods and conditions to produce sulfonated activated carbon is shown in Table 2.7. Previous research primarily used lignin for ACSO₃H catalyst production, resulting in notably low total acidity values. For example, dos Santos *et al.* (2023) yielded only 1.48 mmol/g of total acidity. However, few researches conducted by Lokman (2016), Zhang and Chen (2016) and Fernández *et al.* (2019) suggest that synthesizing ACSO₃H catalysts from cellulose (7.89, 4.43 and 4.45 mmol/g respectively) leads to higher acidity values compared to those from lignin. Notably, there is a lack of research investigating the production of LA using ACSO₃H synthesized from cellulose. Therefore, this study chooses to use cellulose as the precursor material for ACSO₃H synthesis.

Table 2.6: Production of HMF and LA using sulfonated carbon catalyst

Catalyst	Reaction feedstock	Reaction condition	Yield	References
Sulfonated carbon catalyst (1 wt.%)	Cellulose	180 °C, 3 h in hydrothermal	38 wt.% LA	Balasubramanian <i>et al.</i> , (2022)
Activated carbon (40 mg)	Glucose (180 mg)	175 °C, 3 h in MIBK/H ₂ O	1.0 wt.% LA	Bounoukta <i>et al.</i> , (2022)
Sulfonated activated carbon (40 mg)		biphasic system	4.0 wt.% LA	
Sulfonated hydrothermal carbon (5 wt.%)	Cellulose	200 °C, 5 mins in an aqueous system	4.0 wt.% LA	Boonyakarn <i>et al.</i> , (2019)
Phosphoric acid-activated lignin-based solid acid (2 g)	Cellulose residue (4 g)	190 °C, 3 h in MIBK/H ₂ O-NaCl	67.9 mol% LA	Chen <i>et al.</i> , (2022)
Sulfonated carbonaceous solid/lignin-based solid (0.84 g)	Sugarcane (1 g)	140 °C, 6 h in aqueous, water bath heating	38.6 wt.% LA	dos Santos <i>et al.</i> , (2023)
Carbon material Sibunit (10 g)	Cellulose (10 g)	190 °C, 7 h in deionized water	6.0 wt.% HMF	Gromov <i>et al.</i> , (2018)
Sulfonated carbon Sibunit (10 g)			19.7 wt.% HMF	
Lignin-based acid carbon (1.0 g)	Cellulose (1 g)	185 °C, 2 h in hydrothermal reaction	35.6 wt.% LA	Han <i>et al.</i> , (2019)
Sulfonated graphene oxide	Fructose	160 °C, 1 h in batch reactor	61.2 wt.% LA	Lawagon <i>et al.</i> , (2021)
Sulfonated carbonaceous (0.25 g)	Corn straw (0.5 g)	200 °C, 1 h in aqueous, hydrothermal	6.6 wt.% LA	Ozsel <i>et al.</i> , (2019)
Activated Carbon (0.5 g)	Glucose (30 g)	200 °C, 2 h in distilled water (reactor)	2.3 wt.% LA	Upare <i>et al.</i> , (2013)
Sulfonated Activated Carbon (0.5 g)			4.2 wt.% LA	
Sulfonated humins	Cellulose (10 g)	Reaction in the complex solvents	65.9 wt.%	Wang <i>et al.</i> , (2018)

Generally, the production process for ACSO_3H involves two main steps. Firstly, raw materials are carbonized or pyrolyzed to produce activated carbon (AC). Subsequently, the AC is sulfonated by introducing sulfonic groups to produce the ACSO_3H catalyst. The determination of the conditions of the carbonization and sulfonation for the production of ACSO_3H catalyst is important. Carbonization is a thermal treatment technique (such as, microwave-assisted carbonization, hydrothermal carbonization or pyrolysis) that increases the carbon content of raw carbon precursors by removing low molecular weight substances and volatile moisture while sulfonation is a technique used to introduce sulfonic groups in the material (Chong *et al.*, 2021).

Ozsel *et al.* (2019) discovered this phenomenon during the evaluation of carbonization and sulfonation conditions. During the experiment, their study tested the temperatures of 300 °C, 400 °C, and 500 °C in the process of carbonizing wheat straw for 3 hours. They then subjected the carbonized material to sulfonation at 150 °C for 16 hours. The results demonstrated that increasing the carbonization temperature from 300 °C to 500 °C led to a larger surface area, volume, and pore size. However, the catalyst prepared from the carbonized material at 500 °C had a low concentration of acidic sites ($-\text{SO}_3\text{H}$) compared to the catalysts made from carbonized biomass at 300 °C and 400 °C (1.29 mmol/g compared to 1.76 and 1.71 mmol/g, respectively). The findings align with the existing literature by Araujo *et al.* (2019), since they indicate that greater carbonization temperatures result in decreased functionalization efficiency. This is because, at higher temperatures, the carbon sheets form and stack together, creating more rigid and larger carbon structures. This makes it challenging for the $-\text{SO}_3\text{H}$ functional groups to attach during the sulfonation process, resulting in a low overall acid density. Similar to a finding in the study by Nakajima and Hara (2012), they found that the catalytic

performance is significantly reduced when subjected to high carbonization temperatures, typically above 450 °C, due to the expansion of the carbon network. Furthermore, Lokman *et al.* (2014) discover that, 400 °C is the optimum temperature for the direct incomplete carbonization of carbohydrate organic materials, which is necessary to heat the materials in an inert environment to prevent the precursor from turning into ash.

For carbonization time, a study by Lou *et al.* (2012) identified that the carbonization time presented only a slight impact on the catalyst's catalytic activity within the studied range of 0.5–20 hours. Liu *et al.* (2013) conducted a study to investigate the effect of carbonization time on the catalytic activity of a catalyst produced from corn straw for the esterification of oleic acid. The study showed the maximum acid density of 2.64 mmol/g was obtained from the catalyst synthesized for 1 h. A study by Zhang and Chen (2016) shows that the carbonization process of cellulose at 400 °C for 1 hour is already sufficient. Besides, Zhang *et al.* (2020) discovered that the increase in carbonization time leads to a higher degree of carbonization, resulting in the formation of a polycyclic aromatic hydrocarbon structure. This structure then serves as an anchor for the sulfonic acid groups. If the carbon skeleton structure is already formed, further carbonization time may not be required. Thus, drawing from previous research, this study conducted carbonization at 400 °C for 1 hour to synthesize ACSO₃H catalyst.

Similar to the carbonization process, the duration and temperature of sulfonation are also important. Zhang *et al.* (2020) evaluated the effect of sulfonation temperature and reported that the density of acid initially rose as the sulfonation temperature increased from 100-140 °C. However, it thereafter remains relatively constant or may even drop

when the temperature exceeds 140 °C which is mostly due to the occurrence of side reactions, such as multi-sulfonation and sulfone. Flores *et al.* (2019) found that, the temperature during the sulfonation process should not go beyond 150 °C because raising the sulfonation temperature causes the raw materials to undergo graphitization and the carbon sheets to cross-link. This occurs due to the removal of the C-H bonds before the sulfonic acid groups are attached, resulting in a carbon framework that is more rigid which makes the sulfonic acid density reduced. For sulfonation time, Lokman (2016) sulfonated cellulose for 12 hours and resulted in a high total acidity value (7.89 mmol/g). A study by Rechnia-Gorący *et al.* (2018) found that increasing the sulfonation time did not boost the density of sulfonic groups, but the amount of oxygen was increased which led to the reduction of the total acidity. Based on the findings from previous research, it can be concluded that the acidity density of catalysts is directly affected by sulfonation process parameters. However, prolonged sulfonation durations and temperatures have not been found to significantly impact the acidity density of catalysts. Consequently, this study opted to conduct sulfonation at 150 °C for a duration of 12 hours.

The yield of LA was found to be improved by an increase in acidity value although this effect was also dependent on the catalyst's changes after sulfonation. Therefore, more research needs to be done on catalyst characterizations. Furthermore, Brønsted–Lewis dual-acidic catalysts, which are covered in a later section, can be created by impregnating metal catalyst that contain Lewis acid into sulfonated carbon catalyst (Bronsted-Lawry acid).

2.5.3 Synergy of Lewis acid and Brønsted-Lowry acid catalyst

In the context of classical solution chemistry, a Brønsted acid is defined as a species that donates a proton to another species, which subsequently acts as a proton acceptor and acts as a base. Similarly, a Lewis acid is a substance that accepts an electron pair to form a chemical bond, whereas a Lewis base donates an electron pair (*Valadares et al.*, 2023). The Lewis definition is more comprehensive and not limited to solutions or proton transfer reactions. Although the Lewis definition encompasses the Brønsted definition, reactions involving proton transfer are more conveniently described using the Brønsted-Lowry concept.

The synergy of Lewis acid and Brønsted-Lowry acid in bifunctional catalysts has greatly improved the conversion of biomass or cellulose in simultaneous processes. This can even be achieved in a one-pot conversion, which is typically challenging. The bifunctional catalyst created by combining Lewis acid and Brønsted-Lowry acid not only combines the two unique reactions but also modifies the structural characteristics of the two double acid centers (*Azlan et al.*, 2022a). This modification has a major impact on the catalytic behavior of the system. The most commonly used Lewis acids in bifunctional catalysts are metal oxides, metal triflate and metal halides

Table 2.7: Comparison of different techniques to produce sulfonated carbon catalyst

Raw materials	Production method	BET surface area (m ² /g)	Total acidity (mmol/g)	Application	References
Commercial activated carbon	- Treatment with concentrated H ₂ SO ₄ at 150 °C for 6 h	N.a	N.a	Conversion of glucose into LA	Bounoukta <i>et al.</i> (2022)
Eucalyptus tree shed barks	- Carbonization at 600 °C for 1.5 h - Treatment with p-toluene sulfonic acid at 60 °C for 5 h	31.0	0.65	Oleic acid esterification	Yusuff <i>et al.</i> (2022)
Lignin	- Treatment with H ₃ PO ₃ at 60 °C for 12 h	1023.6	2.81	Conversion of cellulose into LA	Chen <i>et al.</i> (2022)
Lignin	- Carbonization at 700 °C for 2 h - Carbonization at 600 & 800 °C for 30 mins - Treatment with concentrated H ₂ SO ₄ at 180 °C for 12 h	N.a	Carbonized at 600 °C: 1.48 800 °C: 0.58	Conversion of sugarcane into LA	dos Santos <i>et al.</i> (2023)
Carbon material Sibunit	- Treatment with concentrated H ₂ SO ₄ at 80 - 250 °C for 10 h	Sulfonated at 80 °C: 344 150 °C: 360 200 °C: 400 250 °C: 221	Sulfonated at 80 °C: 0.14 150 °C: 0.32 200 °C: 0.40 250 °C: 0.62	Conversion of cellulose into HMF	Gromov <i>et al.</i> (2018)
Wheat straw	- Carbonization at 300-500 °C for 3 h - Treatment with concentrated H ₂ SO ₄ at 150 °C for 16 h	Carbonized at 300 °C: 36.4 400 °C: 167.4 500 °C: 306.3	Carbonized at 300 °C: 1.76 400 °C: 1.71 500 °C: 1.29	Conversion of biomass into HMF and LA	Ozsel <i>et al.</i> (2019)
Humins	- Carbonization at 550 °C for 5 h - Treatment with concentrated H ₂ SO ₄ at 120 °C for 10 h	1.9	2.11	Conversion of cellulose into LA	Wang <i>et al.</i> (2018)
Cellulose	- Hydrothermal synthesis with HCl at 195 °C for 20 h - Treatment with concentrated H ₂ SO ₄ at 150 °C for 15 h	272	4.45	Glycerol ketalization	Fernández <i>et al.</i> (2019)

Table 2.7: Continued

Cellulose	- Carbonization at unknown condition - Treatment with concentrated H ₂ SO ₄ at 100 °C for 3 h	1.38	3.12	Esterification of rapeseed oil fatty acids	Malins <i>et al.</i> (2016)
Cellulose	- Carbonization at 400 °C for 12 h - Treatment with concentrated H ₂ SO ₄ at 160 °C for 12 h	8.7	7.89	Esterification of palm fatty acid distillate	Lokman (2016)
Cellulose	- Carbonization at 400 °C for 1 h - Treatment with concentrated H ₂ SO ₄ at 150 °C	1.58	4.43	Conversion of carbohydrates into ethyl levulinate	Zhang and Chen (2016)

A study of the synergistic effects of mineral acids (for Bronsted-Lowry acid) and Lewis acids in the formation of LA has been conducted in the previous studies. According to Yang *et al.* (2013), the combination of Lewis and Brønsted acids exhibited a powerful synergistic catalytic effect in breaking down glucose into LA and the optimal ratio of CrCl_3 in the $\text{CrCl}_3\text{-H}_3\text{PO}_4$ was approximately 0.5. Dallas Swift *et al.* (2015) introduced a synergic catalytic mechanism for the mixed HCl-CrCl_3 system to decompose glucose into HMF. Their findings indicated that the simultaneous presence of Lewis and Brønsted acids in a single container resulted in a significant increase in glucose conversion. Consequently, this leads to an improved yield and selectivity of HMF and LA. Weiqi and Shubin (2017) discovered that the combination of CrCl_3 and H_3PO_4 as a catalyst had a beneficial catalytic impact on the conversion of glucose to LA, in contrast to using only CrCl_3 or H_3PO_4 as catalysts. The maximum LA yield, 56%, was obtained by Lappalainen *et al.* (2019) with Swedish fiber sludge after 60 min at 180 °C with the combination of H_2SO_4 and CrCl_3 . Yang *et al.* (2013) used H_2SO_4 as a source of Bronsted acid and compared several metals for Lewis acid. They found that FeCl_3 produced the highest LA yield (36.0%) compared to CrCl_3 , ZnCl_2 and CuCl_2 .

However, the direct application of homogenous acid as Bronsted acid catalyst comes with a number of issues, including equipment corrosion, challenging recycling and environmental contamination (Hu *et al.*, 2015). Homogenous acid can be replaced by using a solid acid catalyst. Wei and Wu (2018) combined CrCl_3 with HZSM-5 zeolite and the highest LA yield of 64.4 mol% was collected at 180 °C for 180 min. Another strategy performed by Boonyakarn *et al.* (2019) involved combining Lewis acid catalysts, for examples, Fe(III) , Cr(II) , Cr(III) , Cu(II) , Zn(II) , Sn(IV) , and Al(III) salts)

with glucose-derived hydrothermal carbon-based solid acids that functionalized with SO_3H to produce synergistic catalytic effects for the conversion of biomass to LA. These catalysts facilitate reactions at moderate temperatures, hence enhancing the sustainability of LA production and obtaining better LA output.

As discussed before, metal oxides and sulfonated carbon catalysts have great properties and show efficient catalytic activities in LA production. Therefore, the investigation of the synergy for Lewis acid catalysts and Brønsted-Lowry acid catalysts was further extended in this research by utilizing metal oxide and sulfonated carbon catalysts. This synergy was achieved through the impregnation method.

2.6 Cellulose extraction from biomass

Cellulose is the primary structural component of the plant cell wall has a strong molecular structure found in lignocellulosic biomass. Cellulose is formed by long chains of monomeric units which are glucose and these units are connecting via β -glycosidic linkages with reducing and non-reducing ends (Ho *et al.*, 2019). Van der Walls and hydrogen bonds are the primary linkages connecting cellulosic polymers in the form of microfibrils present in amorphous and crystalline forms (Chen *et al.*, 2022).

Hemicellulose is an amorphous, multicomponent polysaccharide characterized by its low molecular weight. This material is made of several components and functional groups including hexoses (D-glucose, D-mannose or D-galactose), pentoses (D-xylose and L-arabinose), acetyl groups, cinnamic, galacturonic acids, acetyl, methyl, and glucuronic (Halder *et al.*, 2019b). The presence of an acetyl group and the branched

structure cause a lack of crystalline structure in hemicellulose. Furthermore, hemicellulose can be easily degraded because of its amorphous nature (Chen *et al.*, 2022). Hemicellulose acts as a physical barrier that prevents cellulose from being degraded by cellulases. Pretreatment methods are required to remove hemicelluloses.

Aside from cellulose and hemicellulose, biomass is composed of lignin. Lignin is complex, amorphous hetero-biopolymer and not soluble in water (Sharma *et al.*, 2019). Lignin is a structurally stable biopolymer composed of three cross-linked phenylpropane (C6–C3) units namely sinapyl alcohol, p-coumaryl alcohol and coniferyl alcohol. This material consists of phenylpropane units joined together by carbon–carbon and aryl–ether linkages. Most of these units are linked by ether bonds (C–O–C) accounting for more than two-thirds of the overall links while the rest of the links are carbon-carbon (C–C) linkages (Singh *et al.*, 2014). The structure of lignocellulosic biomass containing cellulose, hemicellulose and lignin is shown in Figure 2.5. Lignin surrounds cellulose and hemicellulose while cellulose fibers are interlaced with hemicellulose.

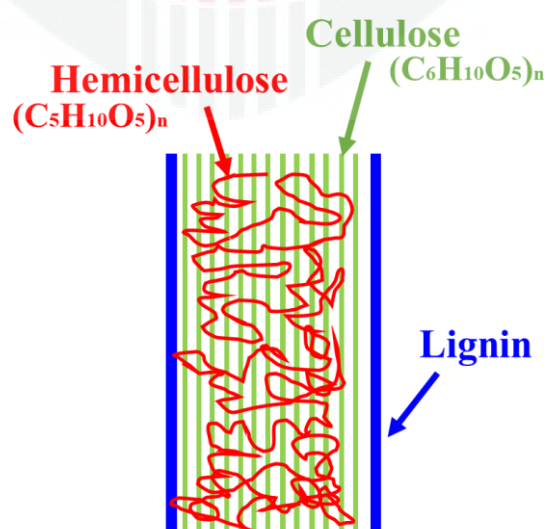


Figure 2.5: The structure of lignocellulosic biomass

The pathway for production of primary precursors such as sugars and secondary precursors (furfural, HMF and LA) directly from biomass at high yields (>80% recovery of C5 and C6 products) is challenging due to complicated methods, high energy demand and/or expensive catalysts (Cai *et al.*, 2014). This is because lignocellulosic biomass including OPEFB possesses a rigid structure primarily attributed to the association between crystalline cellulose microfibrils associating with hemicelluloses and lignin (Fatriasari *et al.*, 2017). Hence, this study focused on the extraction of cellulose from biomass first before being introduced into a one-pot synthesis reaction. Cellulose can be used in many applications such as fuels, chemicals, and the paper and paint industries (Arifin *et al.*, 2016). The first person to discover cellulose was a French scientist named Anselme Payen who in 1837 identified a carbohydrate in a variety of plant materials that yielded a fibrous substance after being purified with acid ammonia treatment and extracted with ether, alcohol or water (Megashah *et al.*, 2018). Considering the complexity of plant structure, isolation of cellulose from lignocellulosic components usually needs harsh conditions. The fibers were subsequently subjected to a multistep pretreatment that increased the cellulose fraction in order to eliminate the non-cellulosic component. Several isolation methods for cellulose extraction such as mechanical treatment to reduce the size of fiber, dewaxing, alkaline treatment as well as bleaching treatment have been investigated.

2.6.1 Mechanical pretreatment

The mechanical pretreatment methods applied in biomass technology include chipping, milling and sieving, which are used to break down the materials into particles ranging from 0.2 to 2.0 mm in size and decrease the crystallinity of the lignocellulosic

materials (Bhatia *et al.*, 2020). Grinding or chipping are the main methods applied to reduce the size of lignocellulosic biomass. Grinding is a method that reduces the size of particles to a maximum range of 0.2-2.0 mm while sieving is utilized to separate chipped and milled samples into various fractions based on their particle sizes (Bhutto *et al.*, 2017).

A study by Ratnakumar *et al.* (2022) revealed the particle size of the initial biomass materials had a notable effect on the characteristics and output of the extracted cellulose. Their research found that, although the cellulose content was found to be high in the powdered biomass with particle size between 150 and 250 μm sample, a greater quantity of isolated cellulose was recorded in the sample with particle size less than 75 μm . It shows that reducing the size of biomass can result in a significant yield of isolated cellulose.

In this study, the biomass was sieved to sizes ranging from 125 to 250 μm , following the methodology demonstrated by Alhaji Mohammed *et al.* (2022) which reported the percentage yields of pure cellulose extracts for particle sizes from 125 μm an 250 μm , were between 25.0% and 52.2%. Furthermore, most previous studies have applied sieving within this range for cellulose isolation from biomass as shown in Table 2.8. However, mechanical pretreatment alone enhances the surface area of biomass without modifying its structure. Scanning electron microscopy (SEM) analysis of two different sizes of OPEFB revealed no impact on its structural after size reduction in the study by Ariffin *et al.* (2008). Hence, chemical pretreatments such as alkaline and bleaching are advisable to apply subsequently to improve both the surface and internal

composition of biomass for the isolation of cellulose. The topic on these methods was addressed in another section (Section 2.6.2).

Table 2.8: Size range of the sieved biomass for cellulose extraction

Biomass	Size range	References
OPMF	Less than 150 μm	Chieng <i>et al.</i> (2017)
Sugarcane	Less than 315 μm	Freixo <i>et al.</i> (2023)
Rapeseed straw	Less than 840 μm	Mirzaee <i>et al.</i> (2023)
Grass straws	Less than 425 μm	Ndwandwa <i>et al.</i> (2023)
OPEFB	Less than 595 μm	Susi <i>et al.</i> (2023)
Almond shell	125 – 500 μm	Alhaji Mohammed <i>et al.</i> (2022)
Pine wood, poplar wood and wheat straw	Less than 310 μm	Zhang <i>et al.</i> (2018)

2.6.2 Chemical process for isolation of cellulose

Various techniques involved in the usage of chemicals have been discovered to isolate cellulose from lignin or other substances. The chemical processes conducted included dewaxing, alkaline pretreatment and bleaching.

Studies by Ogunjobi *et al.* (2023) and Chopra and Manikanika (2021) have emphasized the significance of the dewaxing process in eliminating extractives for cellulose isolation and enhancing the quality of the end products. These extractives include components such as oil, wax, pigments, phenolics, and oil (Owonubi *et al.*, 2021). Solvents such as toluene and ethanol were used in dewaxing process by applying Soxhlet extraction (Ndwandwa *et al.*, 2023). Moreover, in the cellulose isolation process, dewaxing can enhance the removal of hemicellulose in alkaline and bleaching pretreatment which is a subsequent process to the dewaxing method. For example, a study by Kunusa *et al.* (2020) shows that the larger amount of

hemicellulose (47.80%) was removed by alkaline pretreatment from the dewaxed sample compared to the sample without dewaxing (3.86%).

The next methods to extract pure cellulose after dewaxing are alkaline pretreatment and bleaching. Alkaline pretreatment is seen as a feasible technique due to its ability to provide mild reaction conditions, including low temperature and pressure for breaking down complex polymeric biomass. Sodium hydroxide (NaOH) is the optimal alkaline reagent for specifically degrading water-soluble hemicellulose and lignin and from lignocellulosic biomass (Ndwandwa *et al.*, 2023). The use of NaOH treatment that can dissolve non-cellulosic components by breaking the α - and β -aryl ether linkages between hemicellulose and lignin has been applied as the first step in isolating cellulose (Yue *et al.*, 2015). Furthermore, research by Ajayi *et al.* (2023) shows that NaOH effectively eliminated additional contaminants, such as cuticle from the surface of the fiber during the alkaline treatment. The bleaching stage is a procedure performed to break down the remaining lignin in the sample, resulting in enhancing the purity of cellulose and color alterations (Kunusa *et al.*, 2020).

Bhandari *et al.* (2020) isolated microcrystalline cellulose from rice husk through sodium hydroxide treatment followed by bleaching using sodium chlorite. They found that, hemicellulose and lignin were significantly removed from the biomass. Cellulose with a lower crystallinity index was formed and contained 99.68% of carbon and oxygen which are the basic components of a polycrystalline carbohydrate material. Jumhuri *et al.* (2017) also applied NaOH pretreatment followed by a bleaching and they obtained cellulose with a purity of 87%. In addition, FTIR analysis in their study showed a peak at 1742 cm^{-1} which indicates the ester carbonyl groups in the p-

coumaric units of the lignin or carbonyl stretching in the acetyl and uronic ester groups of hemicelluloses were successfully diminished. The isolation of cellulose OPEFB by using 4%-13% NaOH and followed by a bleaching process with a 1.7% NaOCl solution has been carried out by Sayakulu & Soloi (2022). The highest yield of cellulose (89.78%) was collected with 4% NaOH in their study. Nurhidayat (2022) investigated the best conditions for alkaline and bleaching treatment to isolate cellulose. The results in their study demonstrated that the most effective method for isolating cellulose from OPEFB was by subjecting the biomass to a 5% wt. NaOH pretreatment at 90 °C for 1 hour, followed by a bleaching pretreatment using 5% wt. NaClO₂ at 90 °C for 2 hours.

Previous studies have emphasized the significance of dewaxing, NaOH treatment followed by bleaching as crucial steps in the isolation of cellulose. Building upon this knowledge, the current study has applied all methods, employing the optimal conditions determined from prior research to isolate cellulose from OPEFB.

2.7 Pretreatment of cellulose by molten salt hydrates

The conversion of cellulose into LA has garnered significant interest and is now recognized as an important step in biomass processing. However, because of its insoluble in water and tightly packed structure through the strong intra- and intermolecular hydrogen bond, cellulose is often considered a challenging material to work with (Ren *et al.*, 2013). Furthermore, the generation of HMF and LA from cellulose catalyzed by heterogeneous catalysts is limited in the absence of pretreatment. This is primarily because there is a low surface contact area between the

metal oxides and the untreated cellulose in water (Jing *et al.*, 2018). Converting cellulose into HMF and LA using heterogeneous catalysts in a one-pot manner remains a significant challenge. It was reported only 4.6% LA was obtained using a solid acid carbon catalyst in the research by Gromov *et al.* (2018). Although high yields of LA (48.5%) were obtained by Han *et al.* (2019) using a lignin-based solid acid catalyst, γ -valerolactone (GVL) was used as a solvent to improve the solubility and thus the cellulose conversion. According to current theory, the hydrolysis reaction starts with the protonation of the cellulose's glycosidic oxygen and ends with the breaking of the glycosidic bond (Deng *et al.*, 2015). It is challenging for the active acid sites to reach the glycosidic bond since cellulose is insoluble in most solvents due to the large hydrogen bonds that are present in cellulose. Therefore, in order to catalytically break the glycosidic linkages in an aqueous solution, it is typically necessary to pretreat the cellulose.

Molten salt hydrates (MSHs) are currently receiving a lot of interest as effective solvents for biomass and cellulose. MSHs having a water to salt ratio equal to or less than the coordination number of the cations are promising for cellulose dissolution because of their chemical stability, low toxicity, ease of synthesis and high efficiency (Liu *et al.*, 2021). Several literature sources have demonstrated that crystalline cellulose can be effectively broken down into glucose in MSHs with a high yield of approximately 82% utilizing either homogeneous or heterogeneous acid catalysts under mild conditions as shown in Table 2.9. Deng *et al.* (2015) found that glucose yields of less than 90% could be obtained with nearly complete cellulose hydrolysis occurring at temperatures as low as 85 °C and low acid concentrations of H₂SO₄ as a catalyst using LiBr molten hydrate as reaction media. Meanwhile, Wu *et al.* (2020)

used a heterogeneous catalyst and they reported that cellulose can be fully broken down into glucose and oligoglucan by using 2% zeolite (w/w on cellulose) at 140 °C in 3 hours, resulting in a 61% glucose yield. To date, there is a lack of research on the utilization of MSHs to improve the conversion of biomass or cellulose for the synthesis of LA. Nevertheless, a study by Ma *et al.* (2024) achieved success in enhancing the conversion process to produce HMF (44.5%), an intermediate in the cellulose-to-LA conversion process at 170 °C for 20 min using an acidity tunable solid acid AlSiO_x catalyst. Reducing crystallinity is one approach to enhancing biomass or cellulose conversion. In this case, MSHs were used to pretreat the cellulose. According to a previous study, Zhang *et al.* (2023) and Deng *et al.* (2023) successfully reduced crystallinity to 48.7% and 40.1% respectively, by using LiBr as an MSH solution to pretreat cellulose at certain conditions.

However, there is a significant challenge in the separation of the products such as glucose and HMF produced in cellulose conversion because both products are soluble in MSHs solution. Prior research has shown that an additional separation process is required to separate the products, as shown in Table 2.10. Besides, the use of amorphous carbon or zeolites for separation is not recommended as the adsorption selectivity is generally low (Ma *et al.*, 2022). Precipitation using anti-solvents is simple but this method cannot be used for separating glucose (Lara-Serrano *et al.*, 2020). Therefore, another innovative strategy that does not involve separation steps can be used to improve cellulose conversion using MSHs.

Table 2.9: Biomass or cellulose conversion using MSHs solutions

Raw materials	MSHs	MSHs function	Catalyst	Conditions	Results	References
Cellulose	LiBr	Dissolution	H ₂ SO ₄	85 °C, 30 min	82.0% glucose	Deng <i>et al.</i> (2015)
Cellulose	LiBr	Dissolution	None	130 °C, 5 h	90.4% glucan oligomer	Liu <i>et al.</i> (2019)
Cellulose	LiCl	Dissolution	NbPO ₄ /HZSM-5 (in MIBK)	175 °C, 2 h	94.0% LA	Wang <i>et al.</i> (2020)
Cellulose	ZnBr ₂	Dissolution	None	70 °C, 15 min	99.0% amorphous cellulose	Lara-Serrano <i>et al.</i> (2020)
Cellulose	ZnCl ₂	Dissolution	HCl	70 °C, 60 min	84.0% glucose	van den Bergh <i>et al.</i> (2017)
Cellulose	LiBr	Dissolution	HCl	110 °C, 30 min	Cellulose completely hydrolyzed	Pan and Li (2015)
Cellulose	LiBr	Dissolution	AlSiO	170 °C, 20 min	44.5% HMF	Ma <i>et al.</i> (2024)
Cellulose	ZnCl ₂	Pretreatment	None*	25 °C, 16 h	Crystallinity was reduced to 20.0%	Burger <i>et al.</i> (2020)
Cellulose	LiBr	Pretreatment	None*	25 °C, 30 min	Crystallinity was reduced to 19.9%, 98.3% glucose	Huang <i>et al.</i> (2022)
Cellulose	LiBr	Dissolution	ZSM-5 and Beta with SiO ₂ /Al ₂ O ₃	140 °C, 3 h	61% glucose yield	Wu <i>et al.</i> (2020)
Hardwood pulp	LiBr	Pretreatment	None*	25 °C, 60 min	Crystallinity was reduced to 40.1%	Deng <i>et al.</i> (2023)
Nanocellulose	LiBr	Pretreatment	None*	25 °C, 30 min	Crystallinity was reduced to 48.7%	Zhang <i>et al.</i> (2023)
Poplar wood	LiBr	Dissolution	H ₂ SO ₄ and AlCl ₃	120 °C, 1 h	80.0 mol% furfural and HMF	Sadula <i>et al.</i> (2017)
Poplar chips	LiBr	Dissolution	HCl	110 °C, 20 min	48.0 wt% LA	Chen <i>et al.</i> (2022)
Sugarcane bagasse	LiCl	Dissolution	HCl	80 °C, 60 min	79.1% glucose	Yu <i>et al.</i> (2018)

*No catalyst used during pretreatment. Catalyst used only in the reaction after pretreatment.

Moreover, in line with existing literature, the cellulose dissolution mechanism in MSHs differs significantly from that in other cellulose solvent systems such as ionic liquids. It includes processes like defibrillation, deconstruction, and depolymerization. Cellulose defibrillation occurs due to the disruption of the strong intra- and inter-molecular hydrogen bonds in cellulose molecules (Quiroz *et al.*, 2019) while cellulose depolymerization or degradation involves the attack of protonic acid on the glycosidic bonds of cellulose macromolecular chains which need high temperatures (Huang *et al.*, 2020). However, depolymerization of cellulose may increase the cost of MSHs purification for recycling and the issue of product separation as discussed before will happen. Therefore, creating a successful pretreatment method that does not involve cellulose depolymerization would be more beneficial as illustrated in Figure 2.6.

Table 2.10: Separation of products in cellulose conversion using MSHs solutions

Raw materials	MSHs	Products	Separation	References
Cellulose	LiBr	Glucose	No	Deng <i>et al.</i> (2015)
Cellulose	LiBr	Glucan oligomer	Separation by adsorption on amorphous carbon	Liu <i>et al.</i> (2019)
Cellulose	ZnCl ₂	Glucose	Separation by adsorption on zeolite beta.	van den Bergh <i>et al.</i> (2017)
Sugarcane bagasse	LiCl	Glucose	Separation using nanofiltration	Yu <i>et al.</i> (2018)
Poplar wood	LiBr	Furfural and HMF	Separation by extracting furfural and HMF using ethyl acetate	Sadula <i>et al.</i> (2017)
Cellulose	LiCl	LA	Separation by extracting LA using methyl isobutyl ketone	Wang <i>et al.</i> (2020)
Cellulose	ZnBr	Amorphous cellulose	Separation by adding water as an anti-solvent	Lara-Serrano <i>et al.</i> (2020)

As shown in Table 2.9, several studies utilized MSHs solution to pretreat cellulose or biomass. Huang *et al.* (2022) found that microcrystalline cellulose can be almost entirely converted into glucose (98.3%) after being pretreated by lithium bromide hydrates at room temperature which is attributed to the loosened and deconstructed structure of MCC during pretreatment. Burger *et al.* (2020) pretreated cellulose pulp

for 16 hours at room temperature with zinc chloride hydrate, which successfully resulted in a drop in the cellulose pulp's crystallinity from 47% to 20%. Zhang *et al.* (2023) also showed that the cellulose structure of hardwood dissolving pulp was significantly changed into an amorphous structure after LiBr non-dissolving pretreatment for 30 min. Furthermore, Zhang *et al.* (2023) and Deng *et al.* (2023) reported successful reductions in crystallinity to 48.7% and 40.1%, respectively, applying LiBr as the MSH solution under specific conditions. Reducing the crystalline structure of cellulose offers a promising pathway to enhance biomass or cellulose conversion.

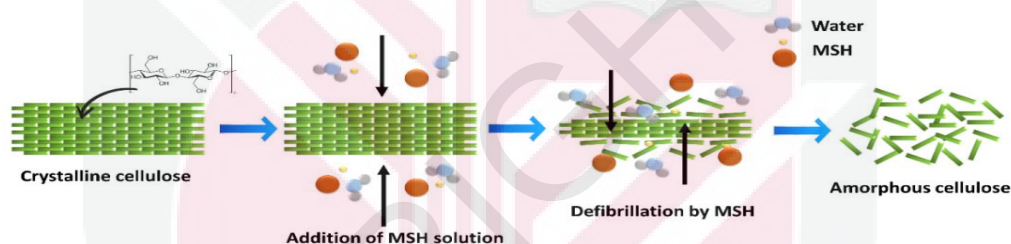


Figure 2.6: Pretreatment of cellulose using MSHs solution

Research has extensively demonstrated that treating cellulose with MSHs effectively reduces cellulose crystallinity and improves its conversion into desired products. While previous studies have demonstrated the effectiveness of MSHs in cellulose pretreatment for glucose production, there exists a significant opportunity to explore their potential for LA production. Furthermore, a notable study conducted by Huang *et al.* (2022) for cellulose conversion into sugars exclusively investigated the use of lithium bromide only, while other MSHs are still unexplored. Therefore, this study aimed to explore the impact of various MSHs such as LiBr, LiCl and ZnCl_2 on cellulose conversion. Additionally, a specific focus on investigating their potential for producing LA was aimed in this research.

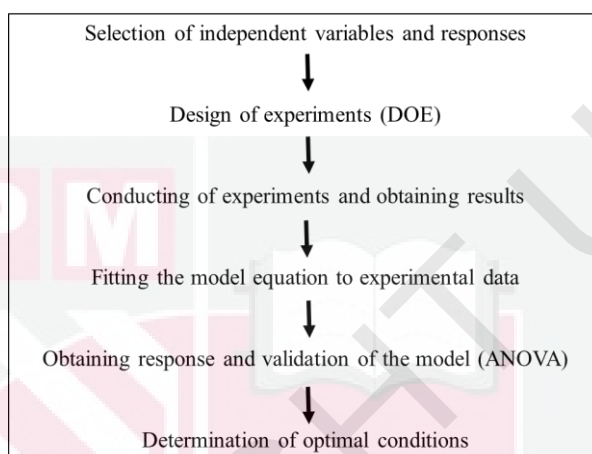
2.8 Optimization of LA yield

Optimization methods are applied across various fields of research to determine solutions that either maximize or minimize specific study parameters. These factors may include minimizing expenses in the manufacture of a service or product, maximizing profits, minimizing the usage of raw materials in production or maximizing production output (Alonso *et al.*, 2020). The example parameters or inputs are reaction temperature, reaction time, pH, type or amount of solvent and types of catalyst. Meanwhile, the outputs might be the yield of products, selectivity, process efficiency or others.

Experiments for optimization are typically conducted by applying and analyzing one parameter while keeping the others constant. This approach is referred to as one variable at a time (OVAT). This technique is primarily applied in academic research due to its structured but easy-to-follow process, which makes this method seem both useful and easy to use. However, the method is actually difficult since the researcher must examine each variable separately and require a substantial number of experiments which can result in significant study expenses. Furthermore, OVAT fails to incorporate the interactions among the chosen factors (Witek-Krowiak *et al.*, 2014).

In order to address those reported problems, a study has been conducted by optimizing an analytical procedure using multivariate statistical techniques. The Response Surface Method (RSM) is used for mathematical modeling in order to develop correlations between numerous inputs and outputs of the process (Panwar *et al.*, 2020). The RSM technique is based on the design of experiments (DOE) which aims to

predict and enhance the performance of complex systems through the use of experiment design, building models and assessment of the importance of independent variables and their interactions (Zhu *et al.*, 2016). RSM can be successfully implemented by following 6 phases of steps:



Examples of DOE software are MODELing Design and Evaluation (MODDE[®]), John's Macintosh Project (JMP[®]), Design-Expert or toolbox applications in languages such as Python, R programming, Minitab and MATLAB (Taylor *et al.*, 2023). Most researchers prefer Design Expert because this software can perform multifactorial data analysis and design experiments in a very user-friendly environment (Gong *et al.*, 2019; Mthembu *et al.*, 2021). Hence, this study used Design Expert to carry out an optimization study to enhance the production of LA.

In recent years, there have been several optimization studies on the production of LA from various raw materials including cellulose. de Guzman and de Leon (2021) study three parameters which are catalyst concentration, time and cellulose loading. Their study presented a maximum yield of 36.2% of LA from cellulose by utilizing a SnCl₂ concentration of 0.2 M under test conditions of 3 hours, 180 °C and 1% w/v cellulose

loading. The highest cellulose conversion into LA (61.9%) was obtained by Rivas *et al.* (2016) who evaluated three parameters (temperature, time and concentration of acid) and the highest amount was obtained at 190 °C operating for 15 min in a medium containing 1 wt% HCl. A study by Ramli and Amin (2015a) optimized LA yield from oil palm biomass using a heterogeneous catalyst. Their study agreed that the important process variables affecting the yield of LA were reaction time, reaction temperature, catalyst loading and biomass loading. However, no research has employed a heterogeneous catalyst for the conversion of cellulose into LA in their optimization study using RSM. In this research, the RSM technique has been used to carry out the optimization of the LA production from OPEFB-based cellulose using the selected sulfonated carbon metal catalyst. Three parameters were evaluated; temperature, time and catalyst loadings.

2.9 Kinetic and thermodynamic studies

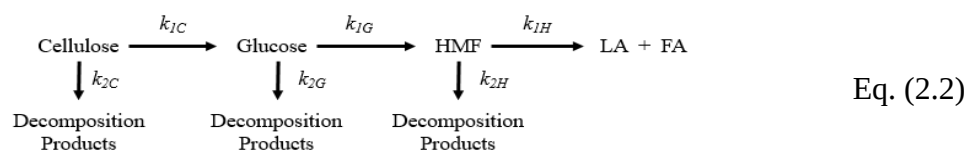
The decomposition of cellulose via hydrolysis reaction into several soluble substances such as glucose, HMF, FA and LA as well as insoluble substances under certain process conditions is not well understood. Considering the challenge of identifying a mechanism for the hydrolysis reaction, it is a common practice to employ a kinetic study for determining the mechanism of the cellulose decomposition. A kinetic study covers an analysis of the rates of chemical reactions, the determination of the factors that affect the rates and the reaction mechanism that governs the reactions (Tan *et al.*, 2019). The reaction rate is determined by the increase or decrease in concentration of the reactant over time as a result of chemical reactions, measured in moles or molecules per unit volume (Donaldson and Wren, 2015; Bokhari *et al.*, 2020).

2.9.1 Kinetic modeling and reaction rates

The first model that was successfully used to determine the kinetics of hydrolysis of lignocellulosic materials was developed by Saeman (1945), who studied the hydrolysis reaction of Douglas fir in a batch reactor. He assumed that the hydrolysis of cellulose reaction experienced two successive first-order reactions, as shown in Eq. (2.1) below. k_1 is the rate constant for the conversion of cellulose into glucose while k_2 is the rate constant for glucose decomposition. The model described the hydrolysis of cellulose into glucose followed by the conversion of glucose into other decomposition products by considering the influence of acid concentration in the hydrolysis reaction. However, this model did not provide detailed information on the conversion process involving the production of LA or humins.



Based on Saeman's kinetic model, Girisuta and co-workers developed a more detailed reaction mechanism of LA formation from cellulose through glucose and HMF (Girisuta *et al.*, 2007). The model as shown in Eq. 2.2 also suggested the possibilities of by-product reactions such as humins by assuming that humins can be derived from cellulose, glucose, and HMF. A dark-brown insoluble substance known as humins was produced. These materials are commonly formed as by-products during the decomposition of glucose and HMF.



Where k_{IC} , k_{2C} , k_{IG} , k_{2G} , k_{IH} , and k_{2H} are rate constants for the reactions. These are assumptions used in the development of the kinetics model (Girisuta *et al.*, 2007).

- (1) The modeling of reaction rate equations is achieved by using the power-law approach instead of a pseudo-first-order approach.
- (2) The reaction rate constants are derived from the modified Arrhenius equations that combine the effects of both acid-catalyst concentration and temperature.
- (3) The cleavage of the β -(1 $\rightarrow$ 4)-glycosidic bond in cellulose to glucose by an acid catalyst is the first step in the acid-catalyzed hydrolysis of cellulose.
- (4) No specific reaction occurs between cellulose and glucose and the decomposition products are formed in a parallel-reaction mode.

Based on their kinetic model, the concentration of the individual compounds (C_{cell} , C_{glu} , C_{HMF} and C_{LA}) as a function of time is represented by the following ordinary differential equations:

$$\frac{dC_{cell}}{dt} = -k_{1C}C_{cell} - k_{2C}C_{cell} \quad \text{Eq. (2.5)}$$

$$\frac{dC_{glu}}{dt} = k_{1C}C_{cell} - (k_{1G} + k_{2G})C_{glu} \quad \text{Eq. (2.6)}$$

$$\frac{dC_{HMF}}{dt} = k_{1G}C_{glu} - (k_{1H} + k_{2H})C_{HMF} \quad \text{Eq. (2.7)}$$

$$\frac{dC_{LA}}{dt} = k_{1H}C_{HMF} \quad \text{Eq. (2.8)}$$

Where k_{IC} , k_{2C} , k_{IG} , k_{2G} , k_{IH} , and k_{2H} are rate constants for the reactions.

The mechanism of LA formation proposed by other researchers was consistent with the model proposed by Girisuta *et al.* (2007) except for the production of humins. They

proposed a simpler model that assumed humins were formed directly by glucose decomposition and not from cellulose or HMF as shown in Table 2.11 (de Guzman and de Leon, 2021; Liang *et al.*, 2017; Lopes *et al.*, 2020b; Wang *et al.*, 2019; Zheng *et al.*, 2017).

Table 2.11: Simpler reaction model for the conversion of cellulose into LA

Mechanism	References
Corncob $\xrightarrow{k_1}$ Glucose $\xrightarrow{k_2}$ HMF $\xrightarrow{k_3}$ LA + FA Glucose $\downarrow k_4$ Humins	Liang <i>et al.</i> (2017)
Cellulose $\xrightarrow{k_1}$ Glucose $\xrightarrow{k_2}$ HMF $\xrightarrow{k_4}$ LA + FA Glucose $\downarrow k_3$ Decomposition products	Lopes <i>et al.</i> (2020b) de Guzman and de Leon (2021)
Glucan $\xrightarrow{k_1}$ Glucose $\xrightarrow{k_2}$ 5-HMF $\xrightarrow{k_4}$ LA + FA Glucose $\downarrow k_3$ Humin	Wang <i>et al.</i> (2019) Zheng <i>et al.</i> (2017)

The following assumptions were made prior to the development of the simpler kinetics models (de Guzman and de Leon, 2021; Liang *et al.*, 2017; Lopes *et al.*, 2020b; Wang *et al.*, 2019; Zheng *et al.*, 2017).

- (1) Each elementary step is pseudo-first order.
- (2) The reactions are homogeneous and irreversible.
- (3) Cellulose undergoes hydrolysis to form glucose before being dehydrated to form the desired intermediate which is HMF.
- (4) A portion of glucose is converted to soluble and insoluble humins.
- (5) HMF undergoes hydration to form LA and FA in the last reaction step.

However, a study conducted by Chang *et al.* (2009); Nzediegwu *et al.* (2021); and Qing *et al.* (2018) proved that humins can also be produced from the conversion of HMF into LA. Hence, their kinetic model was developed by assuming that only cellulose could not be directly converted to humins as shown in Table 2.12.

Table 2.12: Reaction model for LA production involving humins from glucose and HMF

Mechanism	References
<pre> graph LR Biomass -- k1 --> Sugars Sugars -- k2 --> 5-HMF Sugars -- k4 --> HUSP[Humic & Unidentified Soluble Products] 5-HMF -- k3 --> Levulinic acid 5-HMF -- k5 --> HUSP </pre>	Chang <i>et al.</i> (2009)
<pre> graph LR Newsprint[Newsprint (Cellulose)] -- k1 --> Glucose Glucose -- k2 --> HMF Glucose -- k3 --> Humins HMF -- k4 --> LA HMF -- k5 --> Humins </pre>	Nzediegwu <i>et al.</i> (2021)
<pre> graph LR Corncob -- k1 --> Glucose Glucose -- k2 --> HMF Glucose -- k4 --> HUSP[Humins and unidentified soluble products] HMF -- k3 --> LA HMF -- k5 --> HUSP </pre>	Qing <i>et al.</i> (2018)

There are several assumptions made prior to the development of the kinetics models (Chang *et al.*, 2009; Nzediegwu *et al.*, 2021; Qing *et al.*, 2018):

- (1) A pseudo-first-order reaction model.
- (2) The formation of intermediates is negligible.
- (3) The hydrolysis is a series of irreversible reactions from biomass or cellulose to sugars (glucose) then to HMF and finally to LA.
- (4) All the unknown products and humin are by-products.
- (5) LA is mainly produced by the decomposition of HMF, and other possible reaction routines are negligible.

In this study, the reaction kinetics may be represented by the concentration of the individual compounds (C_{cell} , C_{glu} , C_{HMF} and C_{LA}) as a function of time by the following ordinary differential equations (ODEs):

$$\frac{dC_{\text{cell}}}{dt} = -k_{1C}C_{\text{cell}} \quad \text{Eq. (2.5)}$$

$$\frac{dC_{\text{glu}}}{dt} = k_{1C}C_{\text{cell}} - (k_{1G} + k_{2G})C_{\text{glu}} \quad \text{Eq. (2.6)}$$

$$\frac{dC_{\text{HMF}}}{dt} = k_{1G}C_{\text{glu}} - (k_{1H} + k_{2H})C_{\text{HMF}} \quad \text{Eq. (2.7)}$$

$$\frac{dC_{\text{LA}}}{dt} = k_{1H}C_{\text{HMF}} \quad \text{Eq. (2.8)}$$

Where k_{1C} , k_{1G} , k_{2G} , k_{1H} , and k_{2H} are rate constants for the reactions.

The MATLAB software provides a variety of built-in functions for numerically solving ODEs (Horsfall *et al.*, 2021). Previous kinetic studies for LA production applied the numerical method *ode15s* (Kupiainen *et al.*, 2011; Mikola *et al.*, 2019), *ode23s* (Sweygers *et al.*, 2018a) and *ode45* (Jung *et al.*, 2021; Zhao *et al.*, 2019; Martina *et al.*, 2022) by using MATLAB to solve the equations. The *ode45* solver is a suitable solution for non-stiff equations because it offers a favorable trade-off between computational cost and accuracy (Horsfall *et al.*, 2021). Hence, in this study, MATLAB *ode45* has been selected to solve the equations.

In this study, the kinetics for the LA synthesis from OPEFB-based cellulose were investigated as there was no report available previously. The model chosen for this study is based on the fact that all reactions involved in the conversion of OPEFB-based

cellulose into LA are irreversible reactions. The kinetics model proposed by Chang *et al.* (2009), Nzediegwu *et al.* (2021) and Qing *et al.* (2018) demonstrated that the production of humins may come from glucose and HMF. Their models assumed that the cellulose conversion to LA was a pseudo irreversible first-order reaction. The result showed a good fit between the experimental data and the kinetic model. Consequently, their approach was used in the kinetic study for the synthesis of LA from OPEFB-based cellulose.

The best fit model in the previous kinetic studies was determined by using several statistical indices such as sum square errors (SSE), prediction interval (PI), confidence interval (CI), root mean square error (RMSE) and coefficient of determination (R^2). These parameters were used in order to reduce errors and improve the accuracy of predicting models as well as output predictions (Hosseinzadeh *et al.*, 2020). With a known probability, the confidence interval provides the information where the population mean is located (Ross, 2020). This is acceptable if a summary measure for a large population is being pursued. However, this confidence interval is not appropriate if the research is trying to find out the observed value for a specific case. Measuring its mean value of prospective responses is often less important than estimating its actual value (Siegel, 2016). Assuming that the additional observation is collected using the same methodology as the previous data, the prediction interval allows the use of sample data to forecast a new observation with a given probability (Ross, 2020). Prediction interval (PI) accurately predicted future data sets within 99.99% of the time.

The correlation coefficient (R^2) value is not an adequate measure for nonlinear regression (Spiess and Neumeyer, 2010). Most of previous studies applied sum of square error (SSE) (Garcés *et al.*, 2017; Girisuta *et al.*, 2013; Ramli and Amin, 2018). However, SSE is sensitive to outliers. The SSE method is also limited due to the error value, which lacks information regarding the model's goodness of fit (Luo, & Paal, 2023). It provides a measurement of the data's variability that has no significance in the model. Alternatively, the root mean square error (RMSE) is presented under the assumption that the errors are unbiased and correspond to a normal distribution. Therefore, both RMSE and the standard error (SE) assist in presenting a comprehensive overview of the error distribution (Chai and Draxler, 2014). As a result, the statistical tools such as PI, SE and RMSE are claimed to be more accurate in the kinetic studies than those implemented in previous kinetics models such as SSE, CI, and R^2 .

In the previous kinetic studies for LA production, Lopes *et al.* (2020a) obtained RMSE values between 0.440 and 1.043 while Lopes *et al.* (2020b) reported the value of RMSE between 0.003 and 8.275. RMSE was employed by Sweygers *et al.* (2018a) in their study but the values were not reported. A model with a lower RMSE value indicates better accuracy and more accurate predictions. Only Weingarten *et al.* (2012) applied SE in their kinetic study for the LA synthesis but the values were not reported. Similar to RMSE, the best model gave a smaller value of SE (Nguyen *et al.*, 2020).

Table 2.13 shows the trend for kinetic rate of constants, k , from the previous studies. The different trends observed in their literature due to their differences regarding reaction conditions such as temperature, type of catalyst, type of reactors and type of

starting materials used in the research. Some studies showed that temperature can give different trends of k values (Nzediegwu and Dumont, 2021; Lopes *et al.*, 2020b; Chang *et al.*, 2009). However, there are also findings indicating that different temperatures did not affect the trend of k values (de Guzman and de Leon, 2021; Ringgani *et al.*, 2022; Qing *et al.*, 2018; Nzediegwu *et al.*, 2021). Interestingly, most studies found that the k_4 value which refers to the conversion of HMF into LA is the highest value compared to other reactions. Nevertheless, the rate determining step for all previous studies is different as shown below in Table 2.13.

Table 2.13: Kinetic trends for rate constants, k in previous studies

Raw Materials	Temperature	Kinetic Trends	References
Wheat straw	190°C	$k_5 < k_2 < k_3 < k_1 < k_4$	Chang <i>et al.</i> (2009)
	210°C	$k_5 < k_2 < k_1 < k_3 < k_4$	
Cellulose	180°C	$k_1 < k_3 < k_2 < k_4$	de Guzman and de Leon (2021)
	200°C	$k_1 < k_3 < k_2 < k_4$	
Corn-cob	150°C	$k_3 < k_1 < k_2 < k_4$	Liang <i>et al.</i> (2017)
Sugarcane	170°C	$k_4 < k_3 < k_1 < k_2$	Lopes <i>et al.</i> (2020b)
	190°C	$k_3 < k_2 < k_4 < k_1$	
Newsprint waste (cellulose)	180°C	$k_5 < k_1 < k_3 < k_2 < k_4$	Nzediegwu and Dumont (2021)
	190°C	$k_1 < k_5 < k_3 < k_2 < k_4$	
	200°C	$k_3 < k_4 < k_5 < k_1 < k_2$	
Newsprint waste (cellulose)	180°C	$k_5 < k_3 < k_2 < k_4 < k_1$	Nzediegwu <i>et al.</i> (2021)
	190°C	$k_5 < k_3 < k_2 < k_4 < k_1$	
	200°C	$k_5 < k_3 < k_2 < k_4 < k_1$	
Corn-cob	170 °C	$k_3 < k_1 < k_2 < k_5 < k_4$	Qing <i>et al.</i> (2018)
	180 °C	$k_3 < k_1 < k_2 < k_5 < k_4$	
	190 °C	$k_3 < k_1 < k_2 < k_5 < k_4$	
Spirulina platensis Residue	160 °C	$k_1 < k_2 < k_3 < k_5 < k_4$	Ringgani <i>et al.</i> (2022)
	180 °C	$k_1 < k_2 < k_3 < k_5 < k_4$	

k_1 = biomass/cellulose $\rightarrow$ glucose

k_2 = glucose $\rightarrow$ HMF

k_3 = glucose $\rightarrow$ humin

k_4 = HMF $\rightarrow$ LA

k_5 = HMF $\rightarrow$ humin

2.9.2 Thermodynamic studies for LA Synthesis

The activation energy refers to the minimum amount of energy required for a chemical to undergo certain chemical reactions or processes, represented in kcal/mol or kJ/mol (Shahid et al., 2021). Table 2.14 compares the activation energy for LA production from previous studies. The majority of previously reported reaction pathways resemble the proposed kinetic model in this study, given that the formation of humins may also come from glucose and HMF except in the studies by Dussan *et al.* (2013), Lopes *et al.* (2020a) and Liang *et al.* (2017) which did not report the pathway for formation of humin from HMF. It is possible to observe that the values of activation energy for glucose production in all studies are high. The findings indicate that a greater temperature dependence on the production of glucose reactions compared to humins, HMF and LA productions (Lopes *et al.*, 2020b). Most studies found that the activation energy of LA production from HMF is lower compared to other reactions, showing that this reaction is easier than the others. Previous studies have reported that the activation energy for HMF rehydration to LA falls into the range of 24.42 to 121.30 kJ/mol.

Previous research on thermodynamic analysis of LA production was undertaken to a limited extent. All thermodynamic properties such as the entropy change (ΔS), enthalpy change (ΔH) and Gibbs free energy change (ΔG) offer valuable information to explain the reaction phenomenon for LA production. The positive and negative values of ΔH represented exothermic (heat release) and endothermic (heat absorption) reactions (Li *et al.*, 2019). During the process, a positive ΔS° value indicates increased randomness at the solid–solution interface, while a negative ΔS° value indicates the

opposite event of randomness (Sahmoune, 2019). A negative value of ΔG means the reaction will occur spontaneously and thermodynamically favorably. Meanwhile, a positive value of ΔG signifies that the reaction is non-spontaneous, subject to thermodynamic limitations and unfavorable (Yarbaş and Ayas, 2023). To the best of our knowledge, only one research study was conducted to study thermodynamic properties for LA production from oil palm biomass which was performed by Tiong *et al.* (2020). However, a thermodynamic study for LA formation from OPEFB-based cellulose is still absent. Furthermore, the results from their study Tiong *et al.* (2020) need to be substantiated for any missing information.

2.10 Summary

According to the literature review in this chapter, comprehensive insights were provided into the production of LA as a valuable platform chemical. This valuable chemical can be produced from various raw materials, including polysaccharides, monosaccharides and biomass. Based on the mechanism, LA can be generated from cellulose or hemicellulose. Cellulose emerges as a preferred starting material due to its abundance and ease of conversion to LA compared to hemicellulose. The route from cellulose to LA is relatively straightforward, making it an attractive choice for LA production.

In LA synthesis, the choice of catalyst plays a crucial role in determining the efficiency and selectivity of the reaction. Based on the previous studies, heterogeneous catalysts such as metal catalysts and sulfonated carbon catalysts are widely applied for LA

production. A synergy between these two types of catalysts has a good potential to produce LA to enhance catalytic activity and stability.

Considering environmental concerns and sustainability, biomass-derived feedstock is recommended for LA production. Cellulose, a major component of biomass, can be isolated and utilized as a renewable feedstock for LA synthesis. However, the complex structure of cellulose poses challenges in its conversion to LA, necessitating pretreatment processes to enhance reactivity and accessibility. MSHs have emerged as effective solvents for cellulose pretreatment, facilitating the disruption of cellulose structure and improving its suitability for LA production. Optimization of reaction conditions is essential to maximize LA yield and selectivity, necessitating the study of various parameters and kinetic aspects of LA synthesis.

Overall, the literature underscores the importance of selecting appropriate raw materials, catalysts, and process conditions for efficient and sustainable LA production. By leveraging biomass resources, optimizing reaction pathways and employing effective catalysts and pretreatment methods, LA synthesis can be enhanced while addressing green and environmental concerns. Continued research efforts in this area are vital for advancing LA production processes and realizing their full potential in the realm of renewable chemicals.

Table 2.14: Activation energy values (kJ/mol) for the synthesis of LA

Reaction Steps	Kinetic parameter	Activation energy (kJ/mol)							
		Dussan <i>et al.</i> (2013)	Zhao <i>et al.</i> (2019)	Ringani <i>et al.</i> (2022)	Qing <i>et al.</i> (2018)	Nzediegwu and Dumont (2021)	Lopes <i>et al.</i> (2020a)	Liang <i>et al.</i> (2017)	Girisuta <i>et al.</i> (2007)
Biomass/Cellulose → Glucose	k ₁	188.90	39.50	92.53	48.18	10.18	57.50	135.32	151.50
Glucose → HMF	k ₂	155.50	96.80	70.52	45.99	58.79	32.54	134.36	152.20
Glucose → Side products	k ₃	186.20	61.00	28.71	76.32	77.83	37.60	101.58	164.70
HMF → LA	k ₄	121.30	81.40	55.77	57.04	36.45	24.42	96.51	110.50
HMF → Side products	k ₅	n.a	210.00	94.86	67.25	136.25	n.a	n.a	111.30

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

The materials, experimental apparatus and experimental works used to accomplish the goals of the study are briefly outlined in this chapter. The methodology centered on the synthesis of LA from OPEFB by using sulfonated carbon metal catalyst. The screening on different compositions of metal catalysts (Iron and Nickel) was conducted. The best metal composition in catalyst screening is further investigated in order to find the best composition of metals supported on sulfonated carbon catalyst. The physicochemical properties of all synthesized catalysts were studied using FESEM, EDX, BET, XRD, FTIR, ICP, XPS, TGA, XRF and NH_3 -TPD. The overall research flow in this study is summarized in Figure 3.1 which covers catalyst preparation, acid hydrolysis reaction, cellulose dissolution, process optimization and reaction kinetic. Based on the chart, the sequences of experiment consist of sulfonated carbon metal catalyst preparation method and catalytic reaction for LA production from OPEFB-based cellulose using selected catalyst. The details of sequence were discussed on the respective subtopics.

3.2 Materials and chemicals

Detail information such as materials and chemicals disclosed in this section. The biomass which was chosen for this research is OPEFB. The sample was obtained from Sime Darby Plantation, Felda Pulau Carey Selangor as a partially dried raw material. Table 3.1 provides an inventory of chemicals, accompanied by their respective details, which are utilized in the entirety of the study.

Table 3.1. List of chemicals

Chemicals	Supplier	Purity (%)	Usage
Sulfuric Acid	Fisher Scientific	96.0	Catalyst preparation
Sodium Hydroxide	R&M Chemicals	99.0	Catalyst preparation
Iron (III) chloride	R&M Chemicals	99.0	Catalyst preparation
Nickel (II) nitrate	R&M Chemicals	99.0	Catalyst preparation
Ethanol	Systerm	95.0	Catalyst preparation
Acetone	R&M Chemicals	99.5	Catalyst preparation
Cellulose	R&M Chemicals	99.0	Reaction
Toluene	R&M Chemicals	98.0	Cellulose dissolution
Sodium Chlorite	Systerm	96.0	Cellulose dissolution
Lithium Bromide	R&M Chemicals	99.0	Cellulose dissolution
Lithium Chloride	R&M Chemicals	99.0	Cellulose dissolution
Zinc Chloride	R&M Chemicals	98.0	Cellulose dissolution
Glucose	Friendemann Schmidt	99.0	HPLC calibration
Formic Acid	Acros Organic	98.0	HPLC calibration
Levulinic Acid	Sigma Aldrich	99.0	HPLC calibration
HMF	Sigma Aldrich	99.0	HPLC calibration

Ethanol and acetone served as the washing agents for the catalysts. The preparation of calibration curves involved diluting HPLC standards into five concentrations: 200 ppm, 400 ppm, 600 ppm, 800 ppm, and 1000 ppm, which were used for further sample analysis. The required concentration for each HPLC standard was achieved through dilution with ultrapure water.

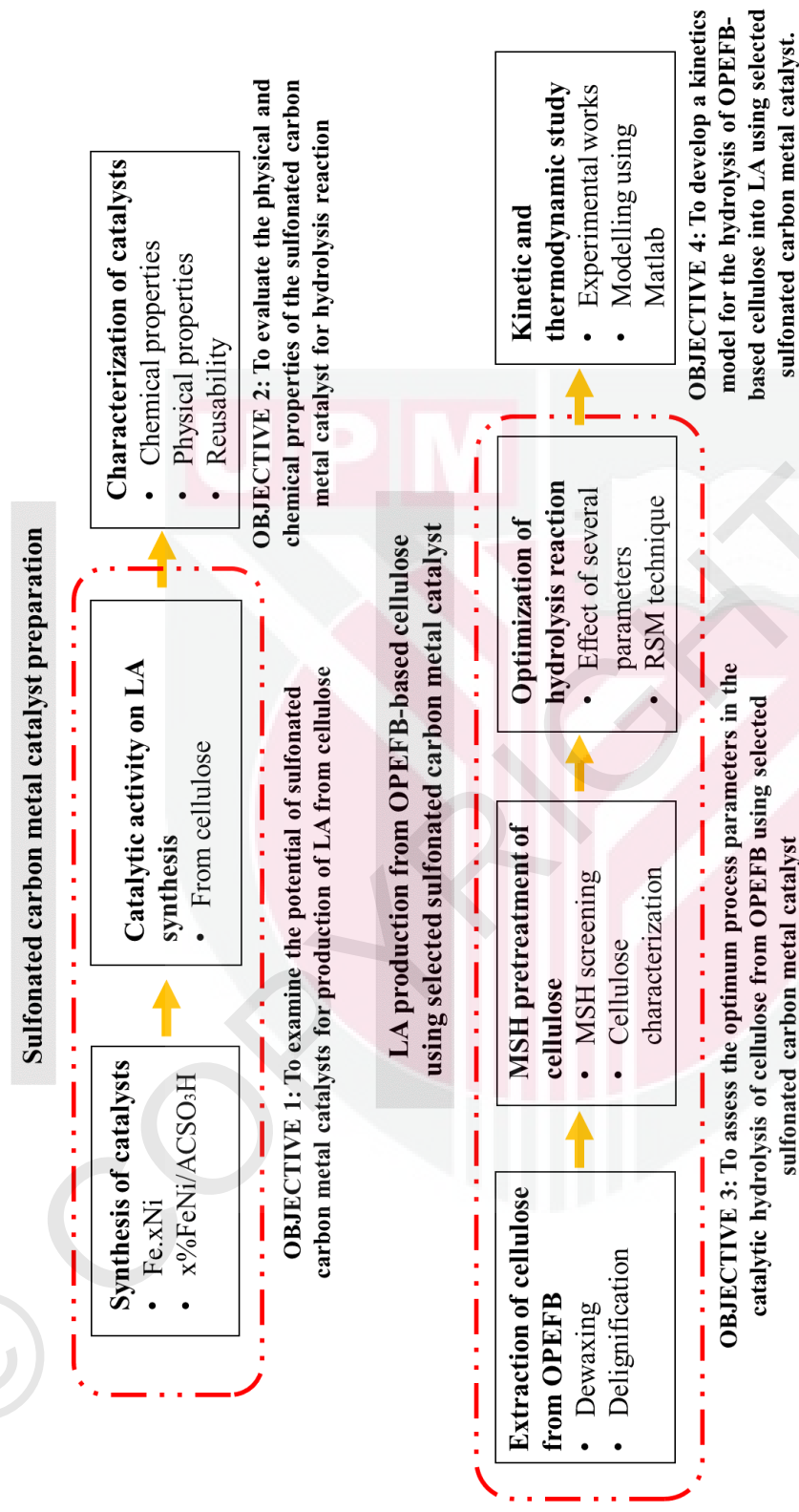


Figure 3.1: Overall methodology for this study

3.3 Catalyst preparation

The preparation of catalyst used in this study involved three stages: first, metal catalysts were made, then sulfonated carbon catalysts, and last, sulfonated carbon metal catalysts. The activation of the catalysts took place in the hydrothermal reactor as shown in Figure 3.2.

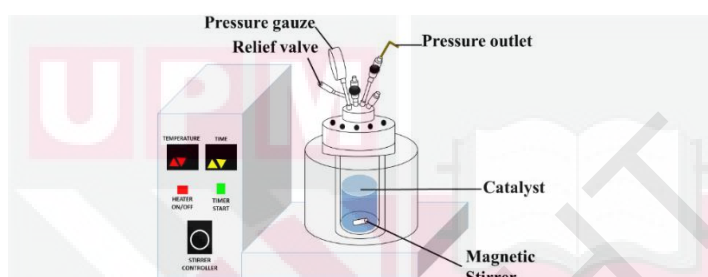


Figure 3.2: Hydrothermal reactor for catalyst activation

3.3.1 Metal catalyst

The method as shown in Figure 3.3 was started with the preparation of iron chloride and nickel nitrate solution. Different loadings of iron (III) chloride and nickel (II) nitrate between 25% to 100% were prepared as shown in Table 3.2. The amount of metal salts used is determined based on the calculation in Appendix A. For Fe₇₅Ni catalyst, 6.05 g iron (III) chloride and 18.58 g nickel (II) nitrate were dissolved in 10 mL distilled water by stirring at the room temperature. A 90 mL mixture of pure ethanol and distilled water (2:1) was added. Then, 10 mL of 6M NaOH was added as a co-precipitate until pH reached neutral. To activate the catalyst, the solution was transferred into a Teflon-lined stainless steel autoclave and subjected to a hydrothermal process at 180 °C for 12 hours. Subsequently, the solution was cooled into room temperature and precipitate was obtained after filtration. The powder was

then washed repeatedly by using pure ethanol and acetone until pH of the filtrate same as the pH of wash water. After that, the catalyst produced was oven-dried overnight. Finally, the sample was calcined at 300 °C for 3 h to obtain iron-nickel metal catalysts. The resultant materials are designated as Fe.xNi while the $\text{Ni}(\text{NO}_3)_2$ metal loading was denoted as x as shown in the Table 3.2 below.

Table 3.2: Different loading of FeCl_3 and $\text{Ni}(\text{NO}_3)_2$

Catalyst	Iron (III) chloride, FeCl_3	Nickel (II) nitrate, $\text{Ni}(\text{NO}_3)_2$
Fe.25Ni	75%	25%
Fe.50Ni	50%	50%
Fe.75Ni	25%	75%
Fe	100%	0%
Ni	0%	100%

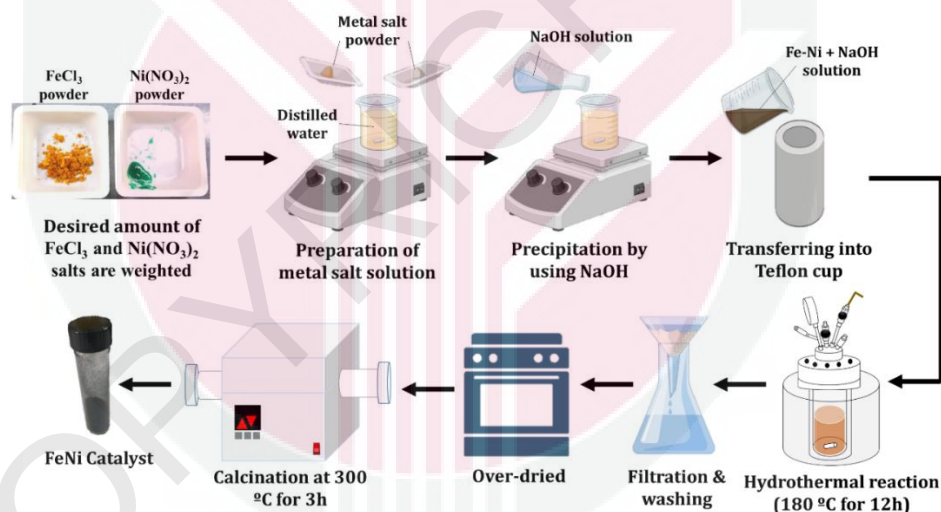


Figure 3.3: Experimental steps for the metal catalyst preparation

3.3.2 Sulfonated carbon catalyst

Sulfonated carbon catalyst was prepared based on a previous study by Zhang and Chen (2016) as shown in Figure 3.4. In a typical process, 5g cellulose powder was carbonized at 400 °C for 1 h under N_2 atmosphere to produce a cellulose-derived amorphous carbon denoted as AC. As for sulfonation treatment, the resulting carbon

was mixed with 98% H_2SO_4 (carbon mass to H_2SO_4 volume ratio at 1:10), followed by heating at 150 °C for 12 hours in a N_2 atmosphere to introduce functional $-\text{SO}_3\text{H}$ groups. Soon afterward, the mixture was diluted with deionized water and cooled to room temperature slowly followed by filtrating and washing with hot deionized water (348 K) until pH of the filtrate same as the pH of wash water. Finally, the resulting catalyst, denoted as ACSO_3H was oven-dried for overnight.

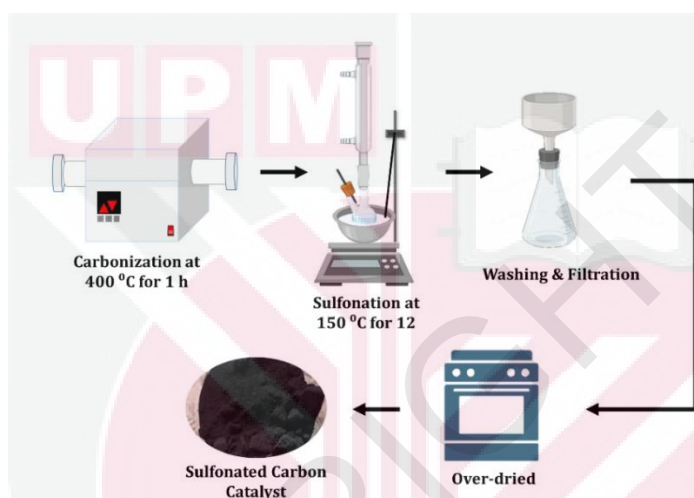


Figure 3.4: Experimental steps for the sulfonated carbon (ACSO_3H) catalyst preparation

3.3.3 Sulfonated carbon metal catalyst

The preparation of the sulfonated carbon metal catalyst was conducted as shown in Figure 3.5. This method involved the impregnation of a specifically chosen Fe.xNi catalyst onto a support composed of sulfonated carbon by referring method by Zhang and Chen (2016) and Zainol *et al.* (2022). The beginning steps were similar to the steps for producing metal catalyst in the section 3.4.1. The metal salt solution containing FeCl_3 and $\text{Ni}(\text{NO}_3)_3$ was prepared followed by the addition of NaOH for precipitation. Both steps were accomplished by stirring at the room temperature. After that, the

sulfonated carbon (ACSO₃H) catalyst was transferred into Teflon cup, dispersed in the 90 mL of ethanol and deionized water and sonicated for 15 minutes. Then, different loadings of Fe-Ni metal solution were added for impregnation of metals with ACSO₃H catalyst. The mixture of both catalysts was subjected to a hydrothermal process at 180 °C for 12 hours. The mixture was cooled into room temperature and precipitate was obtained after filtration followed by oven-dried for overnight. Finally, the sample was calcined at 300 °C for 3 h to obtain iron-nickel doped sulfonated carbon catalysts. Resulting catalysts were designated by adding number at the beginning of each name by following the different loading of Fe-Ni added based on the weight of support (ACSO₃H). For example, 5%FeNi/ACSO₃H is referred to 5% Fe-Ni loading.

Table 3.3: Different loading of Fe-Ni metal in the catalysts

Catalyst	Fe-Ni
5%FeNi/ACSO ₃ H	5%
10%FeNi/ACSO ₃ H	10%
15%FeNi/ACSO ₃ H	15%
20%FeNi/ACSO ₃ H	20%

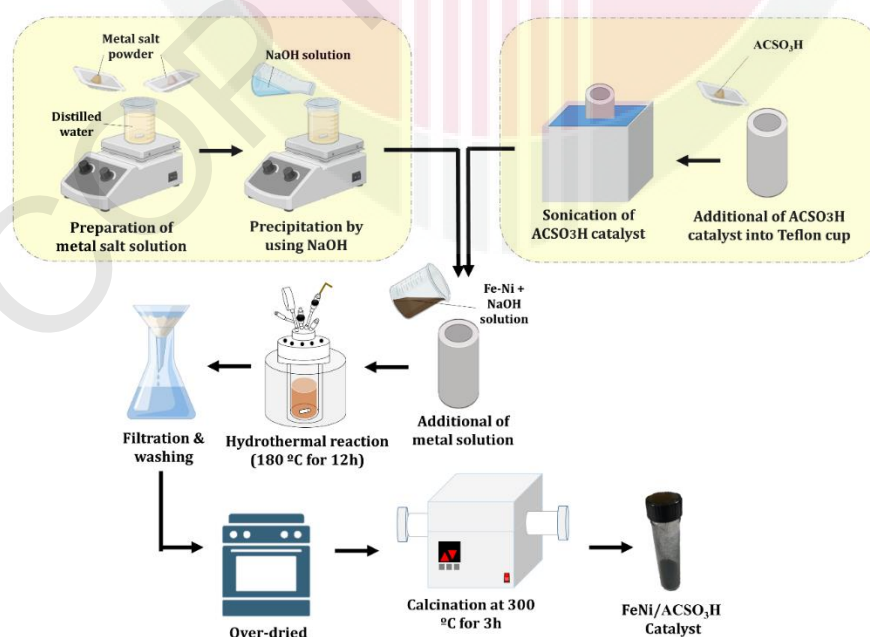


Figure 3.5: Experimental steps for the sulfonated carbon metal catalyst preparation

3.4 Catalyst test by acid hydrolysis reaction

The hydrolysis procedure used to produce LA was carried out in a specially made autoclave reactor. The autoclave was filled with a 50 mL reactant solution comprising 5.0 g of glucose or cellulose and 0.15 g (3%) of synthesized catalyst prior to the catalytic process. Subsequently, the reactor was heated to 180 °C, pressurized with nitrogen, and stirred at 600 rpm for 5 hours. For catalyst screening, the requirements remained unchanged. The reaction liquid was allowed to cool to room temperature when the reaction was finished. Additionally, a blank sample was executed.

3.4.1 Hydrothermal reactor

The reactor setup comprised of a 150mL stainless steel 316 batch reactor (Model name: ACL01-150). This stainless steel is corrosion resistant to sulfuric acid solution. The experimental set up for hydrothermal autoclave reactor is shown in Figure 3.6. To keep the temperature constant, the reactor was equipped with an electrical heater and thermocouple. This reactor has sampling valve to collect the samples. In order to maintain the operational pressure inside the reactor, the six bolts were then tightened to completely closed the reactor before each reaction started.

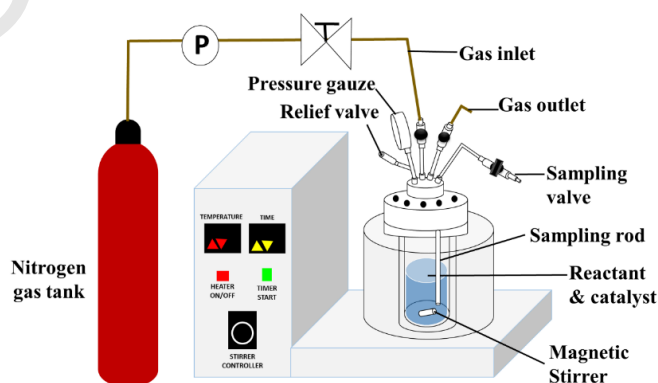


Figure 3.6: Schematic diagram of reactor for hydrolysis reaction

3.4.2 Hydrolysis product analysis

The LA concentration and other degradation products such as glucose, HMF and FA in the water phase were quantified by High Performance Liquid Chromatography (HPLC), model Sykam S 600 Systems. The chromatographic column used was Rezex RFQ Fast Acid (100mm x 7.8mm x 8 mm) of Phenomenex (California, USA) using a cation guard cartridge (Bio-Rad Laboratories). HPLC was run at 85 °C using a mobile phase of 0.01 N sulfuric acid at a flow rate of 1.0 mL/min and using Refractive Index Detector (RID) and UV-vis for detector.

The yields of products were calculated based on the theoretical yield according to Mthembu *et al.* (2021). For glucose yield, the calculation was made as follows:

$$\begin{aligned} & \text{Glucose Yield (\% based on theoretical yield)} && \text{Eq. (3.1)} \\ &= \frac{\text{Conc of glucose } \left(\frac{g}{L}\right) \times \text{volume (L)} \times \text{conversion factor}}{\text{mass of cellulose (g)}} \times 100 \end{aligned}$$

where 0.9 is the conversion factor for glucose (or 162/180). 180 is the molecular weights of glucose and 162 is the molecular weights of the monosaccharide units of cellulose. The calculation for yield of LA, HMF and FA was made based on this equation:

$$\begin{aligned} & \text{Product Yield (\% based on theoretical yield)} && \text{Eq. (3.2)} \\ &= \frac{\text{Conc of product (g/L)} \times \text{volume (L)}}{\text{mass of cellulose (g)} \times \text{conversion factor}} \times 100 \end{aligned}$$

where conversion factor for HMF is 0.77, LA is 0.71 and FA is 0.28 based on their molecular weight per molecular weight of cellulose, where the molecular weight of HMF, LA and FA are 126, 46 and 116 respectively.

In addition, the yield of LA (wt%) was also determined to compare with previous studies which reported the yield in weight percentage. Calculation was made as weight percentages of the LA to the weight of the starting cellulose as followed:

$$LA\ Yield\ (wt\%) \quad \text{Eq. (3.3)}$$

$$= \frac{\text{Weight of LA (g)}}{\text{Weight of cellulose (g)}} \times 100$$

3.5 Catalyst reusability

In the solid acid catalytic system, recycling the catalyst is an important aspect. Glucose was utilized as a reactant to test the sulfonated carbon metal catalyst's effectiveness since it is soluble in water, allowing for the catalyst and product solution to be separated after the reaction (Sweygers et al., 2018a). The optimization of glucose conversion into LA was done to select the best condition of acid hydrolysis for catalyst reusability. Parameters such as temperature, catalyst loading and reaction time were investigated. 5g of glucose was added into the reactor filled with 50 mL distilled water under optimum reaction conditions for five successive runs. After each runs, the catalyst was recovered using centrifugation of the reaction mixture solution at a speed of 3500 rpm for a duration of 15 minutes. The recovered catalyst was then washed twice to eliminate adhered organic impurities and dried in an oven at temperature of 105 °C for 12 h. The amount of metal leached in the reusability study was determined

using ICP-OES analysis. Furthermore, the spent catalyst collected after fifth cycle was characterized by BET and TPD-NH₃ analysis to study the effect on surface area and density of acid sites in the catalyst.

3.6 Preparation of OPEFB-based cellulose

The preparation of cellulose from OPEFB involved the preparation of OPEFB collected from the plantation and the isolation of cellulose from this oil palm biomass waste. Both steps are explained in the section 3.6.1 and 3.6.2 below.

3.6.1 Oil palm empty fruit bunch preparation

OPEFB fibers is chosen as the raw material for this study. The OPEFB was collected directly from the conveyor after the shredding process from Sime Darby Plantation, Felda Pulau Carey, Selangor. After being brought back from the plantation, the shredded OPEFB fibers was washed with tap water to remove the oil and debris on the surfaces. The shredded OPEFB fibers was sun-dried until partially dried and then further oven-dried (Model Memmert 600, Germany) at 105°C for 24 hours or until the moisture content is less than 10%. After the shredded OPEFB fibers was cooled to room temperature, these fibers were grounded (Universal Cutting Mill – Fritsch GmbH, Germany) at Institute of Tropical Forestry and Forest Products (INTROP) and sieved to an approximate length of 125 to 250 µm and then stored in a sealed plastic bag. The flow diagram for preparing biomass as raw materials is presented in Figure 3.7.



Figure 3.7: Flow diagram for biomass preparation

The Van Soest analysis methods which are acid detergent fiber (ADF), neutral detergent fiber (NDF), and acid detergent lignin (ADL), were employed to determine the amount of lignin, cellulose, hemicellulose, and ash in OPEFB (Van Soest *et al.*, 1991). For compositional analysis, prepared OPEFB was sent to the Malaysian Agriculture Research and Development Institute (MARDI), Serdang. The percentage of cellulose, hemicellulose, lignin and extractives were calculated using the Goering and Van Soestt (1970) equation as shown below:

$$\text{Cellulose (\%)} = \text{ADF} - \text{ADL} \quad \text{Eq. (3.4)}$$

$$\text{Hemicellulose (\%)} = \text{NDF} - \text{ADF} \quad \text{Eq. (3.5)}$$

$$\text{Lignin (\%)} = \text{ADL} \quad \text{Eq. (3.6)}$$

$$\text{Extractives (\%)} = 100 - \text{NDF (\%)} \quad \text{Eq. (3.7)}$$

3.6.2 Cellulose isolation from OPEFB

The process of cellulose isolation involved dewaxing, followed by delignification through alkali pretreatment and a bleaching method. The procedure for dewaxing was as follows: selected fibers were placed inside a cellulose thimble weighing 50 g and then introduced into a Soxhlet apparatus. Figure 3.8 displays the specific apparatus configuration used for Soxhlet extraction in the dewaxing procedure. During Soxhlet extraction, OPEFB fibers that have been ground and sieved was immersed in a solvent blend of ethanol and toluene (in a 1:2 ratios) for a minimum of 6 hours or until the solvent turns clear, yielding dewaxed OPEFB lignocellulose fibers. The Soxhlet procedure was performed for roughly 10 to 12 hours, allowing sufficient time for the solvent in the Soxhlet tube to attain the desired clarity.

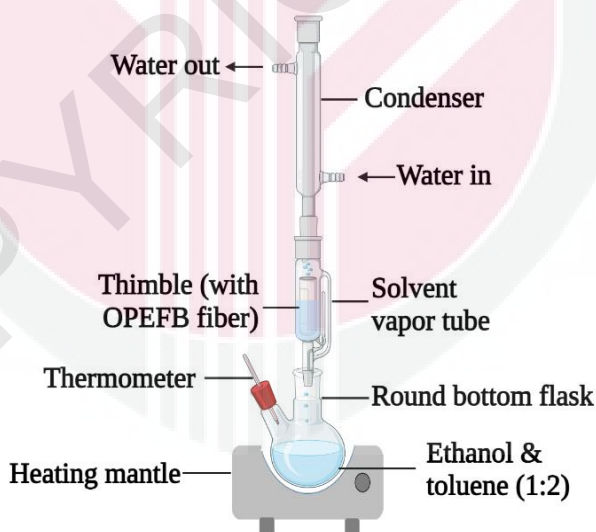


Figure 3.8: Soxhlet extraction for dewaxing process

The large-scale production of cellulose for the next steps was accomplished through the implementation of a batch reaction. Figure 3.9 displays the reactor configuration, which includes an oil-based heating mantle, a stirrer with adjustable rotation and a

condenser. The jacketed glass reactor with a maximum capacity of 5.0 L was used to carry out all pretreatments including alkali pretreatment, bleaching and refluxing.



Figure 3.9: 5.0 L jacketed glass reactor

The entire procedure consisted of three main steps. Firstly, an alkali pretreatment was carried out using a 5% wt NaOH solution at a temperature of 80 °C for a duration of 1 hour. Subsequently, a bleaching pretreatment was performed by utilizing a 5% wt sodium chlorite (NaClO_2) solution at 90 °C for 2 hours and repeated twice to ensure the effectiveness. Lastly, the process concluded with a refluxing step using a 2% HCl solution for 2 hours. Filtration was employed to separate the insoluble fibers residue which was subsequently washed with tap water and finally rinsed with distilled water until it became neutral. As a final step, the fibers were oven dried overnight to eliminate moisture and subsequently ground using a grinder to produce cellulose powder. The cellulose obtained was evaluated for its potential to generate LA. 1g of cellulose was used in the hydrolysis reaction at 160 °C for 2 hours using 0.1g 15%FeNi/ ACSO_3H catalyst. The resulting LA yield was then compared with LA generated from commercial cellulose.



Figure 3.10: Grinder used to grind the cellulose after the treatments

3.7 Non-dissolving pretreatment by molten salt hydrate

A series of MSHs solutions were prepared for non-dissolving pretreatment of cellulose. MSHs used in this study was LiBr, LiCl and ZnCl₂. These solutions were chosen based on their performance in improving the accessibility of cellulose in the previous studies. The preparation of an MSHs solution involved the mixture of MSHs with deionized water in a molar ratio of 1:3 as shown in the first step of experimental setup in Figure 3.11 by referring method by Huang *et al.* (2022). In summary, a mixture consisting of 5 grams of cellulose based-OPEFB and 95 grams of MSHs solution were introduced into a glass container with a capacity of 250 mL. The contents were vigorously shaken for a duration of 10 seconds to ensure uniform blending of the liquid and solid components. Subsequently, mechanical stirring was employed at a speed of 500 rpm, while maintaining a room temperature for 30 minutes. This condition was chosen according to the study by Huang *et al.* (2022). The solids were recovered by filtering them through a 0.22-micron filter membrane under vacuum. The collected cellulose was washed with deionized water until the conductivity of the material was less than 10 $\mu\text{S cm}^{-1}$. The cellulose samples were kept wet in a refrigerator until the

next study. The reusability of selected MSHs solution was also been studied. The liquid obtained after washing and filtration of the selected MSHs-pretreated cellulose was collected. The recover MSHs solution with different reuse times was reused in the pretreatment of fresh OPEFB-based cellulose and the effect of cellulose hydrolysis after the pretreatment was investigated.

The obtained cellulose was tested for LA production. 1 g of cellulose was used in the hydrolysis process at 160°C for 2 h using 0.1 g of a 15% FeNi/ACSO₃H catalyst. The performance of different MSHs pretreated cellulose was evaluated based on the yield of LA. Furthermore, the effects of operating conditions on the reaction of LA production such as temperature, time and catalyst loadings were also investigated to optimize the yield of LA from MSHs-treated OPEFB-based cellulose.

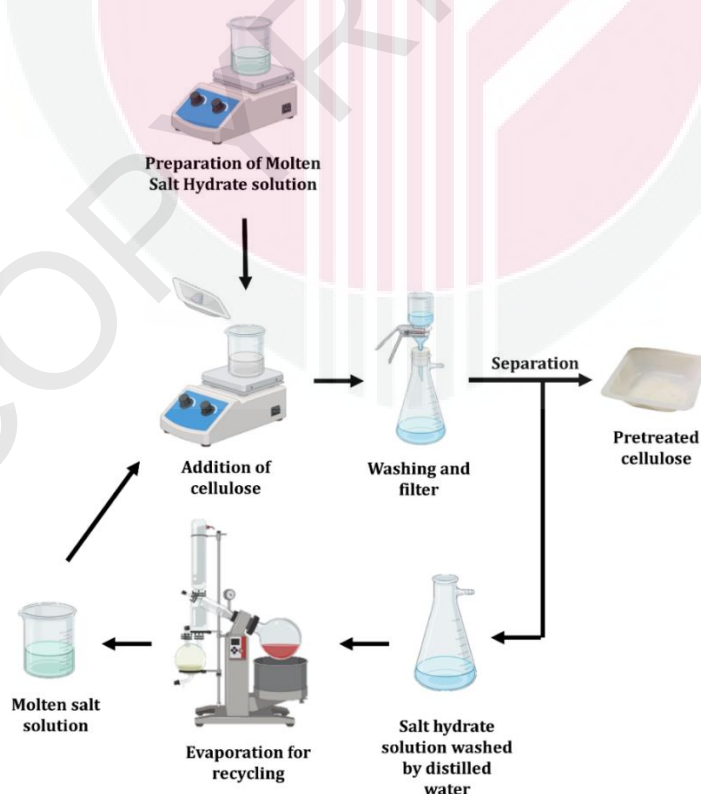


Figure 3.11: Experimental setup for cellulose non-dissolving pretreatment

3.8 Characterization of raw materials and catalyst

The synthesized catalysts were thoroughly characterized to evaluate a comprehensive description of the composition and structure of the catalyst. This includes techniques such as structural analysis (SEM and FESEM), surface area analysis (BET analysis), acidity (TPD-NH₃ analysis), thermal properties (TGA-DTG) and chemical properties (XRD, XRF, EDX, ICP-OES, XPS, FTIR).

3.8.1 Surface area and porosity analysis

The physical properties of catalyst such as pore size distribution, surface area, total pore volume and size were obtained by using Branauer Emmett Teller (BET) method and Barrett–Joyner–Halenda (BJH) method (Abdul Manap *et al.*, 2018). This method was performed using Micromeritics ASAP-2020 instrument (Micromeritics Instrument, Norcross, GA, USA) in Institute of Nanotechnology and Nanoscience, Universiti Putra Malaysia (UPM). This technique is extensively employed in the field of surface study particularly for the determination of solid surface area through the process of physical adsorption of gas molecules onto the surface. The measurement of gas adsorption at incrementally increasing pressure levels enables the estimation of surface area. Nitrogen gas is chosen due to its inert characteristics, ready availability, high purity, spherical shape, tiny molecular size and inexpensive. The nitrogen adsorption-desorption isotherm at a temperature of -196 °C was obtained using the Quantachrome equipment (Autosorb-1 model). The nitrogen gas was physically adsorbed on the surface of the sample at this temperature. The BET equation as shown in Equation 3.8 was employed to describe the relationship between the amount of

adsorbed gas molecule (X_m) at a given relative pressure (P/P_0 , in the range of 0.05 to 0.35) and BET constant (c).

$$\frac{1}{V_a \left[\frac{P_0}{P} - 1 \right]} = \frac{C - 1}{V_m \times C} \left[\frac{P}{P_0} \right] + \frac{1}{V_m \times C} \quad \text{Eq. (3.8)}$$

where P is partial vapour pressure of adsorbate gas in equilibrium with the surface at 77.4 K (b.p. of liquid nitrogen) and P_0 is saturated pressure of adsorbate gas, both in pascals. V_a is volume of gas adsorbed at standard temperature and pressure (STP) [273.15 K and atmospheric pressure (1.013×10^5 Pa)] while V_m is volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, both in millilitres. C is a constant of free energy adsorption or dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample.

3.8.2 Crystallinity analysis

X-ray Diffraction (XRD) is a characterization and identification method for the shape of the lattice structure, the composition of chemical and crystallization degree or amorphous properties of an adsorbent. These properties were determined by Shimadzu, XRD 6000 diffractometer utilizing Cu-K α radiation electrons generated by Philips diffraction X-ray tube with wavelength λ , = 0.1541 nm, voltage of 30 kV and generator current of 30 mA. The scanning of the sample was conducted using an instrument within the set range of theta, spanning from 2° to 60° , at a 4° min^{-1} scan speed. The electron radiation utilized was accelerated with a broad focus 2.7 kW type, specifically applied to the catalyst. The XRD data obtained were processed by using X'Pert High Score Plus software and cross matched the diffraction peaks obtained with

Joint Committee on powder Diffraction Standard (JCPDS) database version 2.6 and International Centre for Diffraction Data (ICDD). The calculation of the degree of crystallinity or crystalline index of the samples can be done using equation as follows:

$$CrI = \frac{\text{area all crystalline peaks}}{\text{area crystalline peaks} + \text{amorphous peaks}} \quad \text{Eq. (3.9)}$$

where CI denotes to crystalline index or degree of crystallinity of material (unitless).

3.8.3 Chemical state analysis

The chemical states and atom concentration on the surface of the catalyst can be analyzed using XPS technique. The analyzes cover the study of the kinetic energy demonstrated by the photoelectrons that are emitted from the sample. The amount of electrons emitted depends on the atom concentration. The analysis was carried out in i-CRIM lab Universiti Kebangsaan Malaysia using XPS AXIS Ultra Kratos (XSAM HS) equipped with hemisphere-type photoelectron energy analyzer. The Mg K α (1253.6 eV) is X-ray source for this analysis. Before conducting the test, a dry solid form catalyst sample weighing 0.5 g was finely ground and pressed into a small aperture within a stainless steel sample stub. The sample is thereafter introduced into the pretreatment chamber and allowed to remain within the pre-vacuum chamber overnight under a pressure of 10⁻⁶ torr. Subsequently, the sample is transferred to the analysis room (SAC room) where the data analysis is performed under a pressure of 5 x 10⁻⁹ torr. The generated peak is subsequently analyzed using the CASA XPS program and cross-referenced with the XPS handbook for the purpose of identifying curve fitting and the background of "serry" type.

3.8.4 Amount of acidity analysis

Acidity strength distribution and total acid site density of the sulfonated carbon metal catalysts were measured by TPD-NH₃ method using the ThermoFinnigan TPDRO 1100 temperature programmed ammonia desorption analyzer at NANOCAT Research Center, Institute for Advanced Studies (IAS), University of Malaya. The pretreatment was performed for 30 minutes under a Nitrogen flow of 20 mL min⁻¹ at 250 °C by placing approximately 50 mg of the sample into a quartz tube to remove moisture. Later, the cleaned catalyst was treated with NH₃ gas for 1 h at room temperature. The excess NH₃ gas on the catalyst surface was purged out with nitrogen gas (30 mL min⁻¹) for 30 min. The ammonia desorption analysis was performed by flowing helium gas (30 mL min⁻¹) with heating from 50 °C to 950 °C with a 10 °C min⁻¹ heating rate. The TPD/R/O 1100 software measured and recorded the amount of ammonia gas desorbed known as the acid density for each sample.

3.8.5 Functional group determination

FTIR analysis was conducted using Thermo Fisher Scientific, Nicolet 6700 infrared spectrophotometer at Institute of Plantation Studies (IKP), UPM. The purpose of the analysis is to determine the functional group presence in the structure of the sulfonated carbon metal catalyst and the raw materials. In preparation for the analysis, the sample was ground into a fine powder using a ceramic mortar and pestle. The spectral measurements of all samples were taken throughout the wavenumber range of 600 to 4,000 cm⁻¹ and the corresponding transmittance values were recorded.

3.8.6 Degradation behaviour analysis

Thermal analysis was performed to investigate the stability, thermal properties and degradation of raw material, cellulose and catalysts. The analysis was conducted using a thermal analyzer Mettler Toledo Model: TGA-DSC HT-3 for both thermal gravimetric analysis (TGA) and differential thermal analysis (DTG) at Faculty of Science, UPM. The weight changes of material as a function of temperature or time were measured by TGA. About 10-20 mg of the cellulose and catalyst sample was weighed and placed in a crucible. The sample was placed inside the furnace and programmed for continuous heating from room temperature to 1000 °C under nitrogen gas with the heating rate set at 10 °C/min flow of 50 mL/min. Furthermore, the TGA analysis was also used to determine the amount of cellulose, hemicelluloses and lignin in OPEFB. Hence, the results obtained can be compared with the proximate analysis.

3.8.7 Morphology structure analysis

Analysis and characterization of raw materials and catalyst morphological structure was performed using scanning electron microscope (SEM), brand Hitachi, model S3400N at Universiti Tenaga Nasional and field emission scanning electron microscopy (FESEM) model JEOL JSM-7600F located in Institute of Bioscience UPM. Both microscopies generate visual representations of a material by directing a focused electron beam onto its surface. 150–500x magnification and an accelerating voltage range of 10–15kV were applied to acquire the scanning images. The sulfonated metal catalyst was mounted onto the SEM stubs which was layered with sticky carbon

tape coated with platinum to reduce electrical charging. The working distance and accelerating voltage were 7.9 mm and 3 kV for the FESEM imaging.

3.8.8 Elemental analysis

FESEM instrument is integrated with an energy dispersive X-ray detector (Oxford INCA X-MAC 51 XMX 0021) to determine elemental concentration of the catalyst. EDX is a quantitative analysis conducted to measure the thickness layer of sample in the form of thin film and the element composition present in a sample. EDX also used for mapping of elements in a sample. The percentage by weight (wt%) of each element in the catalyst sample was figured out and their distribution was shown using spectrum imaging. The working distance and accelerating voltage were 15 mm and 20 kV for the EDX measurement.

The elemental analysis of each support material of the metal catalysts were determined using X-ray Fluorescence (XRF) spectrometer at Department of Chemistry, Faculty of Science, UPM. This instrument is equipped with rhenium anode under energy dispersive mode.

The quantitative determination of spent catalyst was done using the Perkin Elmer (Model: Optima 2000DV) ICP-OES (inductively coupled plasma-organic element sampler) analyzer at Faculty of Science, UPM. This analysis was conducted to determine the amount of metal leaching in the reusability study. The preparation of solutions for the samples was conducted using standard methods often applied in

quantitative chemical analysis. The calibration curves were performed in presence of nickel and iron as internal standard to correct the matrix effects.

3.9 Optimization by Response Surface Methodology (RSM)

For the experimental design, the statistical analysis of response surface methodology (RSM) was carried out to optimize the process conditions for the production of LA from OPEFB-based cellulose by hydrolysis reaction. A rotatable central composite design (CCD) of RSM was chosen to design the experiments. The three independent variables investigated were temperature, catalyst loading and reaction time. Coded and uncoded values for each parameter in the CCD are listed in Table 3.4. The selection of the experimental ranges for the independent parameters was based on the screening of conditions in the Section 3.7.

Table 3.4: Experimental range and levels of the independent variables

Variable	Symbol		Unit	Range and levels		
	Uncoded	Coded		-1	0	1
Reaction Time	t	X ₁	h	1.0	4.5	8.0
Catalyst Loading	load	X ₂	%	5	10	15
Temperature	T	X ₃	°C	160	180	200

All the experiments were designed in a random order as proposed by the software. The design matrix proposed 20 sets of experiments. Table 3.5 shows the design matrix generated by Design Expert software 13.0 (Stat-east Inc., MN. USA). Yield of LA (%) based on theoretical yield and weight percentage as the main product is the ultimate response (R1).

Table 3.5: Experimental design matrix

Run	Factor 1 A: Temperature °C	Factor 2 B: Catalyst Loading %	Factor 3 C: Time h
1	168	13	2.4
2	168	7	2.4
3	192	7	6.6
4	180	15	4.5
5	180	10	8.0
6	168	7	6.6
7	168	13	6.6
8	180	10	4.5
9	180	10	4.5
10	180	5	4.5
11	192	7	2.4
12	200	10	4.5
13	160	10	4.5
14	192	13	6.6
15	180	10	4.5
16	180	10	1.0
17	180	10	4.5
18	180	10	4.5
19	180	10	4.5
20	192	13	2.4

3.10 Kinetic and thermodynamic study

3.10.1 Collection of kinetics experimental data

A study on the kinetics of the hydrolysis of OPEFB based-cellulose into LA was conducted to determine the rate constants, rate of reaction, and order of reaction and activation energy (E_a). The kinetics of the hydrolysis was done under the optimized

operating conditions of 8h reaction time, 2g OPEFB-based cellulose as reactant, 0.1991g catalyst and 60 mL water using the sulfonated metal carbon catalyst (15%FeNi/ACSO₃H). The reaction temperature was varied from 170 °C to 200 °C based on the result from optimization study and temperature screening in the Section 3.9. Due to the reactor limitation, reaction at the temperature above 200 °C cannot be performed. The experimental setup is similar to the experiments for hydrolysis reaction using hydrothermal reactor as shown in Figure 3.2. The operating pressure was maintained constant throughout the reaction to analyze the effect of temperature at specific time intervals. The sampling was performed at specific time intervals and was kept in storage for subsequent HPLC analysis.

3.10.2 Development of reaction model

A kinetic study was performed to understand the conversion pattern of the OPEFB-based cellulose to LA. The reaction started with the hydrolysis of cellulose into glucose which then dehydrated to HMF and finally to LA. The formation of a dark insoluble by-product known as humin invariably happened during the glucose dehydration into HMF and conversion of HMF to LA as shown in the model in the Figure 3.12. The reaction does not consider the production of reversion products and other intermediate compounds due to their low concentration produced throughout the reaction. Rate equations were assumed to follow irreversible pseudo first-order reactions with respect to each component as per the discussion in the literature review chapter and the kinetics model proposed by Chang *et al.* (2009), Nzediegwu *et al.* (2021) and Qing *et al.* (2018).

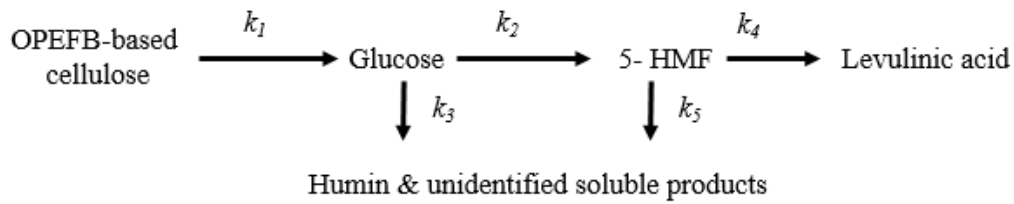


Figure 3.12: Reaction scheme for the conversion of cellulose to LA and the rate constant used for kinetic studies

Based on the previous kinetic model, the derivative rate laws for each conversion step are proposed as follow:

$$\frac{dC_{\text{cell}}}{dt} = -k_1 C_{\text{cell}} \quad \text{Eq. (3.10)}$$

$$\frac{dC_{\text{glu}}}{dt} = k_1 C_{\text{cell}} - (k_2 + k_3) C_{\text{glu}} \quad \text{Eq. (3.11)}$$

$$\frac{dC_{\text{HMF}}}{dt} = k_2 C_{\text{glu}} - (k_4 + k_5) C_{\text{HMF}} \quad \text{Eq. (3.12)}$$

$$\frac{dC_{\text{LA}}}{dt} = k_4 C_{\text{HMF}} \quad \text{Eq. (3.13)}$$

Here, C_{cell} , C_{glu} , C_{HMF} and C_{LA} represents the concentration of cellulose, glucose, HMF and LA at time (t) in g/mol. While k_1 , k_2 , k_3 , k_4 and k_5 are reaction rate coefficients. Eq. (3.10) – Eq. (3.13) were used to evaluate the values of the reaction kinetics parameters. These equations were solved simultaneously using the numerical integration toolbox *ode45* solver in MATLAB software package (R2023a, Mathworks, MA, USA). The *ode45* function is implemented using an explicit Runge-Kutta (4,5) formula (Zhao *et al.*, 2019). MATLAB coding is shown in Appendix G. The reaction rate coefficients were determined by minimizing the errors between the experimental data and the kinetic model using the Standard Error (SE) and Root Mean Square Error

(RMSE). Both are good statistical tools for non-linear regressions. For each component i , standard deviation, (SD_i) standard error (SE_i) and Root Mean Square Error ($RMSE_i$) were calculated as in Eq. (3.14) – (3.16).

$$SD_i = \sqrt{\frac{\sum_{i=1}^n (X_i - \bar{x})^2}{N - 1}} \quad \text{Eq. (3.14)}$$

$$SE_i = \frac{SD_i}{\sqrt{N}} \quad \text{Eq. (3.15)}$$

$$RMSE_i = \sqrt{\frac{1}{N} \sum_{i=1}^n (\text{Predicted}_i - \text{Actual}_i)^2} \quad \text{Eq. (3.16)}$$

where N is the number of data points, x_i is each of the value of the data, $\bar{x}$ is the mean of x_i .

Eq. (3.17) indicates the relationship between the reaction rate constant and the activation energy, expressed by the Arrhenius model.

$$k_i = A_i \times \exp \frac{-E_a}{RT} \quad \text{Eq. (3.17)}$$

where A_i is the frequency factor (min^{-1}), R is the ideal gas constant ($8.314 \text{ J}(\text{mol K})^{-1}$), T the reaction temperature (K) and E_A is the activation energy (J mol^{-1}).

3.10.3 Determination of thermodynamic parameters

Eyring equation which is similar to Arrhenius equation was employed to relate rate constant to temperature based on the transition state theory. The Eyring equation in the Eq (3.18) was applied to evaluate the thermodynamic activation parameters such as activation entropy ($\Delta S^\ddagger$) and activation enthalpy ($\Delta H^\ddagger$). Eq. (3.18) gives a plot of $\ln(k/T)$ against $1/T$ for evaluating both $\Delta H^\ddagger$ and $\Delta S^\ddagger$. The Gibbs free energy of activation was determined from Eq. (3.19). From the equation, h is Plank's constant (6.626×10^{-34} J·s), k_B is the Boltzmann's constant (1.381×10^{-23} J·K⁻¹), R is gas constant (8.3145 J·mol⁻¹·K⁻¹) and k is the rate constant at reaction temperature T .

$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad \text{Eq. (3.18)}$$

$$\Delta G^\ddagger = -RT \ln \frac{kh}{T k_B} \quad \text{Eq. (3.19)}$$

CHAPTER 4

RESULT AND DISCUSSION

4.1 Introduction

This chapter details the results and discussions of the study based on the four main objectives defined in chapter 1. The first objective covers the performance of sulfonated carbon metal catalysts on the production of LA from cellulose and glucose while the second objective covers the characterization of these catalysts. These two objectives are presented under section 4.2 for metal catalyst and 4.3 for sulfonated carbon metal catalyst. The optimization of LA yield from OPEFB-based cellulose represents the third objective. In this part, the result for extraction of cellulose from OPEFB, pretreatment of this cellulose with MSHs and the optimization of this reaction using Response Surface Methodology (RSM) are discussed. Finally, the last section explores the kinetics and thermodynamics of hydrolysis reaction for the production of LA from OPEFB-based cellulose.

4.2 Performance & characterization of catalyst Fe.xNi

This work aimed to synthesize the best metal catalysts for the production of LA from cellulose. Commercial cellulose or glucose was used as a raw material for the screening of selected catalysts. Based on previous studies, two metals catalysts were chosen namely Nickel (Ni) and Iron (Fe) metals. Both prepared metals are addressed

as Fe and Ni only for all catalysts. The combination of this catalyst was addressed as Fe.xNi catalyst, while x referred to the loadings of Nickel in the catalyst, for example, Fe.25Ni was 25% nickel and 75% iron in the catalyst. The characteristics of the catalysts are described first followed by the assessment of the catalytic activity.

4.2.1 Structural, phase, and chemical component

The XRD profiles of metal catalysts are shown in Figure 4.1. A broad diffraction peak was presented at 2θ (21.7°, 33.185°, 35.585°, 38.98°, 49.485°, 54.085° and 62.485°) which correspond to the diffraction planes (012), (104), (110), (113), (024), (116) and (214), respectively in all catalysts except Ni catalyst. The position and relative strength of diffraction peaks closely match the standard data for hematite, Fe₂O₃ (JCPDS file No. 33-0664), giving further evidence of the high purity of the synthesized Fe₂O₃. These findings were corresponding to the research by Hassan *et al.* (2020) and Li *et al.* (2016). XRD result also presents five main peaks at 37.3°, 43.1°, 64.8°, 75.3° and 79.5° in all catalysts except Fe catalyst, which correspond to the (111), (200), (220), (311) and (222) planes of NiO (JCPDS NO. 47-1049), respectively. The XRD pattern for NiO is similar to the findings from Fazlali *et al.* (2019) and Xu *et al.* (2021). The XRD patterns indicate that elements Fe and Ni in all catalysts presented not in the form of single metal but metal oxide.

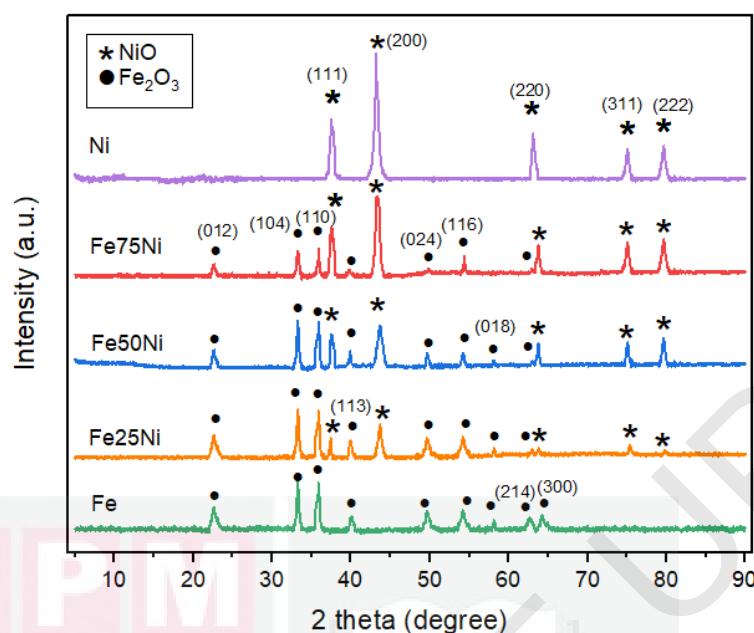


Figure 4.1: XRD analysis for Fe, Ni and Fe.xNi catalysts

The functional groups available on the catalyst were identified using FTIR and results are displayed in Figure 4.2. The peaks observed at 455 cm^{-1} is assigned to the stretching and bending vibrations of Fe–O bonds in $\alpha\text{-Fe}_2\text{O}_3$ (Dutt *et al.*, 2018). The intense absorption peaks observed at 526 cm^{-1} are attributed to the vibrational modes of the Fe–O bond (Aziz *et al.*, 2020). Both peaks are present in all metal catalysts except the Ni catalyst, indicating that Fe metal was successfully incorporated, hence, presented in the mixed metal catalysts. The appearance of strong vibrations at 525 cm^{-1} suggests the presence of Ni–O bonds in the fingerprint area (Moavi *et al.*, 2021). The region at approximately 3340 cm^{-1} is associated with hydroxyl group (OH) activities, which is supported by the study conducted by Salim *et al.* (2021). Based on the research by Saravanakkumar *et al.* (2018), the band observed at around 1100 cm^{-1} can be attributed to the stretching mode of the Ni–O–Ni bond. In conclusion, the result obtained from the FTIR spectrum proved that the existing functional groups associated with both Ni or Fe in the catalysts produced and is consistent with the XRD findings.

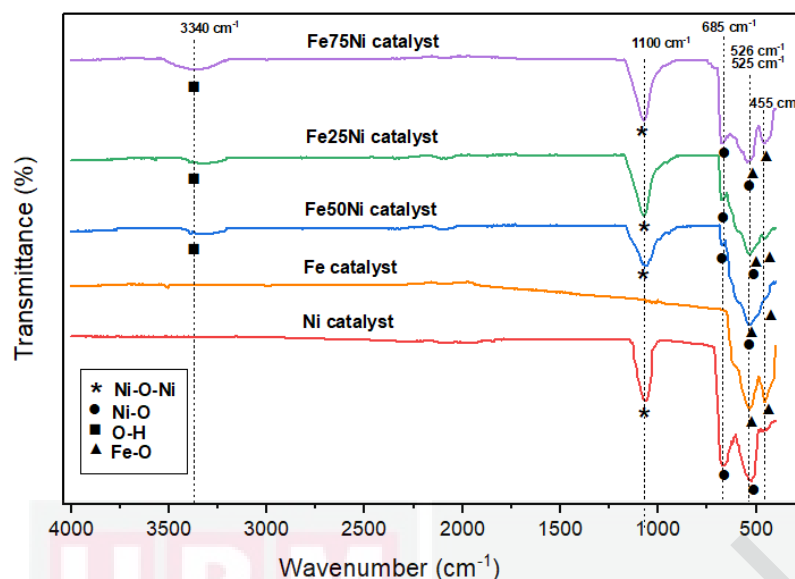
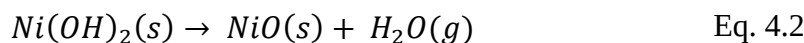
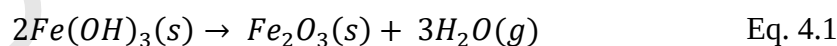


Figure 4.2: FTIR analysis for Fe, Ni and Fe.xNi catalysts

The TGA and DTG of metal catalysts are shown in Figure 4.3 to demonstrate the weight losses of catalysts with increasing temperature. TGA result reveals a first-step weight reduction occurring below 100 °C for all catalysts, which can be attributed to the removal of both physically adsorbed water and the dehydration of surface hydroxyl groups (Abdullah *et al.*, 2016). The second step occurred as a result of the breakdown of hydroxyl metal into metal oxides at temperatures ranging from 200 to 400 °C. These chemical reactions are similar to the findings by Feyzi and Hassankhani (2011) and Pinto *et al.* (2019). These reactions were also confirmed by XRD analysis and expressed as:



Based on equation 4.1, calcination of iron (II) hydroxide ($\text{Fe}(\text{OH})_3$) at high temperature produced iron (III) oxide (Fe_2O_3). $\text{Fe}(\text{OH})_3$ is a product of the precipitation of iron (III) chloride (FeCl_3) with NaOH as shown in Equation 4.3. Meanwhile, calcination of

nickel (II) hydroxide (Ni(OH)_2) at high temperatures generated nickel oxide (NiO). Similar to Fe(OH)_2 , Ni(OH)_2 is the product formed by precipitation of $\text{Ni(NO}_3)_2$ with NaOH expressed in equation 4.4. Furthermore, TGA results demonstrate that all prepared Fe_xNi catalysts were stable up before 200 °C as shown in Figure 4.3(c)-(e) and suitable for production of LA as this reaction performed at the range of temperature.

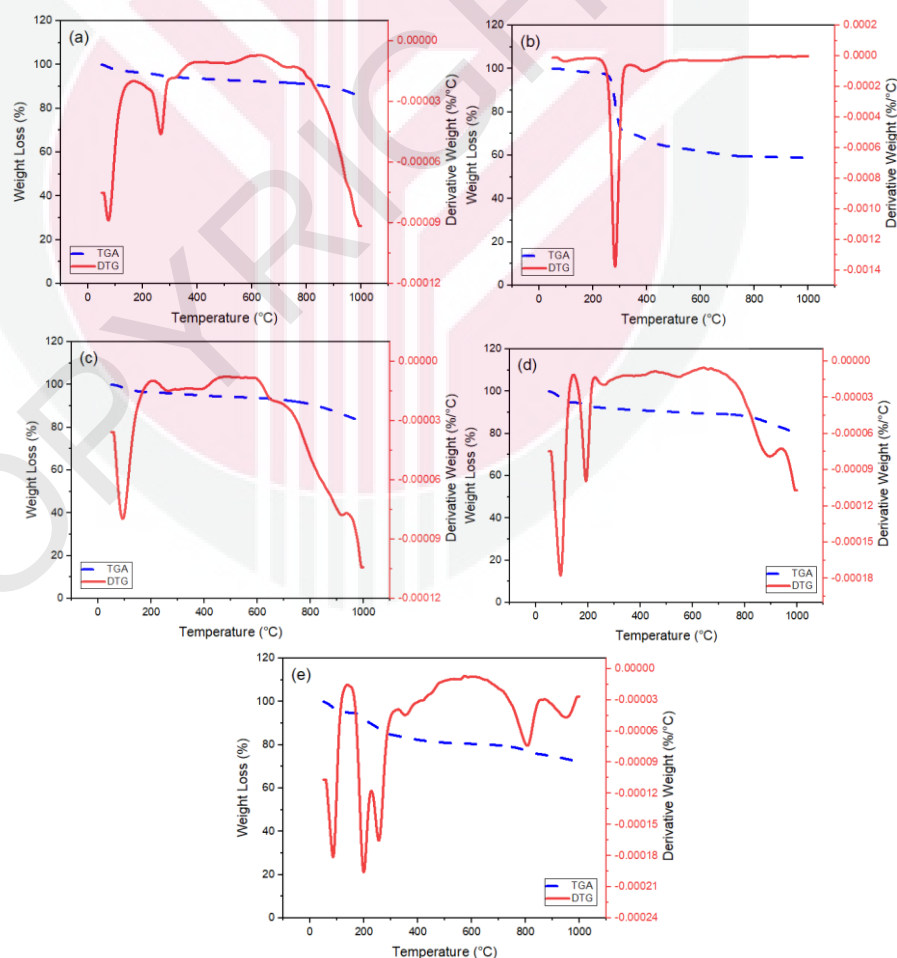


Figure 4.3: TGA and DTG curves of catalyst (a) Fe, (b) Ni, (c) Fe.25Ni, (d) Fe.50Ni and (e) Fe.75Ni

For deeper understanding, the catalyst was analyzed by XPS to identify the chemical oxidation states of the surface species in terms of iron, oxygen and nickel. Fe.75Ni catalyst was selected for this analysis. The wide scan was carried out between 0 and 1200 eV of energy binding as shown in Figure 4.4(a).

The XPS spectra in Figure 4.4(b) reveal that the catalyst exhibited a Ni $2p_{3/2}$ peak at a binding energy of around 852.25 eV, indicating the presence of Ni^{2+} . Additionally, Ni $2p_{1/2}$ peaks were observed at a binding energy of 870.25 eV, which is attributed to Ni^{3+} (Chu *et al.*, 2020). Moreover, the peaks at 858.50 eV and 877.51 eV are ascribed to satellite peaks of the Ni species (Ramu *et al.*, 2021). The Fe $2p$ core-level XPS spectrum in Figure 4.4(c) exhibits two shakeup satellites at 714.9 and 717.7 eV, along with two strong peaks at 722.33 and 710.05 eV. These peaks correspond to the Fe $2p_{1/2}$ and Fe $2p_{3/2}$ peaks, respectively, which are the characterization of Fe^{3+} and closely match the peaks observed in Fe_2O_3 (Zhang *et al.*, 2022).

The main component of Fe_2O_3 and NiO in the sample is further confirmed by the O 1s signal of the XPS spectrum as illustrated in Figure 4.4(d) which can be divided into two peaks. The peak located at 528.35 eV corresponds to Ni-O bonds while those located at 531.07 eV refer to Ni-O or Fe-O bonds, similar to the findings by Jiang *et al.* (2017). Consequently, the developed catalyst consisted of NiO and Fe_2O_3 which has already been confirmed via XRD analysis.

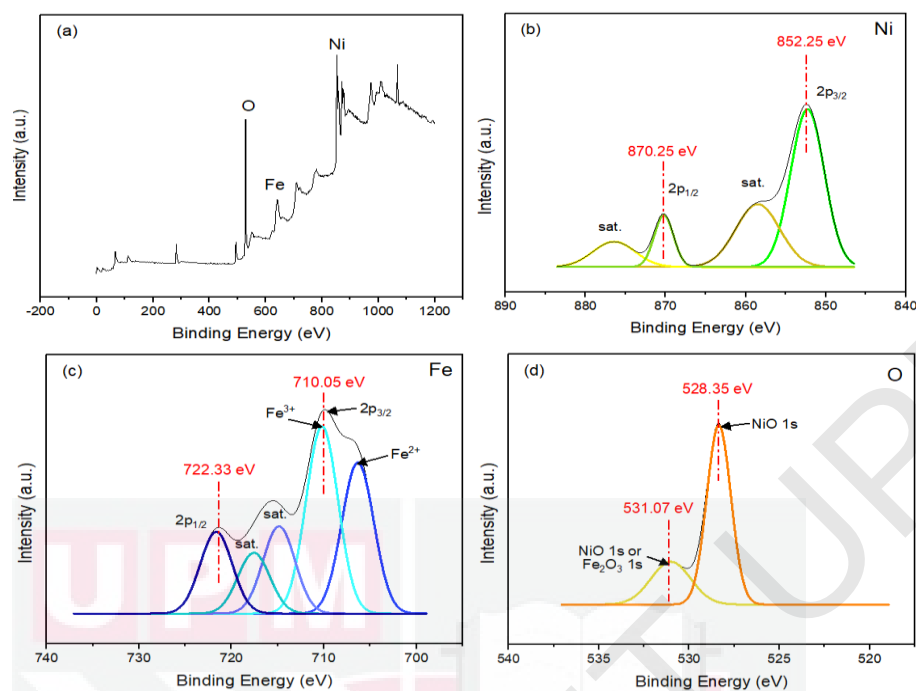


Figure 4.4: XPS analysis of Fe.75Ni catalyst (a) wide scan (b) Ni 2p (c) Fe 2p and (d) O 1s

4.2.2 Surface area and porosity

The textural characteristics of all catalysts obtained from N₂ adsorption-desorption isotherms are provided in Table 4.1. The BET-specific surface areas of Fe.25Ni, Fe.50Ni, Fe.75Ni, Fe and Ni catalysts were found to be 33.09, 15.89, 48.17, 5.63 and 52.96 m²/g, respectively. It indicated that Fe.75Ni and Ni catalysts exhibited a higher surface area than the other metal catalysts. The trend of surface area follows Ni > Fe.75Ni > Fe.25Ni > Fe.50Ni > Fe. It is observed that the BET surface area increased as NiO content increased which is similar to the findings by Hu and Teng (2010). The BET surface area of the Ni catalyst is 52.96 m²/g. The result is compared to NiO catalysts from the other studies as Ni catalyst in this study is typically referred to a NiO catalyst based on the XRD findings before. The surface area of NiO catalyst in this study is lower than Tong *et al.* (2015)(188 m²/g) but higher than Xu *et al.* (2021)(28.4 m²/g). It is postulated that the different preparation methods especially the

heating technique might affect the catalyst porous structure, for example, Tong *et al.* (2015) used longer time for thermal preparation of NiO catalyst. Nevertheless, in the case of mixed metal catalysts, the surface areas declined to 15.89 – 48.17 m²/g with further increase in the Fe content. This could be attributed to the accumulation of Fe₂O₃ crystallites validated in the XRD result which is discussed in a section above (Section 4.2.1). The large surface area of Fe.75Ni and Ni catalysts can be effectively associated with their significant pore volume (> 0.10 cm³/g), which is mostly attributed to the increased amount of liquid nitrogen adsorbed (Azri *et al.*, 2021).

The surface area differences between Fe.25Ni and Fe.50Ni catalysts can be comprehended through investigating particle dispersion and aggregation, pore structure or size and synergistic effects between the metals. The BET surface area of Fe.25Ni is measured to be 33.09 m²/g and it was expected that the particles of Fe and Ni are evenly distributed at this composition. This effective dispersion ensures that more surface sites are exposed and accessible, leading to an increased surface area (Feng *et al.*, 2021). Meanwhile, Fe.50Ni, with a BET surface area of 15.89 m²/g, indicates that at a higher Ni content (50%), the particles was expected to aggregate more, leading to larger clusters. This aggregation results in a decrease in surface area as the surface sites become less accessible (Dwivedi *et al.*, 2020). Upon analyzing the pore structure and size, it is shown that Fe.25Ni exhibits a reduced pore volume of 0.0340 cm³/g and a smaller pore size of 3.60 nm, suggested a finely distributed porous and more compact and structure. Smaller and more numerous pores lead to a higher surface area. In contrast, Fe.50Ni shows an increase in pore volume (0.0478 cm³/g) and a much larger pore size (8.24 nm). This indicates a transition towards a reduction in the number of pores while increasing their size. The existence of larger pores and

possible voids resulting from aggregation lead to a lower surface area as the specific surface area reduces (Tee et al., 2022). At lower nickel concentration (25%), it was expected that there may be an ideal interaction between iron and nickel, resulting in improved dispersion and limiting substantial particle development, which can be attributed to synergistic effects. Nevertheless, at higher Ni content (50%), these synergistic effects may become less noticeable, leading to increased particle aggregation. As a result, a reduced surface area for the Fe.50Ni catalyst was reported compared to Fe.25Ni.

In the case of pore properties, Table 4.1 presents the pore sizes or diameters of catalysts varying from 3.60 to 8.24 nm which are produced by various catalytic metals and indicated as mesoporous materials. Nanoporous materials are categorized into three primary types based on pore size: microporous materials (pore size < 2 nm), mesoporous materials (pore size 2–50 nm), and macroporous materials (pore size > 50 nm), as explained by IUPAC (Kamari and Ghorbani, 2021). According to Table 4.1, the Ni and Fe.50Ni catalysts showed similar pore diameters ranging from 8.04 to 8.24 nm. The Fe.50Ni exhibited a high pore diameter even though the pore volume was low most likely due to the adsorption of liquid nitrogen occurring on the external surface area rather than filling the micropores (Azri *et al.*, 2021).

Table 4.1: Physical properties of Fe.xNi catalysts

Catalyst	^a BET Surface Area (m ² /g)	^a Pore Volume (cm ³ /g)	^a Pore Size/ Diameter (nm)
Fe.25Ni	33.09	0.0340	3.60
Fe.50Ni	15.89	0.0478	8.24
Fe.75Ni	48.17	0.1141	6.44
Fe	5.63	0.0110	4.63
Ni	52.96	0.1677	8.04

^aDetermined by using BET analysis.

The N₂ adsorption-desorption isotherms are shown in Figure 4.5 while Figure 4.6 illustrates pore size distribution curves. These results revealed the type IV isotherms for all catalysts, indicating the mesoporous structure of the catalysts. The presence of a desorption hysteresis loop (H3 type), which is related to slit-shaped pores, confirms the coexistence of mesopores (2–50 nm) (Hassan *et al.*, 2020). The H3 classification is specific to solid materials composed of flexible non-rigid aggregates or agglomerates of plate-like particles, resulting in extensive non-uniform slit-shaped pores (Hassan *et al.*, 2020).

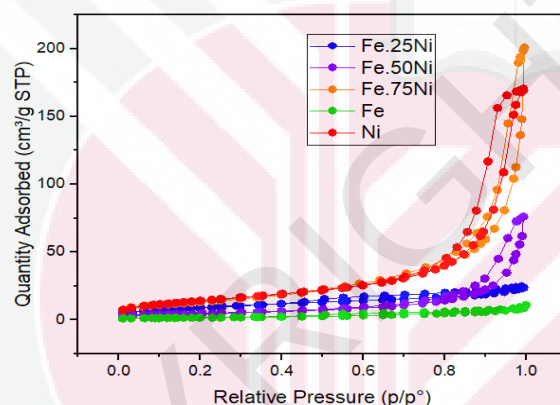


Figure 4.5: Isotherm profiles of Fe, Ni and Fe.xNi catalysts

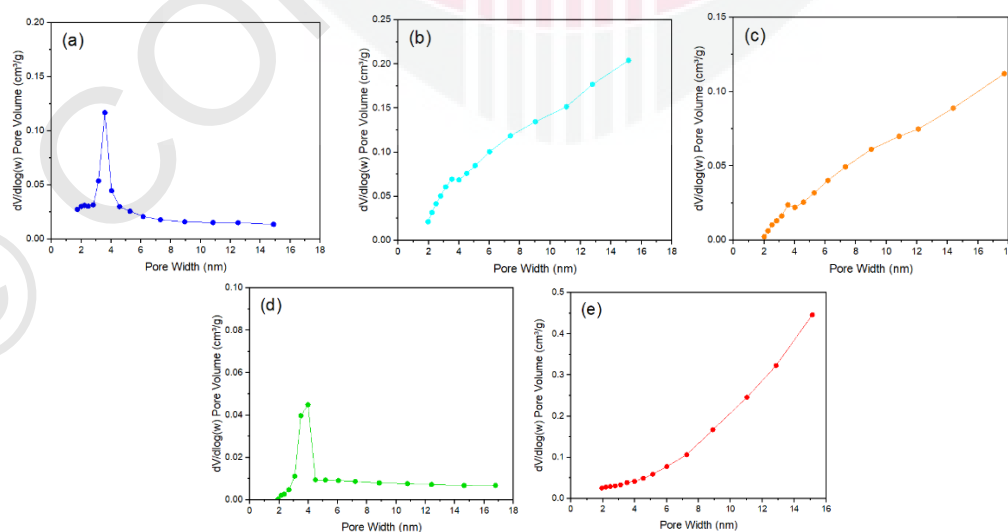


Figure 4.6: Distribution of pore volume of (a) Fe.25Ni (b) Fe.50Ni (c) Fe.75Ni (d) Fe and (e) Ni catalysts

The pore size distribution curve in Figure 4.6 shows that the average pore sizes of all metal catalysts are within the range of 2–18 nm. For Ni, Fe.50Ni and Fe.75Ni catalysts, the pore size distribution gave a climbing peak observed at the high-pressure region, indicating the presence of prominent mesoporous characteristics in these catalysts (Ramachandran *et al.*, 2019). The likewise trend for pore size distribution of Fe in Figure 4.6(a) and Fe.25Ni in Figure 4.6(d) are observed due to the blockage of pore when the amount of Fe was high.

4.2.3 Acid sites properties

The corresponding acidity (amount of ammonia uptakes) is presented in Table 4.2. The acidity data in Table 4.2 ranks Ni > Fe.75Ni > Fe.50Ni > Fe.25Ni > Fe. As reported by XRD analysis, Fe catalyst is referred as Fe₂O₃ while Ni is referred as NiO so the comparison with previous studies was done by comparing the total acidity of Fe₂O₃ and NiO in other findings. It can be inferred that Fe possesses slight weak acidic sites properties, while Ni showed highest weak acid sites with total acidity (15.7199 mmol/g). Indeed, the total acidity for Fe₂O₃ obtained from this study is lower than a report by Preda *et al.* (2022) which reported 2.60 mmol/g while Atius and Astuli (2021) reported the value for total acidity of Fe₂O₃ was 1.75 mmol/g. However, the values are only slightly different. The inclusion of NiO species enhances the presence of acidic sites in the catalytic system, which is also confirmed by Hafriz *et al.* (2022). The acidity strength is determined by the quantity of adsorbed NH₃ at various desorption temperatures, where weak acidity refers to desorption temperatures below 573 K, medium-strong acidity refers to desorption temperatures ranging from 573 K to 773 K, and strong acidity corresponds to desorption temperatures above 773 K

(Huang *et al.*, 2016). The ammonia desorption profiles of metal catalysts are displayed in Figure 4.7. The presence of weak, medium and strong acid sites in the Fe.75Ni catalyst is evident from the broader and more strong NH_3 desorption peaks obtained in the temperature range of 473-1273 K which confirms a higher concentration of acid sites in this catalyst compared to other mixed metal Fe.xNi catalysts. The observed profile for Ni catalyst shows the highest peak of weak acids indicating that the catalyst is rich with weak acid from Lewis acid species. The inclusion of iron and nickel in the catalyst promotes the development of Lewis acid sites (Zainol *et al.*, 2020). After the incorporation of Ni with Fe, the peaks for medium and strong acids were increased which made the catalysts high with both weak and strong acid sites of Lewis acid species.

Table 4.2: Acidity data of Fe.xNi catalysts

Catalyst	Amount NH_3 adsorbed ^a (mmol/g)			Total
	Weak acid	Medium acid	Strong acid	
Fe.25Ni	0.6624	0.55754	2.1286	3.3664
Fe.50Ni	1.4350	1.0036	1.9118	4.3504
Fe.75Ni	9.811	2.5288	4.8328	8.3427
Fe	0.9909	0.2069	0.3990	1.5968
Ni	6.6633	6.3402	2.7164	15.7199

^a NH_3 -TPD desorption peak for all catalysts.

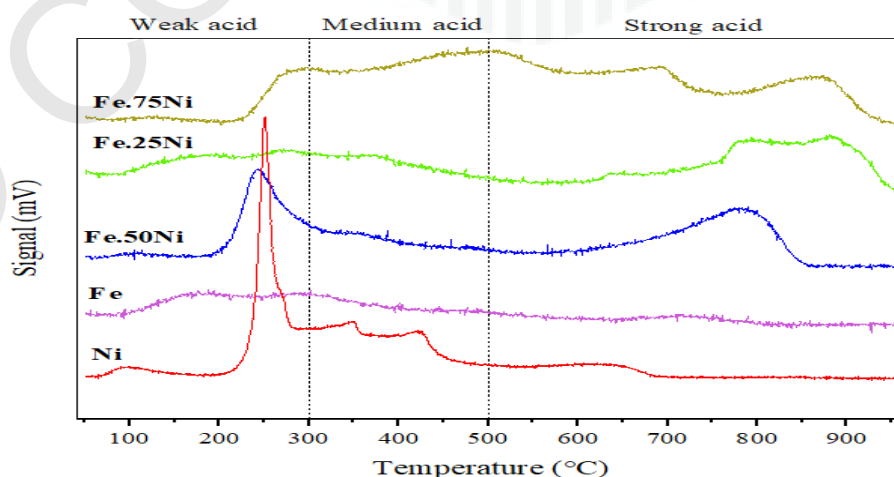


Figure 4.7: NH_3 -TPD patterns of Fe and Ni catalysts

4.2.4 Surface morphology

FESEM images were captured at 10,000x to examine the changes in the catalyst surface morphology for single metal and mixed metal catalysts. All the particles for Fe and Ni catalysts in Figure 4.8 look spherical shape and exhibit some degree of agglomeration. This agglomeration may be due to their magnetic character, whereby distinct parts or particles of matter attract and come into close proximity with one another (Rahimi *et al.*, 2020). The particles exhibit non-uniformity, potentially attributed to particle agglomeration (Gnana *et al.*, 2019). Previous studies demonstrated that the spherical metal oxides have been widely used in various applications because this spherical structure represents the most naturally stable form (Boyjoo *et al.*, 2016). For metal oxides, spherical morphology offers several benefits which include good mechanical properties, a high surface area-to-volume ratio, enhanced dispersion due to charge stabilization and the capability for easy coating with other substances such as supports which are beneficial for catalytic reaction (Boyjoo *et al.*, 2016). Zhu *et al.* (2021) also found that the spherical metal oxides in their study had better mass transfer ability, which is also an important factor in catalytic processes.

Insignificant changes were observed between single metal (Fe or Ni) with Fe.75Ni catalyst suggesting that the combination of iron and nickel in the Fe.75Ni catalyst does not significantly alter the morphology structure of the catalyst. The catalyst elemental composition (recorded in weight percent) was analyzed using EDX measurement and the results are reported as a bar chart in Figure 4.8.

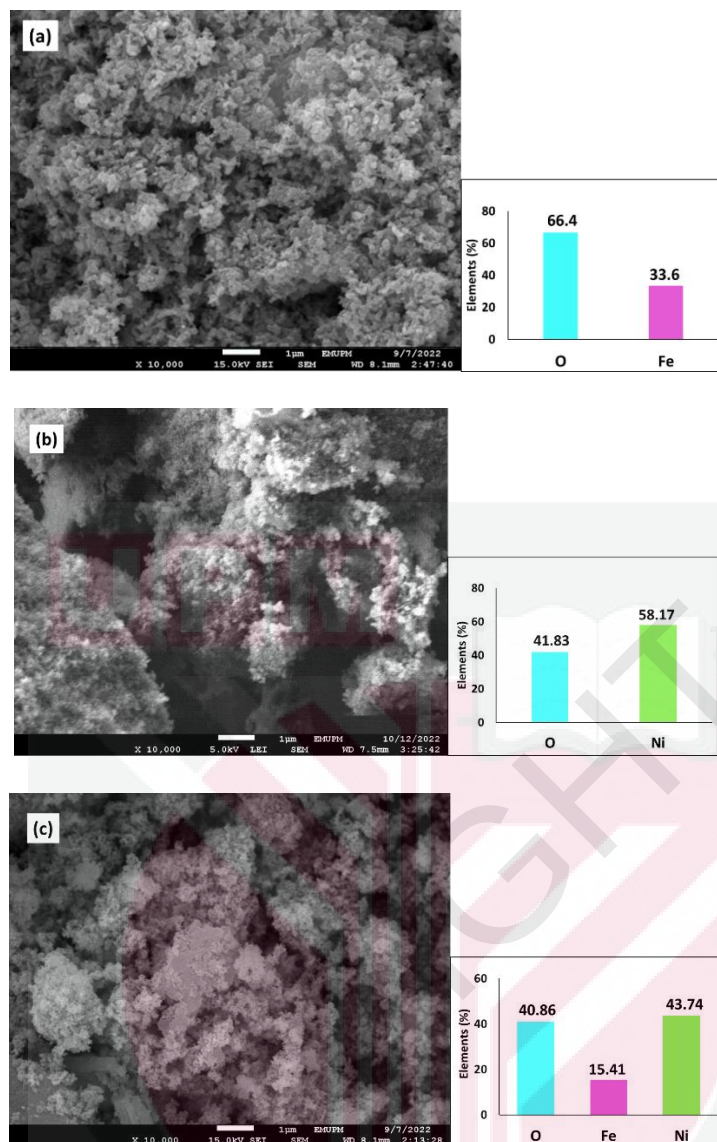


Figure 4.8: FESEM images and EDX analysis for (a) Fe catalyst (b) Ni catalyst and (c) Fe.75Ni catalyst

EDX spectroscopy obtained for Fe.75Ni proves that NiO and Fe_2O_3 metal oxide were successfully incorporated in the catalyst. Nonetheless, the results demonstrate that the Ni content was only 43.74%, not the expected 75%, while Fe comprised 15.41% instead of the intended 25%. This deviation may be due to the presence of oxygen in the formation of NiO or Fe_2O_3 . The results without oxygen can be observed in the XRF data as demonstrated in Table 4.3, where only the amount of Fe and Ni are reported. Although the XRF results do not present exact amounts as actual composition values,

the minor variations are within an acceptable range. It can be concluded that the precipitation method is a practical and efficient method for introducing metal catalysts.

Table 4.3: Elemental composition of Fe.xNi catalysts determined by XRF

Catalysts	XRF analysis (wt.%)			Actual composition value (wt.%)	
	Fe	Ni	Others	Fe	Ni
Fe	98.2	-	1.9	100.0	-
Ni	-	99.8	0.2	-	100.0
Fe.25Ni	73.2	24.5	2.3	75.0	25.0
Fe.50Ni	51.9	47.4	0.8	50.0	50.0
Fe.75Ni	22.4	77.1	0.46	25.0	75.0

In addition to EDX analysis, the mapping images for the element distribution of the Fe.75Ni catalyst are shown in Figure 4.9. The element mapping consists of iron, nickel and oxygen which can be referred to NiO and Fe₂O₃ metal oxide. The distribution of Fe, Ni and O on the catalyst surface can be clearly identified in this catalyst from the mapping image. Indeed, majority of Fe and Ni homogenously distributed on the catalyst surface.

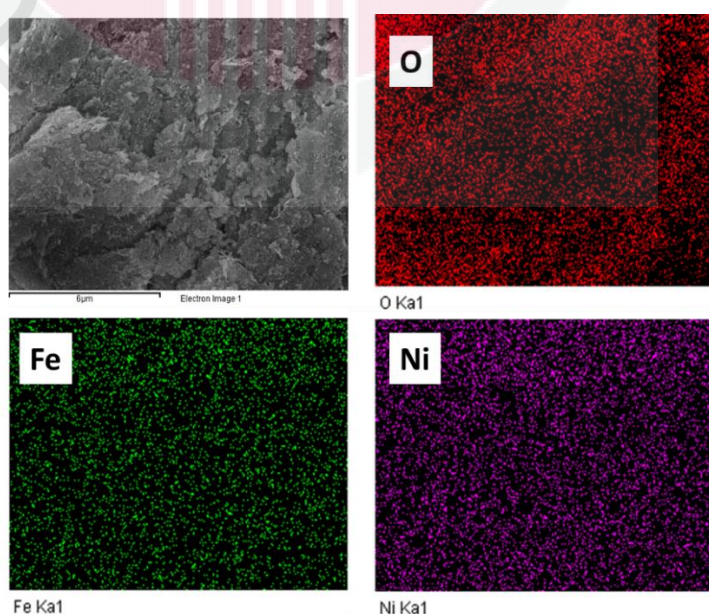


Figure 4.9: EDX mapping for Fe.75Ni

4.2.5 Conversion of cellulose and glucose into levulinic acid

The catalytic activity of Fe and Ni catalysts in producing LA and other intermediate products was evaluated using two different raw materials. The amounts of products were analyzed using HPLC as described in Section 3.4.2. The performance of catalysts was compared using cellulose and glucose as shown in Figure 4.10(a) and 4.10(b) respectively. Catalyst screening was conducted by comparing the catalytic activity of Fe, Ni, Fe.25Ni, Fe.50Ni and Fe.75Ni catalysts. The catalytic activity was conducted at a temperature of 180 °C for 5 h of reaction time.

In this research, the main product was LA. FA is theoretically generated in equal molar quantities to LA through the rehydration of HMF (Zarin *et al.*, 2022). For the synthesis of LA from cellulose, the highest amount of LA (10.51 %) based on theoretical yield was obtained from Fe.75Ni catalyst and the yield based on weight percentage was 7.52 wt.%. The LA yield trend from cellulose was Fe.75Ni > Ni > Fe.50Ni > Fe.25Ni > Fe. Meanwhile, the trend of LA produced from glucose was Fe.75Ni > Fe.25Ni > Fe.50Ni > Ni > Fe. For glucose, the highest yield of LA (32.32 %) of theoretical was achieved also from the Fe.75Ni catalyst with the yield based on weight percentage at 20.82 wt.%. In order to confirm the role of the catalyst, an experiment using blank sample without Fe.xNi catalyst was also conducted. The yield of HMF and LA from glucose were 0.04% and 7.33% of theoretical, respectively and the result of HMF and LA yield from cellulose were 0.11% and 0.92% based on theoretical yield, respectively. The huge difference between the reaction with and without Fe.xNi catalyst confirmed the role of this catalyst in the reactions.

The results from both raw materials (cellulose and glucose) indicate that Fe.75Ni is the best catalyst. The physicochemical characteristics of the catalysts, such as their porosity and acidity are related to the distribution of the products from the reactions. This catalyst has a high value of acidity and large acid sites which can be seen from TPD-NH₃ analysis. The chemical route of cellulose or glucose to LA necessitates a high concentration of acid sites (Weiqi and Shubin, 2017). Even though the highest acidity value was achieved by the Ni catalyst, the type of acidity also impacted LA production (Zarin *et al.*, 2022). In this case, a combination of Fe and Ni catalysts produced highly strong Lewis acid, while Ni only produced weak Lewis acid. The pore size of the catalyst also could have affected the yield of LA from cellulose or glucose. Furthermore, the size of mesopores among the metals catalysts (3.60-8.24 nm) was smaller compared to the cellulose molecule (40–300 μm) (Kian *et al.*, 2020) but larger than the glucose molecule (0.54 to 0.97 nm) (Yang *et al.*, 2008). Therefore, during the cellulose conversion process, the reaction could only take place outside the Fe-Ni catalysts because cellulose was unable to pass through the catalysts' pores. After cellulose was transformed into glucose, the molecules may enter the catalysts.

In addition, a low amount of LA from the catalyst with greater Fe loading can be assumed due to the production of an additional by-product such as lactic acid, similar to the findings by Ramli and Amin (2015b). The amount of FA was lower than LA for all reactions. This state may have occurred as a result of the breakdown of FA under the reaction conditions. A study by Ya'Aini *et al.* (2013) found that FA has been seen to undergo breakdown into carbon monoxide (CO), carbon dioxide (CO₂), water (H₂O), and hydrogen gas (H₂) under conditions of heat and acidity. As seen in Figure 4.10, glucose and HMF as intermediates were still present in the final products. Hence,

optimization of the reaction should be carried out by selecting the best conditions or modifying the catalysts to optimize the conversion which was explored in the following parts.

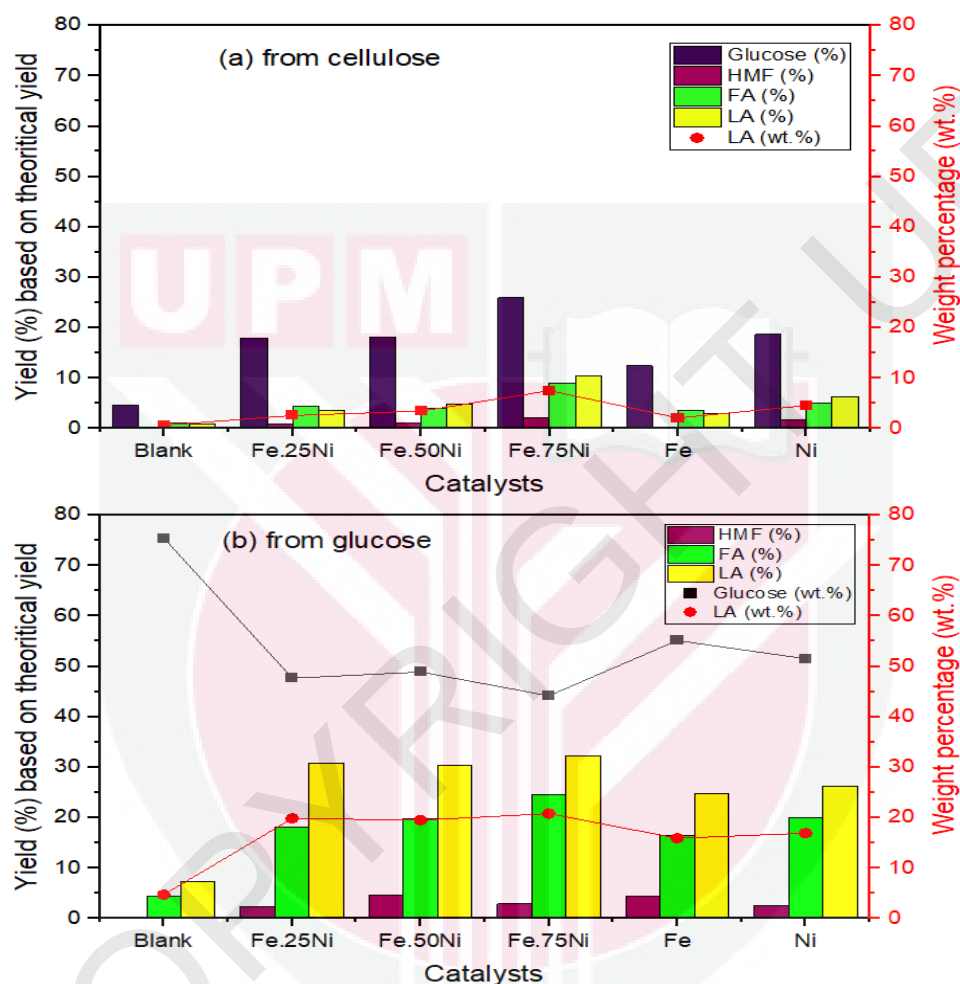


Figure 4.10: Product yields (%) based on theoretical yield and LA yield (wt%) from cellulose (a) and glucose (b) using Fe.xNi catalysts. Reaction conditions: 5 g cellulose or glucose, reaction temperature 180 °C, reaction time 5 h, catalyst dosage 0.15 g

4.2.6 Summary

In conclusion, based on the catalytic screening of different loadings of Fe and Ni, Fe.75Ni has been found to exhibit a promising activity compared to other catalysts (Fe, Ni, Fe.25Ni, Fe.50Ni). The highest LA yield based on theoretical (10.51 %) or

7.52 wt.% based on weight percentage was obtained from cellulose at a reaction temperature of 180 °C, reaction time of 5 h and 0.15g catalyst loading. The huge difference between the yield of LA from cellulose with and without Fe.xNi catalyst (0.92 % based on theoretical yield) confirmed the role of this catalyst in the reactions. From the results, it is concluded that LA production over mixed metal catalyst is predominantly affected by the catalyst acidity while the surface area derived from this catalyst provided the catalytic sites. Therefore, this catalyst was selected for impregnation with support in the next part. Furthermore, the reaction from glucose under the same conditions and using similar catalyst demonstrated higher amount of LA (32.32% based on theoretical yield or 20.82 wt.%) which indicated that cellulose need to be pretreated to enhance the conversion process.

4.3 Performance & characterization of FeNi/ACSO₃H catalyst

The objective of this study was to synthesize the best-sulfonated carbon metal catalysts for LA production from cellulose. Similar to the preceding study, commercial cellulose or glucose was utilized as the raw material for the catalyst screening process. Fe.75Ni as the best catalyst in the previous study was selected to impregnate into sulfonated carbon (ACSO₃H) catalyst. AC refers to activated carbon while ACSO₃H is sulfonated activated carbon. The combination of this catalyst was addressed as x%FeNi/ACSO₃H catalyst, while x referred to the loadings of Fe.75Ni in the catalyst, for example, 5%FeNi/ACSO₃H was 5% Fe.75Ni in the catalyst. The study of the characteristics is described first, followed by the evaluation of catalytic activity based on LA yield.

4.3.1 Structural, phase and chemical component

Figure 4.11 presents the XRD pattern of (a) AC and ACSO₃H, and (b) FeNi/ACSO₃H with different loadings of Fe.75Ni metals. XRD results for AC and ACSO₃H displayed a single broad diffraction peak and weak diffraction peaks at $2\theta = 10-30$ and $2\theta = 35-50$ which can be attributed to C(002) and C(101), respectively. The initial peak of the C(002) plane is typically assigned to amorphous carbon, which is composed of disordered polycyclic aromatic carbon sheets, while the C(101) plane's low-intensity peak is typically attributed to the graphitic structure of carbon (Lokman *et al.*, 2015). Both peak intensity of the ACSO₃H catalysts were diminished compared to AC influenced by the sulfonation process and remained as an amorphous form. This results from the corrosive nature of the strong acid, which impacts the carbon structure by altering its chemical bonds (Zainol *et al.*, 2021). Unfortunately, the peaks were diminished upon the introduction of metals to form sulfonated carbon metal catalysts (FeNi/ACSO₃H) similar to the results from the study by Abdullah *et al.* (2020). By comparing the intensities of absorption bands associated with Lewis and Bronsted-Lowry acid sites, it can be inferred that the acidity of the FeNi/ACSO₃H is primarily influenced by the Lewis acid sites. Additionally, there is a trend indicating that the strength of the Lewis acid increases proportionally with higher Fe and Ni content in the catalysts which can be confirmed by the result from the TPD-NH₃ analysis.

The XRD pattern of the FeNi/ACSO₃H catalysts is also illustrated with several diffraction peaks (012), (104), (110), (113), (024), (116), and (214) presented at 2θ (21.7°, 33.185°, 35.585°, 38.98°, 49.485°, 54.085° and 62.485°). This pattern was assigned to the standard data for hematite, Fe₂O₃ (JCPDS file No. 33-0664), providing

additional proof of the high purity of the synthesized Fe_2O_3 , which aligned with the XRD results from Li *et al.* (2016) and Hassan *et al.* (2020). XRD result also demonstrated five main peaks which were located at 37.3° , 43.1° , 64.8° , 75.3° and 79.5° in all catalysts, which ascribed to NiO (JCPDS NO. 47-1049), (111), (200), (220), (311) and (222) respectively. The XRD pattern for NiO is similar to the findings from Xu *et al.* (2021) and Fazlali *et al.* (2019).

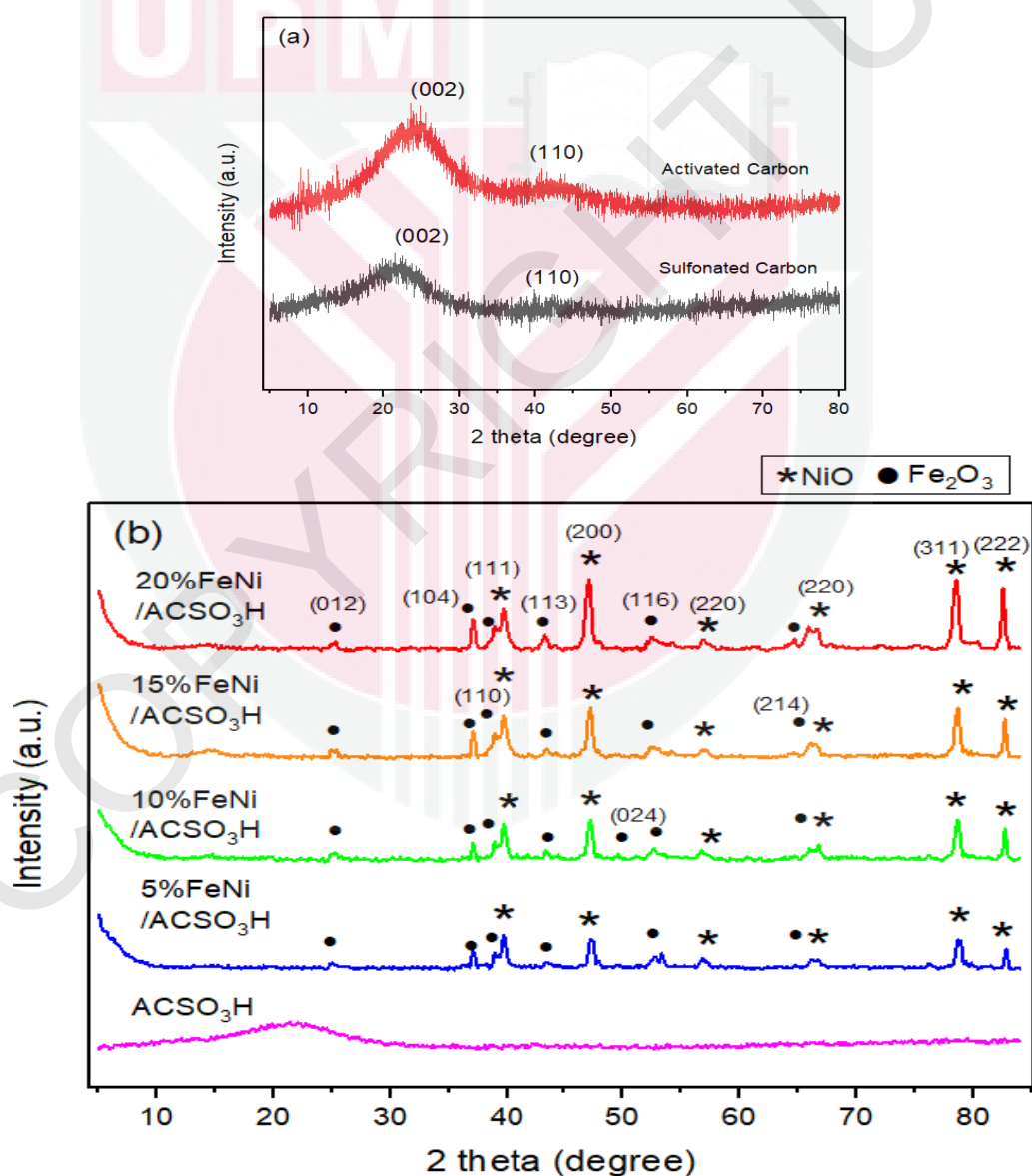


Figure 4.11: XRD analysis for (a) carbon catalysts and (b) FeNi/ACSO₃H catalysts

The studies on chemical functional groups exhibited in sulfonated carbon metal catalysts were conducted using FTIR analysis as shown in Figure 4.12. The peaks detected at 455 cm^{-1} can be attributed to the bending and stretching vibrations of Fe–O bonds in $\alpha\text{-Fe}_2\text{O}_3$ (Dutt *et al.*, 2018). The significant absorption peaks detected at 526 cm^{-1} are similarly ascribed to the vibrational modes of the Fe-O bond (Aziz *et al.*, 2020). All metal catalysts except for the Ni catalyst, exhibited both peaks, indicating the successful presence of Fe metals in all mixed metal catalysts. The occurrence of intense vibrations at a frequency of 525 cm^{-1} confirms the existence of Ni–O bonds within the fingerprint region (Moavi *et al.*, 2021). The spectral band of about 3340 cm^{-1} corresponds to the vibrational activity of hydroxyl groups (OH) which probably belong to the hydroxyl group of water adsorbed on the surface of the catalysts, as evidenced by the research carried out by Salim *et al.* (2021). The absorption peaks at 1152 cm^{-1} corresponded to the symmetric expansion vibration of the S=O bond in SO_3H (Tian *et al.*, 2020). The occurrence of two prominent peaks at wavenumbers of 1117.39 cm^{-1} and 1013.04 cm^{-1} can be assigned to the symmetric stretching of O-S-O and the asymmetric stretching of O-S-O, respectively. This confirms the presence of a sulfonic group ($-\text{SO}_3\text{H}$) covalently bound to a polyaromatic carbon structure after the sulfonation reaction (Mavakumba *et al.*, 2018). Meanwhile, the catalyst 100%FeNi did not show any of these peaks. The absorption bands observed at a wavenumber of 1579 cm^{-1} are indicative of the presence of C = C bonds in aromatic carbon compounds while the significant peak at 1710 cm^{-1} is attributed to C=O bonds from carboxylic acid (Araujo *et al.*, 2021). Overall, these findings are consistent with other studies documented in the scientific literature (Tian *et al.*, 2020) (Mavakumba *et al.*, 2018) (Moavi *et al.*, 2021).

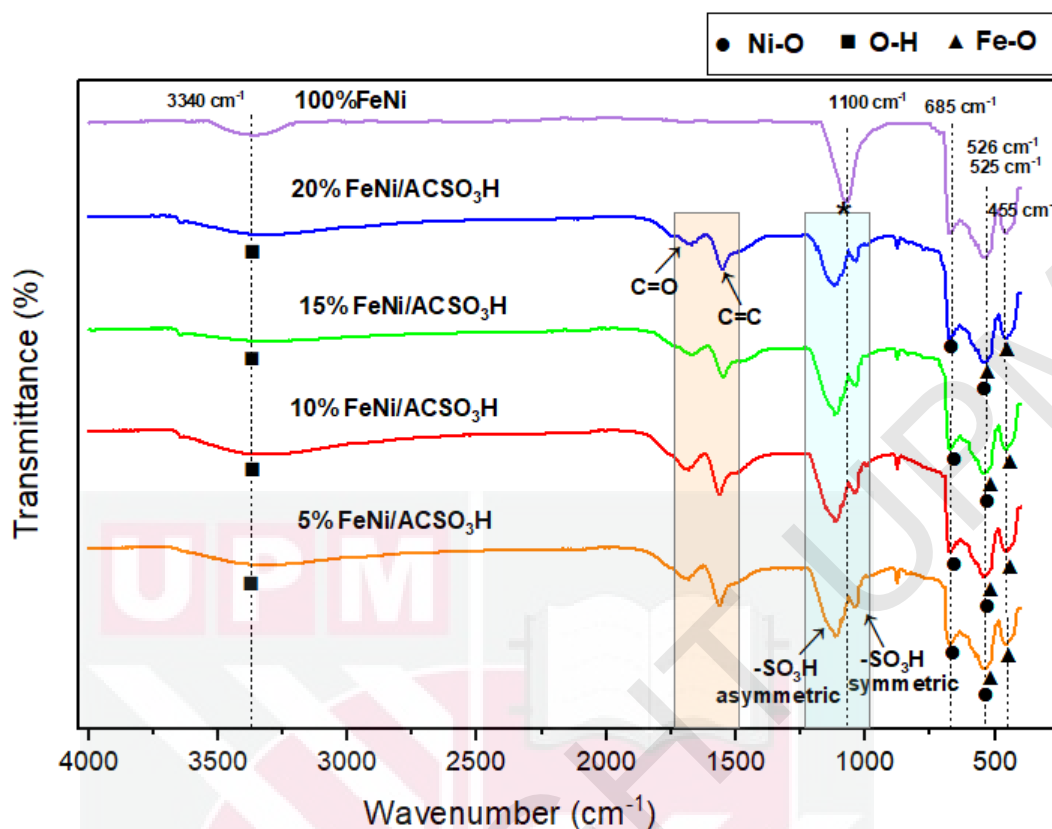


Figure 4.12: FTIR analysis for FeNi/ACSO₃H catalysts

The thermal stabilities of the AC, ACSO₃H and sulfonated carbon metal catalysts were examined by TGA under air flow at a heating rate of 10 °C min⁻¹ from 50 to 1000 °C as presented in Figure 4.13. The weight losses are presented as a function of temperature. The weight loss at temperatures below 200 °C is attributed to the evaporation of water absorbed by the catalyst (Thushari *et al.*, 2019). There is a clear variation in the water content throughout the series, with all sulfonated samples showing higher water content than plain AC (less hydrophilic). It can be concluded that the sulfonating treatment greatly enhances the hydrophilicity of the surface by introducing sulfonic groups (Bounoukta *et al.*, 2021).

The AC catalyst in Figure 4.13(a) showed a steady and gradual weight loss (<30 wt.%) as the system's temperature increased at the range of 400 to 800 °C. This weight loss

is likely caused by the slow desorption and breakdown of C-C, O-H and C-O bonding on the carbon structure following carbonization at 400 °C since the optimum temperature for direct carbonization of carbohydrate organic materials is 400 °C (Lokman *et al.*, 2014).

Meanwhile, the sulfonated carbon (with and without metals) showed another peak as illustrated in Figure 4.13(d)-(g) and. The degradation of -SO₃H groups resulted in a weight loss which was observed at temperatures of 400 °C, similar to the findings reported by Lokman (2016). TGA result for ACSO₃H shows that -SO₃H groups remained stable at a reaction temperature of up to 300 °C. At temperatures between 450-800 °C the oxygenated functional groups decompose (Sangsiri *et al.*, 2022). TGA results demonstrate that all prepared FeNi/ACSO₃H catalysts were stable before 800 °C as shown in Figure 4.13(c)-(f). As a comparison, 100%FeNi catalyst as metal only also displayed in the Figure 4.13(c). There was a noticeable degradation happened in the 100%FeNi sample between 200-300 °C as a result of the breakdown of hydroxyl metal into metal oxides Pinto *et al.*, (2019). However, the degradation in this temperature range was minimal in the FeNi/ACSO₃H catalysts, likely due to the lower metal content in these catalysts.

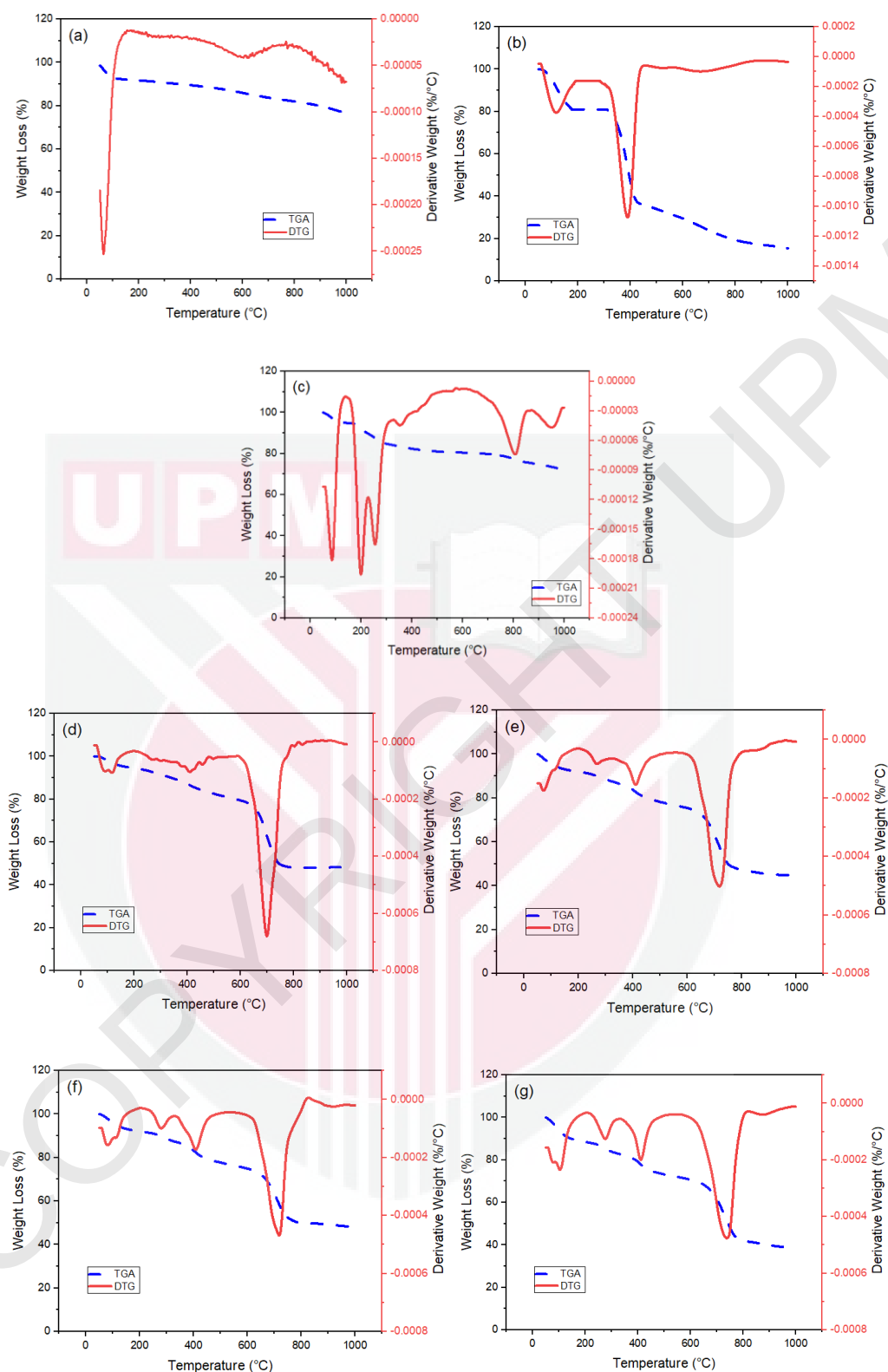


Figure 4.13: TGA and DTG curves of catalyst (a) AC (b) ACSO₃H (c) 100%FeNi (d) 5%FeNi/ACSO₃H (e) 10%FeNi/ACSO₃H (f) 15%FeNi/ACSO₃H and (g) 20%FeNi/ACSO₃H

To further study the chemical bonding state and composition of the FeNi/ACSO₃H catalyst, X-ray photoelectron spectroscopy (XPS) analysis was carried out by selecting 15%FeNi/ACSO₃H as a sample. The obtained XPS spectra were convoluted based on the reference C 1s at 284.5 eV in a narrow scan.

As shown in the XPS spectra in Figure 4.14(b) for the catalyst, the Ni 2p_{3/2} peak appeared at a binding energy around 852.25 eV assigned to Ni²⁺ and Ni 2p_{1/2} peaks appeared at a binding energy of 870.25 eV were assigned to Ni³⁺ (Chu *et al.*, 2020). Moreover, the peaks at 858.50 eV and 877.51 eV are ascribed to satellite peaks of the Ni species (Ramu *et al.*, 2021). In Figure 4.14(c), the catalyst sample exhibits two peaks at 709.81 eV and 720.41 eV, which correspond to the Fe 2p_{1/2} and Fe 2p_{3/2} peaks, respectively, indicating the existence of Fe³⁺ ions. Additionally, there are peaks observed at 718.9 eV and 732.9 eV, which are satellite peaks associated with Fe³⁺ ions in Fe₂O₃ (Wang *et al.*, 2021).

Figure 4.14(d) demonstrates that the O 1s spectra of the catalysts can be divided into three peaks, which have binding energies of 529.01, 530.80 and 531.77 eV, respectively. These peaks represented lattice oxygen (O_α) and chemisorbed oxygen (O_β) of the metal oxides (Meng *et al.*, 2023; Niu *et al.*, 2021). The O 1s region presented peaks at 530 eV for C-O (Rokhum *et al.*, 2022). Besides that, the signal with a binding energy of 531.7 eV may also be conclusively attributed to the existence of Ni-O or Fe-O bonds, similar to the findings by Jiang *et al.* (2017). Based on the literature, peak for -SO₃H is also located at 531.77 eV presented by S-O bonds (N. Li *et al.*, 2019).

It was found that XPS spectra for C 1s peaks in Figure 4.14(e) include three peaks that are attributed to the C-C or C=O with binding energy for 284.22 eV, C-O (285.69 eV), C=O (287.4 eV). This finding is similar to the study by Sangsiri *et al.* (2022) and Ferreira *et al.* (2020). Tohdee *et al.* (2021) found a peak at binding energy of 286.00 eV for C-S bond but this peak did not prominently appear in this study. It was assumed that, the peak overlapped with the peak at binding energy 287.86 eV. The peaks observed at 168.07 eV and 169.02 eV in the high-resolution S 2p spectra depicted in Figure 4.14(f) can be assigned to S 2p_{3/2} and S 2p_{1/2}, respectively which provides additional confirmation of the successful incorporation of –SO₃H groups (Zhang *et al.*, 2020). Consequently, the XPS result shows the successful sulfonation and metal impregnation in the catalyst which was already confirmed via XRD analysis.

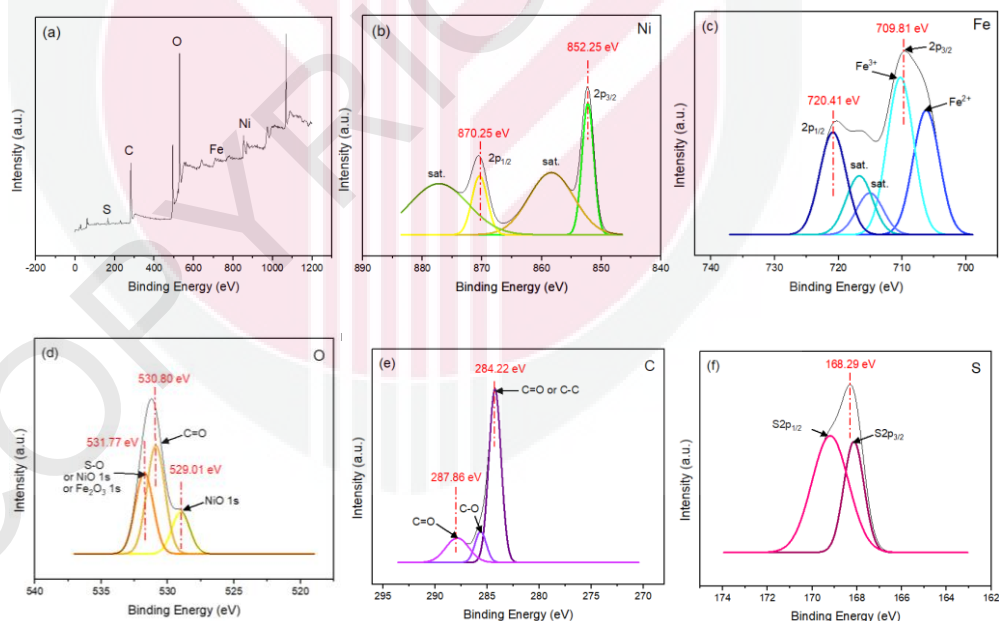


Figure 4.14: XPS analysis of 15%FeNi/ACSO₃H catalyst (a) wide scan (b) Ni 2p (c) Fe 2p (d) O 1s (e) C 1s and (f) S 2p

4.3.2 Surface area and porosity

The BET surface area, pore volume and average pore size for Fe and Ni metal catalysts are summarized in Table 4.4.

Table 4.4: Physical properties of FeNi/ACSO₃H catalysts

Catalyst	^a BET Surface Area (m ² /g)	^a Pore Volume (cm ³ /g)	^a Pore Size/ Diameter (nm)
AC	4.83	0.0169	5.03
ACSO ₃ H	1.24	0.0179	5.36
100%FeNi	48.17	0.1141	6.44
5%FeNi/ACSO ₃ H	13.62	0.0300	5.89
10%FeNi/ACSO ₃ H	17.76	0.0443	6.23
15%FeNi/ACSO ₃ H	10.68	0.0327	6.83
20%FeNi/ACSO ₃ H	16.30	0.0515	7.82

^aDetermined by using BET analysis.

The increasing of surface area is greater in 10%FeNi/ACSO₃H > 20%FeNi/ACSO₃H > 5%FeNi/ACSO₃H > 15%FeNi/ACSO₃H > AC > ACSO₃H, respectively. The BET surface area for AC is 4.83 m²/g, however, after being sulfonated with sulfuric acid, the surface area declined to 1.24 m²/g. This happened due to the introduction of acidic constituents into the existing pores of the AC (Abdullah *et al.*, 2020). Furthermore, the removal of C single bonds and C bonding between the crystalline structures in activated carbon after the sulfonation process also contributed to the decrease in surface area (Dehkhoda and Ellis, 2013). Chen *et al.* (2022) also claimed that the surface of activated carbon was effectively modified by grafting sulfonates, achieved through the selective disruption of mesoporous structures. Pore sizes for both AC and ACSO₃H catalysts are 2–50 nm, which explains the mesoporous type of pores. Figure 4.15 illustrates the N₂ adsorption-desorption isotherms for AC and ACSO₃H

catalysts, which revealed the type IV isotherm with a hysteresis loop typical for mesoporous materials for both catalysts.

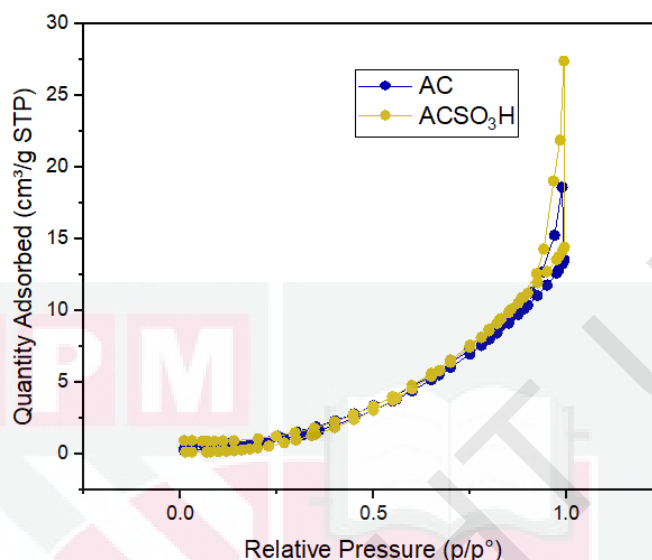


Figure 4.15: Isotherm profile of AC and ACSO₃H catalysts

Interestingly, the surface areas for the sulfonated activated carbon catalysts were increased after doping with metals, suggesting that their surface had more pores and active sites to support the reaction (Ibrahim *et al.*, 2020). Ya'Aini *et al.* (2019) concluded that the existence of these metal particles on a well-distributed activated carbon surface result in a significant increase in the specific surface area. Catalysts with high specific surface area was successfully produced by Chen *et al.* (2022) which resulted in the high hydrolysis activity for the synthesis of LA.

When a small quantity of FeNi (5-20%) were impregnated into the ACSO₃H framework, the FeNi particles are evenly distributed on the surface and inside the pores of the ACSO₃H. The dispersion of metal particles in the composite resulted in an increase in the total surface area, as the metal particles contribute their own surface area, as reported in the previous section for Fe₇₅Ni surface area. Introducing FeNi

particles into the ACSO_3H surface can result in the formation of additional porosity (Ronduda et al., 2022). The interaction between the metal particles and the carbon support can result in the formation of new pores or the expansion of pre-existing ones, therefore enhancing the surface area.

The $\text{FeNi}/\text{ACSO}_3\text{H}$ catalyst only consists of a weight ratio of just 5-20% FeNi . The ACSO_3H matrix constitutes the remaining 80-95% and possesses a significantly reduced surface area of $1.24 \text{ m}^2/\text{g}$. The overall surface area is determined by taking a weighted average of the high surface area of FeNi and the low surface area of ACSO_3H . Furthermore, the FeNi particles have the capability to block a portion of the pores within the ACSO_3H matrix and may also undergo some degree of agglomeration, so diminishing the overall surface area that is functional (Abdullah et al., 2020). Despite FeNi having a high surface area of $48.17 \text{ m}^2/\text{g}$, its inclusion in the ACSO_3H matrix results in a reduction of accessible surface area due to these effects.

Furthermore, the pore size distribution of $\text{FeNi}/\text{ACSO}_3\text{H}$ catalysts exhibits the mesoporous structure centered at 2 nm. Based on IUPAC, nanoporous materials are classified into three primary types based on pore size: microporous materials (pore size $< 2 \text{ nm}$), mesoporous materials (pore size $2\text{--}50 \text{ nm}$) and macroporous materials (pore size $> 50 \text{ nm}$) (Kamari and Ghorbani, 2021). Based on Table 4.4, the pore diameters for all $\text{FeNi}/\text{ACSO}_3\text{H}$ catalysts were slightly higher than those of AC and ACSO_3H . It was due to the obstruction of micropores by metal oxides and consequently, the average pore size was greater due to the presence of additional mesopores in the catalyst (Ramli and Amin, 2015b).

Figure 4.16 presents the N₂ adsorption-desorption isotherms for FeNi/ACSO₃H while pore size distribution is illustrated in Figure 4.17. The results indicated that all catalysts exhibited a type IV isotherm with type 3 hysteresis (H3), which suggests the presence of a mesoporous structure in the catalysts in line with the IUPAC classification. The catalyst's type III isotherm suggests that the adsorbed molecules tend to form clusters, in other words, as the pressure or concentration increases, the amount of gas adsorbed on the catalyst surface continues to increase without any limit, and its relative saturation approaches unity (Azri *et al.*, 2020). All FeNi/ACSO₃H catalysts exhibited pore sizes ranging from 2 to 18 nm. Nevertheless, all catalysts demonstrated a climbing peak in terms of pore size distribution except for 20%FeNi/ACSO₃H. As the metal loading increased over the optimum value (15%FeNi/ACSO₃H), pore blockage and agglomeration of NiO particles on support occurred and the pore volume started to decrease (Shamsuddin *et al.*, 2021). The pore volume for 20%FeNi/ACSO₃H catalyst manage to reach up to 0.10 cm³/g compared to other catalysts. Hence, the pore volume of 20%FeNi/ACSO₃H was still higher than other catalyst presented in Table 4.4

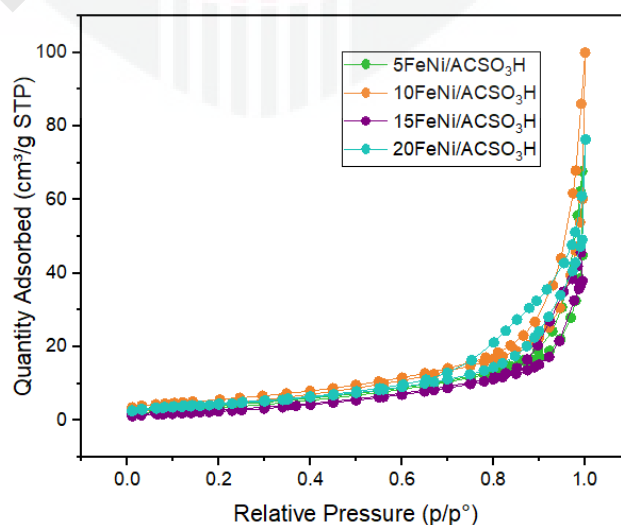


Figure 4.16: Isotherm profile of 5-20%FeNi/ACSO₃H catalysts

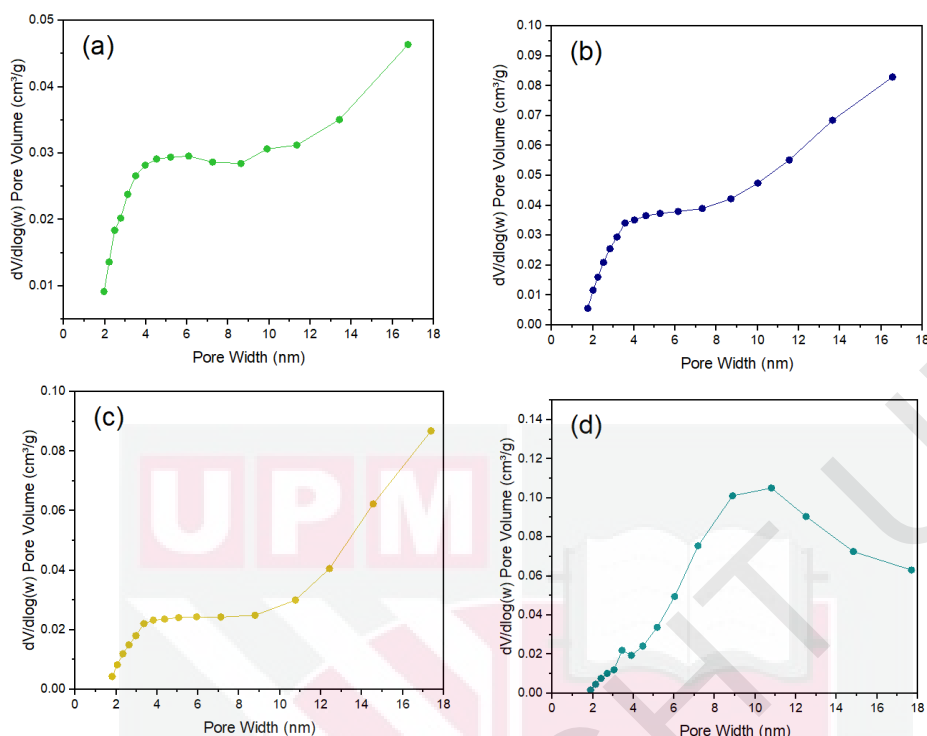


Figure 4.17: Distribution of pore volume of (a) 5%FeNi/ACSO₃H (b) 10%FeNi/ACSO₃H (c) 15%FeNi/ACSO₃H and (d) 20%FeNi/ACSO₃H

4.3.3 Acid sites properties

The corresponding acidity (amount of ammonia uptakes) is reported in Table 4.5. The acid sites in the catalysts are certainly a consequence of the sulfonation process, given that the acid density obtained in non-sulfonated AC was relatively low, measuring 2.2493 mmol/g. An increase in total acid density values is noticed after sulfonation, reaching a maximum of 9.4060 mmol/g. The acid density of the prepared AC is slightly lower than that of the activated carbon catalyst prepared by Lokman (2016) which was 2.4500 mmol/g. After sulfonated, the total acid density in this study is slightly higher than their study (7.8900 mmol/g). It is also worth mentioning that the total acid density of the ACSO₃H from this study was higher compared to the sulfonated hydrothermal carbon catalyst (7.15 mmol/g) from Wen *et al.* (2020) and sugar-derived sulfonated

carbon catalysts (5.31 mmol/g) produced by Rokhum *et al.* (2022). The enhanced acid density can be attributed to the increased surface area and bimodal porosity of macroporous and mesoporous structures, which facilitate the incorporation of a significant number of SO₃H groups onto the carbon lattice (Lokman, 2016).

The total NH₃ adsorption of FeNi metal only was 8.3427 mmol/g, with 9.811 mmol/g assigned to weak acids, 2.5288 mmol/g to medium acids, and 4.8328 mmol/g to strong acids. However, when this FeNi catalyst was impregnated into ACSO₃H, the overall adsorption of NH₃ significantly rose, especially for very acidic substances. An example was the compound 5% FeNi/ACSO₃H, which had a total adsorption capacity of 20.4752 mmol/g, with a significant increase in the adsorption of strong acids to 16.1033 mmol/g. This trend continued with higher doping levels, where 20% FeNi/ACSO₃H achieves the highest total NH₃ adsorption of 25.6783 mmol/g, including 14.5744 mmol/g for strong acids.

Ni or Fe loaded onto the ACSO₃H increases the acid amount significantly. It was expected that the total acidity would increase as the metal concentration increased. However, the total acidity value for 15%FeNi/ACSO₃H slightly lower than 10%FeNi/ACSO₃H. This phenomenon may be attributed to the non-uniform dispersion of the NiO and Fe₂O₃ metals across the surface of the catalyst, leading to the agglomeration of these metals and subsequently obstructing the active sites on the catalysts (Wijaya *et al.*, 2021).

There is no catalyst that impregnated NiO and Fe₂O₃ into sulfonated carbon catalyst to compare with this study. Santi *et al.* (2022) doped NiO into activated carbon and the

total acidity was only 3.05 mmol/g. Meanwhile, Soltani *et al.* (2019) doped NiO into a sulfonated carbon catalyst but only obtained 3.10 mmol/g total acidity which is very low compared to this study. It is envisaged that the sulfonation agents and method used in sulfonation can affect the acidity of the catalyst since their study used different acids. Furthermore, the utilization of different carbon precursors, which could result in varying degrees of attachment of sulfonic active groups may also contribute to the different values of acidity (Lim *et al.*, 2020).

Table 4.5: Physical properties of FeNi/ACSO₃H catalysts

Catalyst	Amount NH ₃ adsorbed ^a (mmol/g)			Total
	Weak acid	Medium acid	Strong acid	
AC	N.D	0.9976	1.2517	2.2493
ACSO ₃ H	1.3742	0.1392	7.8926	9.4060
100%FeNi	9.811	2.5288	4.8328	8.3427
5%FeNi/ACSO ₃ H	1.5655	2.8064	16.1033	20.4752
10%FeNi/ACSO ₃ H	1.9302	4.0908	17.8478	23.8688
15%FeNi/ACSO ₃ H	2.4460	4.4232	15.7525	22.6217
20%FeNi/ACSO ₃ H	2.4774	8.6235	14.5744	25.6783

^aNH₃-TPD desorption peak for all catalysts.

The amount of NH₃ adsorbed at various desorption temperatures is used to determine the acidity strength: weak acidity, which occurs below 573 K, medium-strong acidity, which occurs between 573 K and 773 K, and strong acidity, which occurs above 773 K (Huang *et al.*, 2016). The ammonia desorption profiles of AC and ACSO₃H catalysts are illustrated in Figure 4.18. The graph depicted one peak for the ammonia desorption that appeared for the AC catalyst. In contrast, the ACSO₃H catalyst exhibited an additional desorption peak within 150 to 300 °C temperature range. There are two types of Brønsted acid sites are present: weak Brønsted acid sites at

lower temperatures and strong Brønsted acid sites at higher temperatures (Lokman *et al.*, 2015).

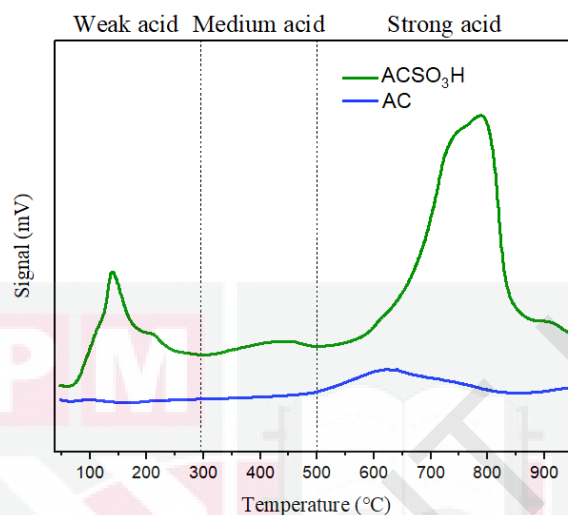


Figure 4.18: NH₃-TPD patterns of AC and ACSO₃H catalysts

Figure 4.19 demonstrated the ammonia desorption profiles of FeNi/ACSO₃H catalysts which revealed the presence of a broad peak in the strong region indicating strong acidity in all catalysts. The NH₃-TPD profile indicated small intensity peaks in the region between 90-300 °C assigned to the NH₃ desorption from weak acid sites in 20%FeNi/ACSO₃H catalyst only. Additional sharp NH₃ desorption peaks at 300-500 °C in all catalysts suggested medium acid sites. For the 20%FeNi/ACSO₃H catalyst, the weak and medium acid sites can be observed from the relatively broader and intense NH₃ desorption peaks in the range between 200-500 °C, which confirmed a higher number of acid sites in this catalyst. The presence of iron and nickel in the catalyst contribute to the formation of Lewis acid sites (Zainol *et al.*, 2020).

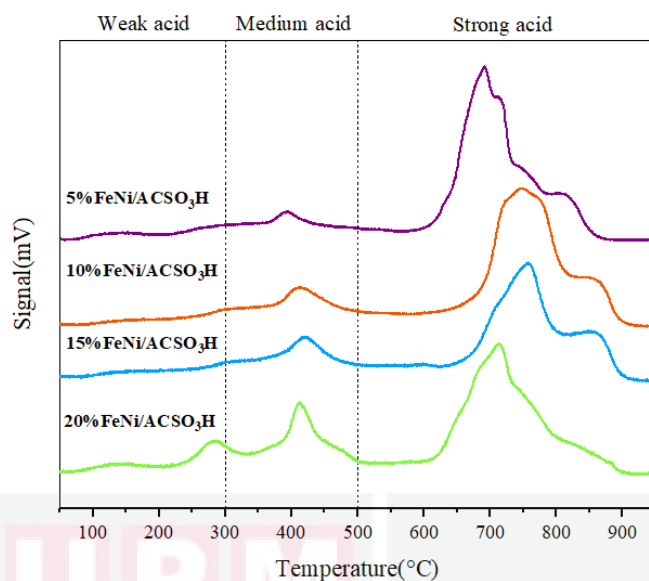


Figure 4.19: NH₃-TPD patterns of FeNi/ACSO₃H catalysts

4.3.4 Surface morphology

Figure 4.20 reveals the surface morphologies of AC and ACSO₃H catalysts at the 1 μ m scale. Irregular and aggregation well-developed tube-like shapes were observed in the AC catalyst. The morphological changes of AC was observed after sulfonation with sulfuric acid. Applying a high concentration acid treatment resulted in surface damage to the AC material, leading to the formation of a cracked surface structure which can be attributed to the degradation of chemical bonding (Zainol *et al.*, 2021). Furthermore, a large number of irregularly sized pores are produced, similar to the research by Mardina *et al.* (2021). EDX result in Figure 4.20 demonstrates the presence of the sulfur (S) component after the sulfonation process, which indicated the existence of the -SO₃H functional groups on the activated carbon catalyst.

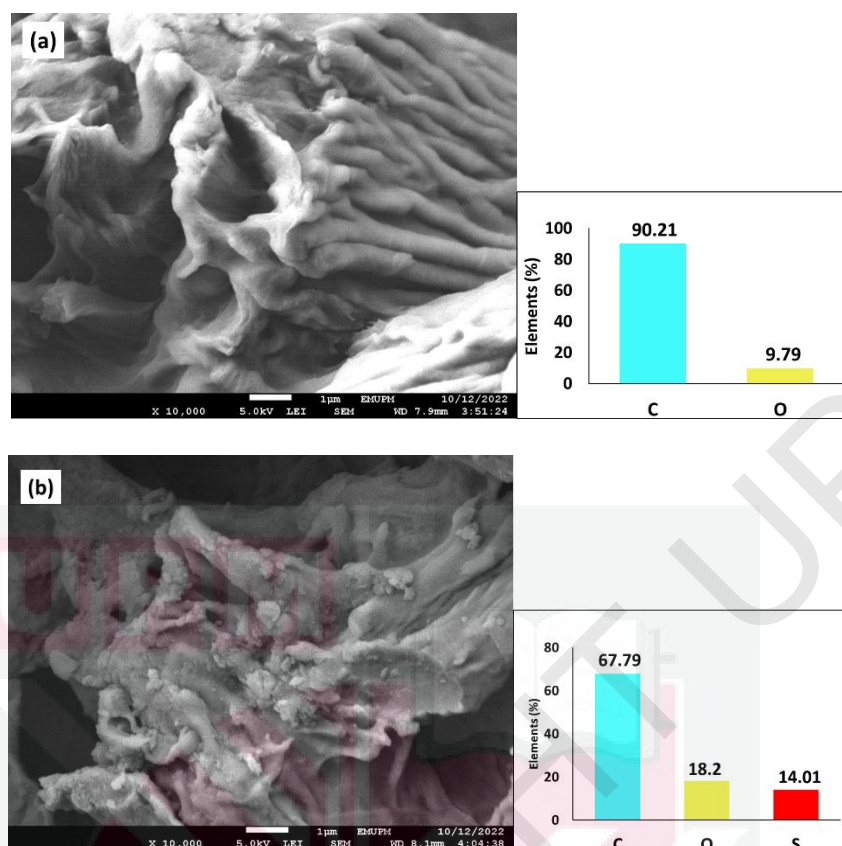


Figure 4.20: FESEM and EDX images of (a) activated carbon and (b) sulfonated activated carbon

FESEM image of 15%FeNi/ACSO₃H is presented in Figure 4.21(b). For comparison before the impregnation of metal catalyst into sulfonated carbon catalyst, an FESEM image of Fe₇₅Ni catalyst was also provided in Figure 4.21(a). The morphological structure of Fe₇₅Ni catalyst clearly exhibits a spherical shape, as illustrated by Fe₂O₃ and NiO metal oxide. The distinctive morphology is also evident in the 15%FeNi/ACSO₃H catalyst images, which exhibit small highly developed tubular structures that corresponding to sulfonated carbon (Kumar *et al.*, 2019). The presence of C, O, S, Fe and Ni metals in the XRD result confirmed the successful impregnation of Fe and Ni metal into the ACSO₃H catalyst.

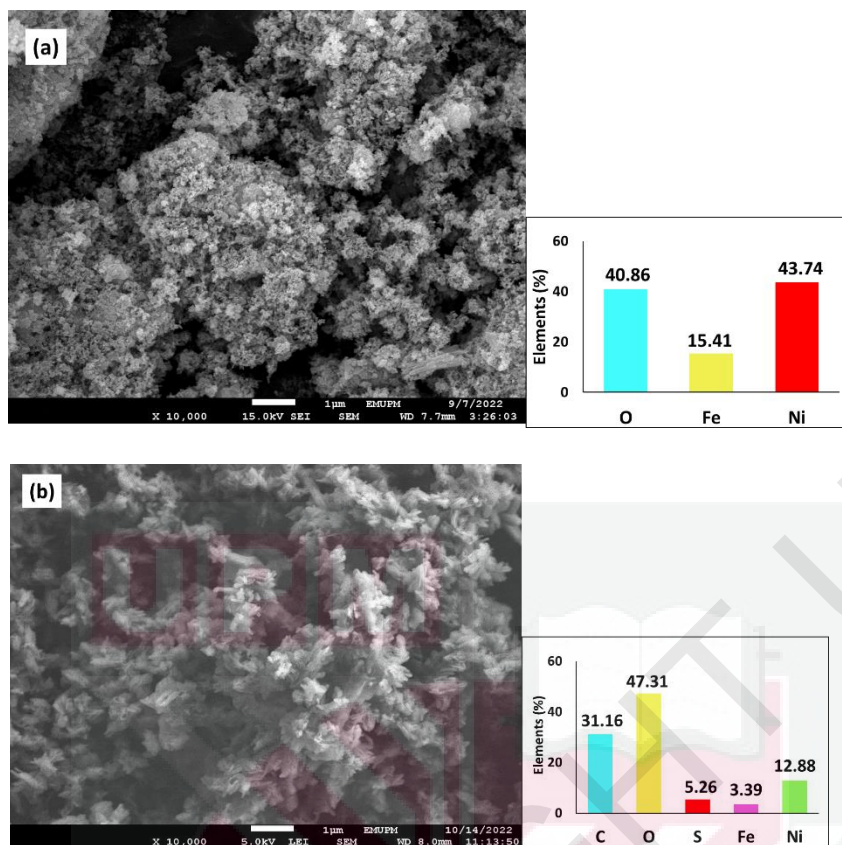


Figure 4.21: FESEM and EDX images of (a) 100%FeNi and (b) 15%FeNi/ACSO₃H

The elemental mappings shown in Figure 4.22 reveal that the S, C, O, Fe and Ni elements exist in 15%FeNi/ACSO₃H catalyst, implying that the –SO₃H, Fe₂O₃ and NiO groups are homogeneously loaded onto the surfaces of the catalyst.

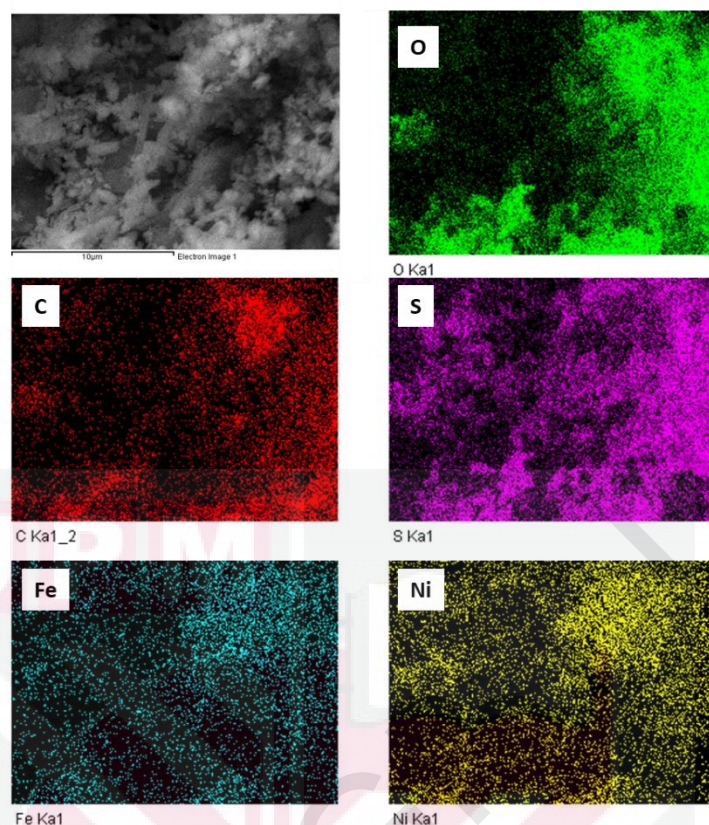


Figure 4.22: EDX mapping for 15%FeNi/ACSO₃H

4.3.5 Catalyst screening

The conversion of cellulose into LA was evaluated by using different compositions of Fe and Ni metals loaded onto sulfonated carbon catalysts which were selected based on the previous studies. The amounts of products were analyzed using HPLC as described in Section 3.4.2. Furthermore, the effects of several operating parameters for a conversion of glucose were also studied and discussed.

Activated carbon (AC) and sulfonated carbon (ACSO₃H) catalysts were utilized to produce LA and other products. As shown in Figure 4.23, the introduction of the sulfonic group through sulfonation enhanced the yield of LA. Based on the theoretical

yield, LA produced from AC was only 1.09 % (based on theoretical) which was equal to 0.78 wt.%. When a sulfonated carbon catalyst was used, the amount of LA increased to 5.91 % of theoretical (4.35 wt.%). Specifically, the higher acidity of ACSO_3H contributes to an increased production of LA compared to AC (Li *et al.*, 2014b).

The yield of glucose from cellulose in Figure 4.23(a) increased when using ACSO_3H catalyst (33.14%) compared to AC catalyst (16.01%) which indicated the conversion of cellulose into glucose was better when using ACSO_3H catalyst. The conversion of cellulose into glucose is challenging due to the significantly limited porosity and surface area, which hinders the adsorption of cellulose and the transfer of glucose during reactions (Yang *et al.*, 2021). The pore size of the catalyst also could have affected the yield of LA from cellulose or glucose. Furthermore, the size of mesopores among the metals catalysts (3.60-8.24 nm) was smaller compared to the cellulose molecule (40–300 μm) (Kian *et al.*, 2020) but larger than the glucose molecule (0.54 to 0.97 nm) (Yang *et al.*, 2008). Liu *et al.* (2013) managed to obtain 35.0% glucose from cellulose when using sulfonated sucrose-carbon at a lower temperature (140 °C). The utilization of ionic liquid in their study assisted the cellulose conversion by dissolving this material. Meanwhile, Figure 4.23(b) shows that, when glucose was used as a starting material, the weight of glucose was reduced from 52.3 wt.% (using AC catalyst) to 40.57 wt.% when using ACSO_3H catalyst. This indicated that the conversion of glucose into other materials such as fructose or HMF occurred faster when utilizing ACSO_3H catalyst.

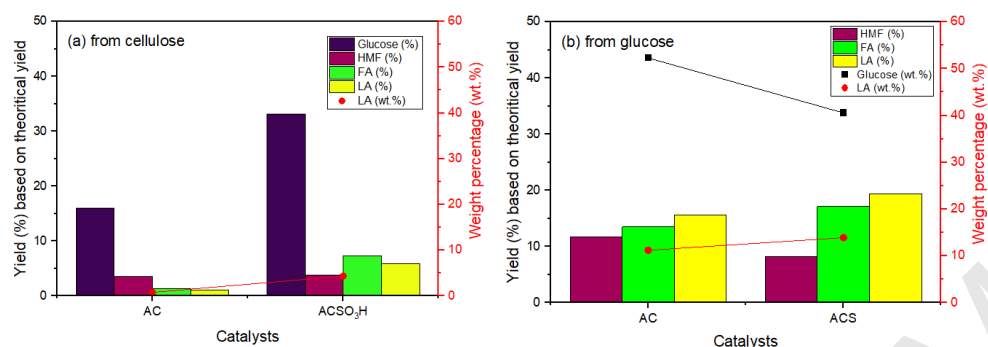


Figure 4.23: Product yields (%) based on theoretical yield and LA yield (wt%) from cellulose (a) and glucose (b) using AC and ACSO₃H catalysts. Reaction conditions: 5 g cellulose or glucose, reaction temperature 180 °C, reaction time 5 h and catalyst dosage 0.15 g

A proposed method to enhance the yield of HMF and LA was done involved the utilization of an external Brønsted acid in conjunction with a Lewis acidic metal catalyst. Different loadings of Fe and Ni metals were impregnated into sulfonated carbon and these catalysts were referred to as sulfonated carbon metal catalysts (FeNi/ACSO₃H). The evaluation of these catalysts in the production of glucose, HMF, FA and LA was also done by utilizing two different raw materials. The efficiency of these catalysts was compared by utilizing cellulose and glucose, as depicted in Figures 4.24(a) and 4.24(b) accordingly.

Generally, LA yields after impregnation with metals were higher than the sulfonated carbon catalyst discussed before. 15%FeNi/ACSO₃H catalyst produced the highest yield of LA from both cellulose and glucose. 16.76 % LA (based on theoretical yield) with 12.00 wt.% yield based on a weight percentage collected from this catalyst for cellulose. Meanwhile, glucose yielded 50.70 % LA yield based on theoretical (32.65 wt.%) by using this catalyst. As observed in Figure 4.24, increasing metal loadings up to 15% increased the yield of LA. However, further increasing to 20% FeNi decreased the amount of LA. As previously reported, this could be attributed to the presence of

the most reactive Lewis acid sites, which facilitate the production of humins (Ramli and Amin, 2015c). Therefore, it is presumed that the conversion of cellulose or glucose into LA on FeNi/ACSO₃H catalyst is mainly determined by the acidity of the catalyst and the active catalytic sites originating from sulfonated carbon catalyst.

When evaluating the catalytic performance of metal FeNi only compared to FeNi impregnation into ACSO₃H catalysts, notable enhancements were observed using cellulose as the feedstock. The utilization of a 100% FeNi catalyst resulted in a glucose yield of 25.93%, while HMF (2.18%), FA (9.02%), and LA (10.51%, 7.52% mass) exhibit comparatively lower yields. Conversely, when FeNi was impregnated into ACSO₃H, the conversion efficiency was enhanced. This led to a decrease in glucose yield, but a significant increase in the yields of HMF, FA, and LA. As an example, the 5%FeNi/ACSO₃H catalyst obtained a glucose yield of 7.89%, which was quite low. However, this catalyst demonstrated greater yields for HMF (5.87%), FA (12.88%), and LA (13.29% or 9.51% wt.%). This trend continues with higher loading of FeNi levels, with 15% FeNi/ ACSO₃H showed the highest LA yield (16.76%) and LA mass% (12%). The results suggested that the addition of ACSO₃H greatly improves the catalytic performance, resulting in enhanced efficiency and selectivity when compared to only FeNi catalyst. The observed trends were further supported by similar enhancements in catalytic performance when glucose was used as the raw material.

Figure 4.24 shows that the yield of LA was low but yield of glucose was also low for the conversion of cellulose into LA, indicating the challenges associated with cellulose degradation. This propose that there was still some cellulose that has not been converted into glucose yet. In contrast, when initiated with glucose, the remaining

glucose was also low but high amount of LA can be observed as the product from hydrolysis of glucose, highlighting the relatively easier degradation of glucose compared to cellulose (Wang et al., 2020). The presence of hydrogen bonds within and between cellulose chains causes a highly crystalline structure to form. This structure limits the ability of catalysts to access the $\beta(1 \rightarrow 4)$ glycosidic linkages (Guan *et al.*, 2021).

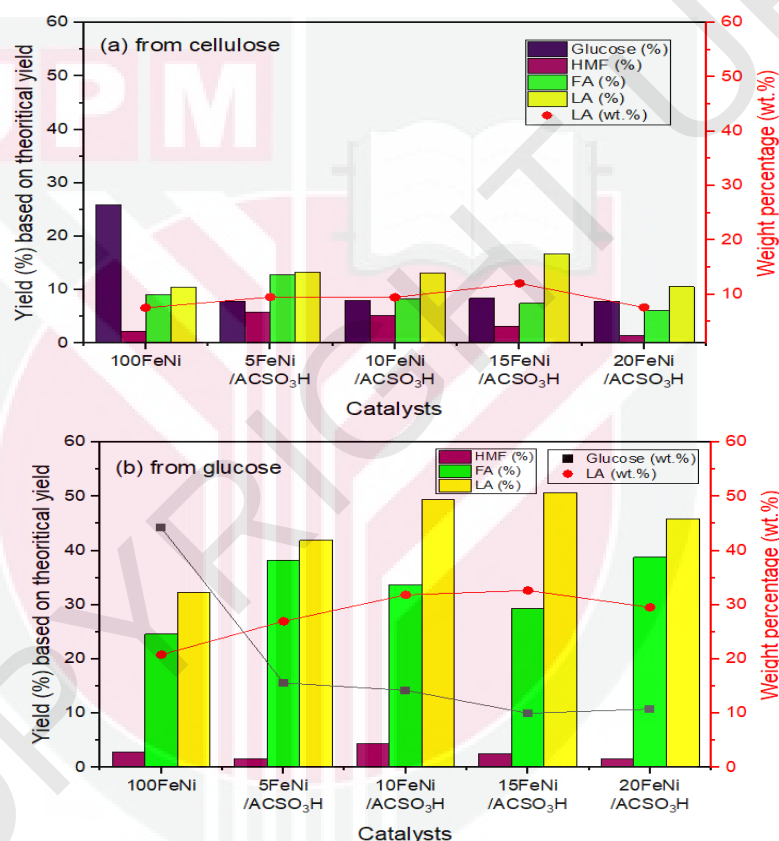


Figure 4.24: Product yields (%) based on theoretical yield and LA yield (wt%) from cellulose (a) and glucose (b) using FeNi/ACSO₃H catalysts. Reaction conditions: 5 g cellulose or glucose, reaction temperature 180 °C, reaction time 5 h and catalyst dosage 0.15 g

4.3.6 Optimization study of LA from glucose

The effects of experimental parameters such as temperature, reaction time and catalyst loadings on the production of LA were investigated. Glucose was selected as a starting

material in this part of the study. In this case, utilization of glucose made it easier, as it is completely soluble in water, allowing for feasible separation of the solid catalyst. Additionally, a reusability study of the catalyst was carried out after obtaining an optimized condition. 15%FeNi/ACSO₃H catalyst was used because this catalyst produced the highest yield of LA.

The conversion of cellulose to LA is significantly influenced by the reaction temperature. Generally, a temperature ranging from 150 to 200 °C is necessary to convert cellulose into LA (Shi *et al.*, 2021b). Therefore, it is crucial to find the most favorable temperature for the conversion of cellulose into LA using a sulfonated carbon catalyst in this study. Figure 4.25 shows that, an increase in reaction temperature from 120 to 200 °C resulted in a rise in the LA production. This trend contrasts with the findings from Shi *et al.* (2021a) which showed that increasing the temperature to more than 180 °C reduced the LA yield. It was assumed that their study had already identified optimized temperature, but this current research still needs to increase the temperature until it reaches the optimum conditions. However, due to the reactor limitation, the temperature beyond 200 °C was not doable. As seen in Figure 4.25, the weight percentage of glucose decreased when temperature increased. The yield of HMF was increased in reaction temperature from 120 to 160 °C and then decreased when the temperature was beyond 160 °C. This trend indicated that, glucose was successfully converted into HMF and LA was rapidly produced from HMF when the temperature increased. The yield of LA at the temperature of 200 °C was assumed to be not optimum because HMF was still present in the final products. However, a study from Ma *et al.* (2021) presented that the yield of LA had a substantial rise, increased from 8.94% to 50.40%, in response to an increase in reaction temperature

from 160 to 200 °C. Subsequently, their study found that further increases in reaction temperature beyond 200 °C led to a gradual decline.

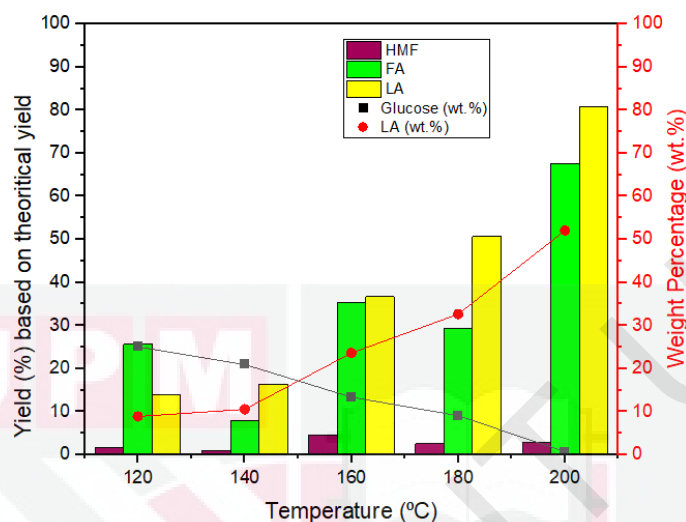


Figure 4.25: Product yields (%) based on theoretical yield and LA yield (wt%) from glucose at different temperatures using 15%FeNi/ACSO₃H catalysts. Reaction conditions: 5 g glucose, reaction time 5 h and catalyst dosage 0.15 g

Figure 4.26 shows the effects of catalyst dosage on the production of LA. When the catalyst dosage increased from 0.05 to 0.10 g the LA yield increased from 56.5% to 86.2% and the yield of HMF decreased significantly from 2.83% to 1.29%. This is due to the increase in the number of catalytic active sites available in the catalysts which promotes the production of LA (Chen *et al.*, 2022). An excessive quantity of catalyst can result in the increasing of unwanted products (Cheng *et al.*, 2022). Humic compounds generated from the side reactions can accumulate on the surface of the catalyst, thereby limiting the desired reactions and affecting the LA synthesis (Xu *et al.*, 2023).

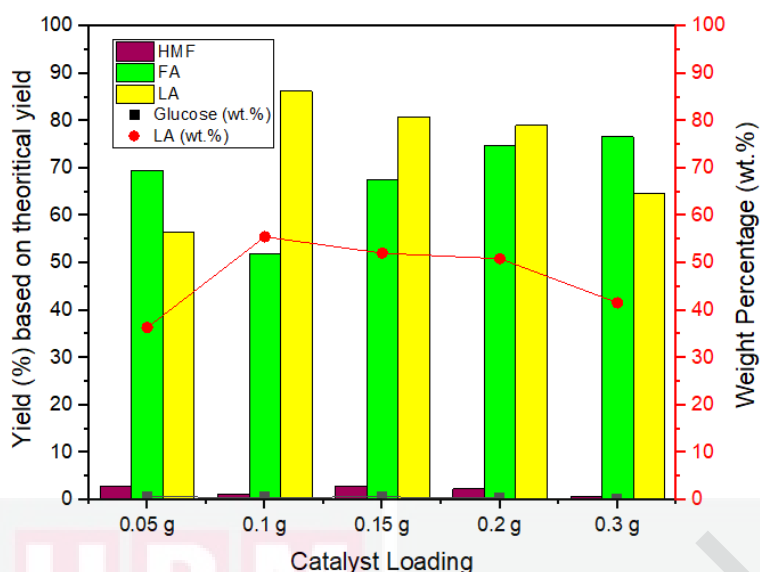


Figure 4.26: Product yields (%) based on theoretical yield and LA yield (wt%) from glucose using different loadings of 15%FeNi/ACSO₃H catalysts. Reaction conditions: 5 g glucose, reaction temperature 200 °C and reaction time 5 h

As shown in Figure 4.27, when the reaction time increased from 3 to 5 h, the yield of LA noticeably increased from 62.7% to 86.2% (based on theoretical yield) with a weight percentage of 55.54 wt.%. However, further increasing the reaction time up to 8 h and 10 h resulted in a gradual decline in the yield of LA from 86.2% to 77.2% and then to 71.8% (based on theoretical yield). The weight percentage of LA collected at 8 h and 10 h were 49.73 wt.% and 46.25 wt.%, respectively. Prolonged reaction time has led to polymerization of the products which causes a decrease in the yield of the desired chemicals (Ma *et al.*, 2021). Furthermore, humins can be generated when the reaction time is prolonged (Yan *et al.*, 2008). The deposition of humin on the surface of the catalyst can cause catalyst deactivation (Chen *et al.*, 2022).

In summary, highest yield of LA was produced from glucose after optimized the reaction conditions (temperature, reaction time and catalyst loading). 86.2% (based on theoretical yield) or a weight percentage of 55.54 wt.% of LA was achieved at 200 °C

reaction temperature using 0.10 g 15%FeNi/ACSO₃H catalyst and 5 hours of reaction time. This condition was further applied for the following reusability study.

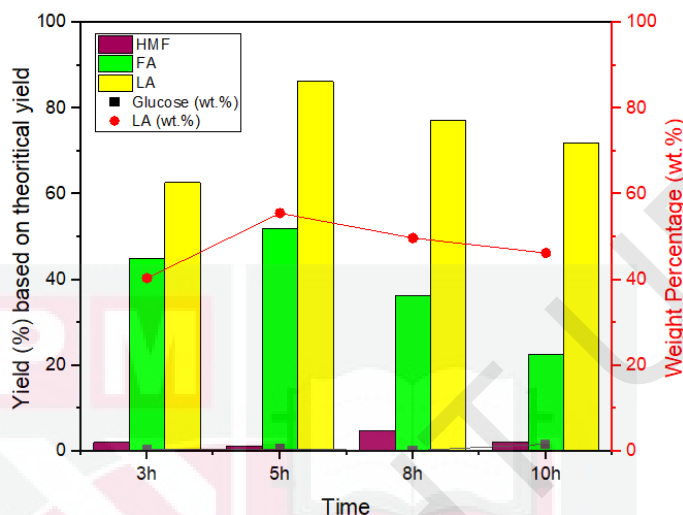


Figure 4.27: Product yields (%) based on theoretical yield and LA yield (wt%) from glucose at different times using 15%FeNi/ACSO₃H catalysts. Reaction conditions: 5 g glucose, reaction temperature 200 °C and catalyst dosage 0.10 g

The stability and reusability of a sulfonated carbon metal catalyst used in this study are essential due to the risk of metal leaching and catalyst deactivation. Glucose was utilized as a reactant to test the sulfonated carbon metal catalyst's effectiveness since it is soluble in water, allowing for the catalyst and product solution to be separated after the reaction (Sweygers et al., 2018a). The reaction conditions used for reusability study were selected based on the optimization study for conversion of glucose into LA. The reusability of the optimized sulfonated carbon metal catalyst was assessed over five consecutive cycles to examine its deactivation and ability to be reused without reactivation. Figure 4.28 shows that the activity of the catalyst decreased gradually after each cycle. Repeated reaction cycles were carried out using the optimum catalyst and at the optimum temperature 200 °C for 5 h using 0.10g sulfonated carbon metal (15%FeNi/ACSO₃H) catalyst. When each reaction cycle was over, the spent catalyst

was collected by centrifugation and washed with hexane and methanol to get rid any polar or non-polar impurities on the surface of the catalyst. The LA yield dropped from 86.2% of theoretical (55.54 wt.%) to 80.96% (52.14 wt.%) after the second reaction cycle. The yield of LA based on theoretical yield further dropped to 79.37% (51.12 wt.%) and 71.53% (46.06 wt.%) after the third and fourth reaction cycles, respectively. The reaction proceeded further to another run, however, the yield of LA reduced to 31.69% only which equals 20.41 wt.%. Hence, this finding has shown that the synthesized catalyst can be reutilized for a maximum of four reaction cycles with relatively good catalytic activity. The sulfonated carbon catalyst used in the research by Mavakumba *et al.* (2019) also demonstrated that it can be effectively utilized for up to 4 cycles. In this research, the regeneration of the catalyst was done by washing and filtering only, without calcination similar to a study by Aliyu *et al.* (2024). This is because a high temperature of calcination (more than 500 °C) is needed to reactivate the catalyst (Zhao *et al.*, 2018). Performing high temperature can degrade the sulfur group, so sulfonation is essential to re-introduce this group in the catalyst (Kang and Yu, 2018). In order to evaluate the changes that happened in the catalyst after the reactions, the spent catalyst was analyzed in term of physical and chemical properties.

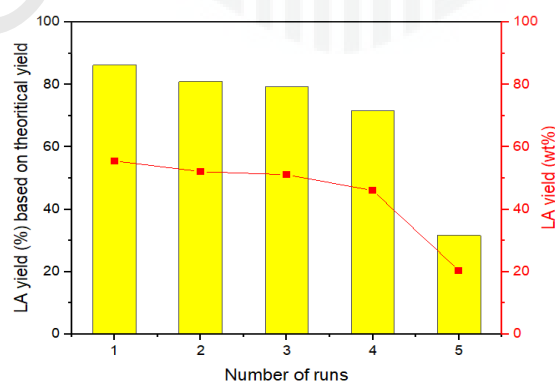


Figure 4.28: Reusability study of 15%FeNi/ACSO₃H catalysts. Reaction conditions: 5 g glucose, reaction temperature 200 °C, reaction time 5 h and catalyst dosage 0.10 g

Table 4.6 shows that BET surface area, pore volume and pore size of the catalyst dropped, which may be assigned as the cause for the decline in activity. The leaching of SO₃H could be confirmed by TPD-NH₃ analysis. Meanwhile, the leaching of Fe and Ni elements from Fe.75Ni catalyst was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and the data is tabulated in Table 4.7. The total acid content dropped sharply from 23.38 µmol/g for the fresh catalyst to 11.61 µmol/g for the spent one. The decrease in LA yield after each reuse can be due to the leaching of active sites, which was assumed to occur during the cleaning of the catalyst using hexane and methanol after each re-utilization (Mavakumba *et al.*, 2019).

Table 4.6: Physical properties of fresh and spent catalysts

Catalyst	^a BET Surface Area (m ² /g)	^a Pore Volume (cm ³ /g)	^a Pore Size/ Diameter (nm)
Fresh Catalyst	10.68	0.0327	6.8328
Spent Catalyst	5.81	0.0294	5.1907

^aDetermined by using BET analysis.

Table 4.7: Chemical properties of FeNi catalysts

Catalyst	Total amount NH ₃ adsorbed ^a (µmol/g)	Fe (wt.%) ^b	Ni (wt.%) ^b
Fresh Catalyst	23.38	4.01	13.62
Spent Catalyst	11.61	2.37	4.91

^aNH₃-TPD desorption peak for all catalysts.

^bICP-OES analysis

4.3.7 Summary

In this chapter, the best loading of Fe and Ni metals was successfully impregnated with sulfonated carbon catalyst based on the findings from several analyses such as XRD, FTIR, EDX and XPS. It was found that the production of LA from cellulose with a

maximum LA yield of 16.76% (based on theoretical yield) and a weight percentage of 12.00 wt.% was achieved at 200 °C reaction temperature using 0.10 g 15%FeNi/ACSO₃H catalyst and 5 hours of reaction time. Generally, the LA synthesis from cellulose was still low due to the incomplete degradation of cellulose. To increase the yield of LA, cellulose should be modified or pretreated. Due to the limitation of cellulose dissolution, glucose was used for reusability study. Since the catalyst can be used for up to four reaction cycles with no loss of catalytic activity, it has shown to have a very positive economic impact on the chemical reaction.

4.4 Production & pretreatment of OPEFB-based cellulose

This study aims to evaluate the effect of pretreatment on the cellulose produced from OPEFB for the production of LA. OPEFB mainly consists of lignocellulosic materials such as cellulose, hemicellulose and lignin. The cellulose was firstly isolated from the OPEFB and later pretreated with several MSHs to enhance the yield of LA. LiBr, LiCl and ZnCl₂ were the selected MSHs and their effects on the LA yield from OPEFB-based cellulose was evaluated. To obtain high yield of LA, several parameters such as reaction time, reaction temperature and the effect of catalyst loading on LA production from OPEFB-based cellulose were also investigated.

4.4.1 Characterization of OPEFB

Figure 4.29 shows a prepared OPEFB sample according to the method described in Section 3.7.1 where the fiber was washed and screened to remove unwanted materials, ground and sieved to an approximate length of 123–250 µm.



Figure 4.29: OPEFB sample after dried, ground and sieved

The proximate analysis in Table 4.8 indicates the findings of analysis by neutral detergent fiber (NDF), acid detergent fiber (ADF), acid detergent lignin (ADL) and ash. These data are shown as percentages, representing the composition per 100 grams of OPEFB or on a dry basis. Based on the results obtained from the proximate analysis, the content of cellulose, lignin, hemicellulose, ash and extractives was calculated by using the formula given (Eqs. (3.3) – (3.6)) in Sections 3.7.1 in Chapter 3.

Table 4.8: Proximate analysis of OPEFB

Analysis	Content (%)
Acid Detergent Fiber (ADF)	56.76
Neutral Detergent Fiber (NDF)	77.43
Acid Detergent Lignin (ADL)	14.82

*The proximate analysis data from MARDI for this study was issued by the Agriculture Chemical Analysis Laboratory (D10), Food and Agriculture Analysis Laboratory Program, Technical Services Centre.

Table 4.9 shows the amount of cellulose, hemicellulose, lignin, ash and extractives expressed as percentages based on a quantity of 100 g of OPEFB (or on a dry basis) in comparison with several recent studies. The cellulose content in OPEFB fibers in this research compares well with the range reported in the literature, with values ranging from

39.90% to 48.60%. The hemicellulose content was also consistent with values recorded by previous studies which varied from 13.30% to 29.80%. Nevertheless, it is important to mention that the amount of lignin in our study (14.82%) is generally lower in comparison to some previous studies, where the lignin content may have reached as high as 25.20% from a study by Zarin *et al.* (2022). The amount of extractive is high in this study compared to other reports, hence, the dewaxing method is needed to remove the extractives for subsequent usage of OPEFB (Mthembu *et al.*, 2023).

The observed variations in chemical composition among different studies can be explained by several reasons, such as harvesting technique, growth conditions and biomass storage (Pasangulapati *et al.*, 2012). The processing technique and analytical procedures during the chemical composition analysis of biomass also can affect the results (Biswas *et al.*, 2014). Given that lignocellulosic materials represent a substantial amount of biomass, it is crucial to assess the chemical composition prior to performing any experiment. Understanding the chemical composition of OPEFB fibers is important for further isolation of cellulose to remove hemicellulose, lignin and extractive.

Table 4.9: Compositional analysis of OPEFB

Research	Materials (%)			
	Cellulose	Hemicellulose	Lignin	Extractive
This study*	41.94	20.67	14.82	22.57
Masran <i>et al.</i> (2020)	40.30	19.90	22.90	16.90
Nurhidayat (2022)	42.38	23.84	20.20	-
Zarin <i>et al.</i> (2022)	41.00	13.30	25.20	20.50
Risanto <i>et al.</i> (2023)	39.90	25.80	22.10	12.20
Ajayi <i>et al.</i> (2023)	44.60	29.80	21.40	4.13
Harahap <i>et al.</i> (2020b)	48.60	28.10	23.40	-

* '-' Not determined.

The thermogravimetric curves of lignocellulosic biomass exhibit four different stages of primary decompositions, characterized by the reduction in weight of the biomass materials (hemicellulose, cellulose and lignin) and the loss of moisture. After the removal of moisture up to a temperature of 150 °C, the decomposition of the three biomass lignocellulosic components is observed. Hemicellulose undergoes degradation at temperatures ranging from 230 to 290 °C, while cellulose degrades at temperatures between 290 and 370 °C (Díez *et al.*, 2020). However, the decomposition peak of lignin was broader in comparison to the decomposition peaks of hemicellulose and cellulose due to the lower reactivity of C-C bonds in lignin (Halder *et al.*, 2019a). In the last stage, the slow and constant decomposition of the complex compound lignin occurred at the temperature of 370 to 900 °C (Reza *et al.*, 2020). According to the TGA result shown in Figure 4.30, the cellulose content is approximately 38.98% (stage III), the hemicellulose content is 21.41% (stage II), and the lignin content is 10.45% (stage IV). The values for cellulose, hemicellulose and lignin in the proximate analysis were 41.94%, 20.67% and 14.82%, respectively, which are not markedly different from these results. The content of residue collected from TGA analysis is 23.41% which is almost equal to the result from proximate analysis.

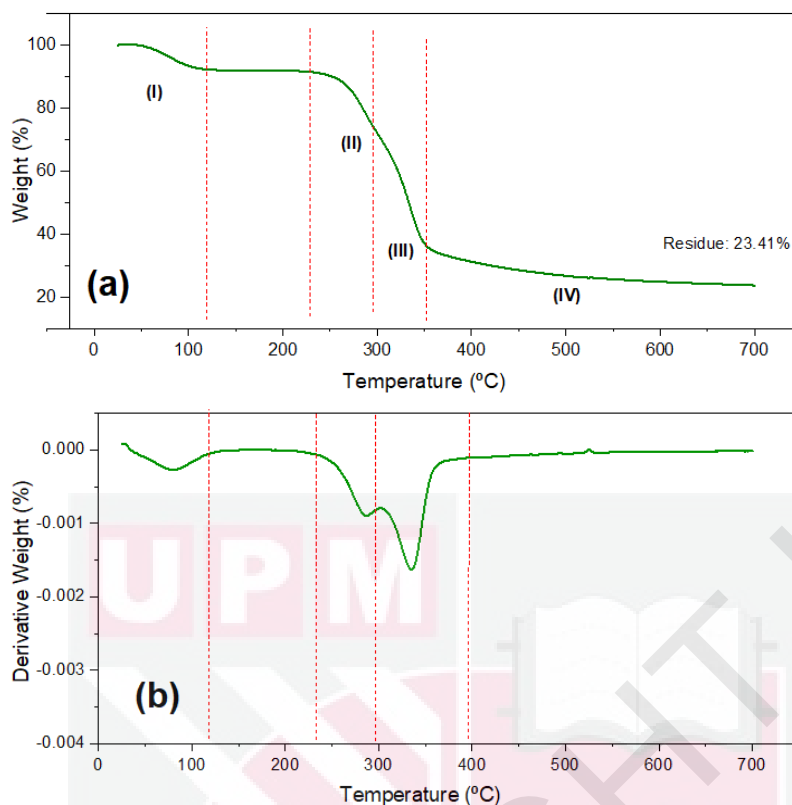


Figure 4.30: TG (a) and DTG (b) Curve for prepared OPEFB

4.4.2 Characterization of cellulose isolated from OPEFB

Figure 4.31 shows the physical appearances of raw OEFB fiber and cellulose obtained from OPEFB fiber through an isolation process by applying a dewaxing technique, treatment using NaOH, bleaching treatment using NaClO₂ solution and refluxing using HCl solution, which are described in Chapter 3 Methodology. The original color of raw OPEFB fiber changed from brown to white after the isolation process due to the removal of hemicellulose and lignin materials (Rahman *et al.*, 2017). A study carried out by Ng *et al.* (2015) also confirmed that the success of the isolation process can be determined by a distinct change in color, typically transitioning into a white powder.

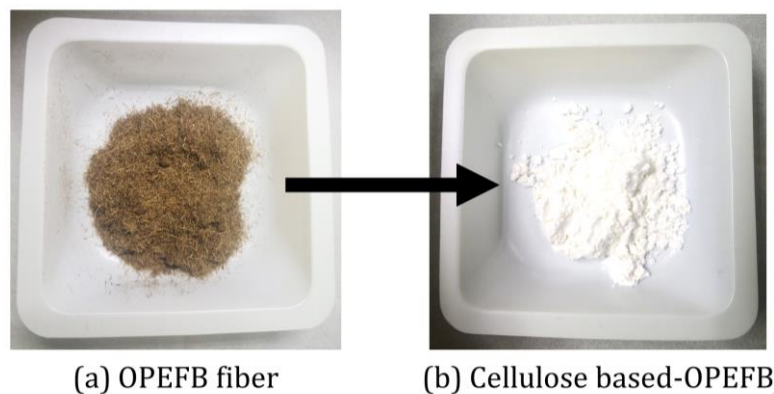


Figure 4.31: OPEFB fiber and cellulose produced from OPEFB

Meanwhile, the evaluation based on chemical properties can be observed from the analysis of TGA, XRD and FTIR. The purpose of TGA analysis is to differentiate the decomposition of hemicellulose and cellulose materials between the OPEFB sample with isolated cellulose from OPEFB (OPEFB-based cellulose). As discussed before, hemicellulose undergoes degradation at temperatures ranging from 230 to 290 °C, while cellulose degrades at temperatures between 290 and 370 °C (Díez *et al.*, 2020). Meanwhile, lignin degrades at a temperature above 400 °C (Mohamad Haafiz *et al.*, 2013). The decomposition of the materials in the samples is clear in the TGA and DTG curves shown in Figure 4.32. The TGA result for the OPEFB-based cellulose sample demonstrates different decomposition trends compared to the OPEFB sample.

A degradation peak that corresponds to the thermal breakdown of cellulose occurs in both samples within a limited temperature range of 290 to 370 °C similar to the previous studies. However, the decomposition peak within the temperature 230 to 290 °C which refers to hemicellulose degradation only appeared in the OPEFB sample, suggesting that no hemicellulose is available in the isolated cellulose (OPEFB-based cellulose) sample. The disappearance of this peak proved that alkaline and bleaching

treatment successfully removed unstable hemicellulose (Chieng *et al.*, 2017). The result is also consistent with the TGA result for isolated cellulose obtained in the study by Ajayi *et al.* (2023) and Mirzaee *et al.* (2023), wherein only cellulose degradation was observed. The high residual weight in the OPEFB-based cellulose indicates that this sample high contains inorganic material, such as ash, that cannot be decomposed during TGA analysis (Norazli *et al.*, 2023).

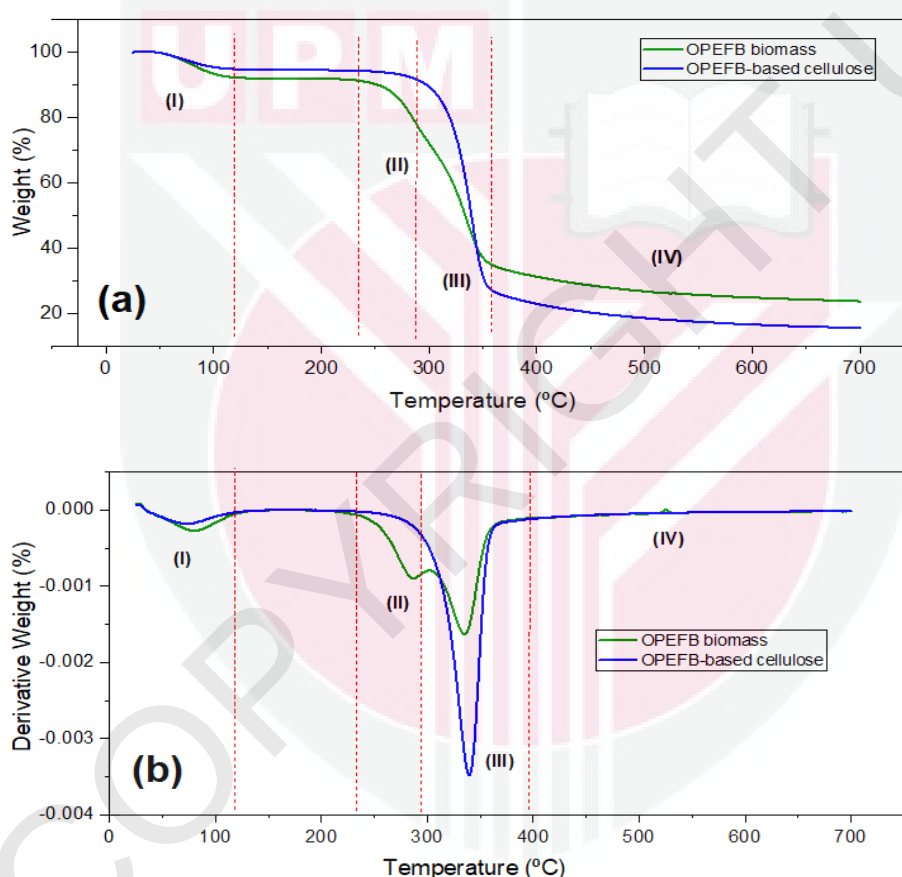


Figure 4.32: Comparison of TGA curve (a) and DTG curve (b) for OPEFB biomass and OPEFB-based cellulose

FTIR spectra for OPEFB-based cellulose are presented in Figure 4.33 with raw OPEFB sample provided alongside for comparative purposes. Peaks around 3200-3400 cm^{-1} in both samples assigned to the O–H stretching vibration of the hydrogen-

bonded hydroxyl group in the cellulose molecule (Ogunjobi *et al.*, 2023). Furthermore, C–H stretching groups of cellulose were seen at 2885 cm^{-1} in both samples. The presence of significant micro-cellulose content is confirmed by the C–OH vibration in both samples, which exhibits a very intense band at 1032 cm^{-1} (Alhaji Mohammed *et al.*, 2022). The peak at 1373 cm^{-1} present in the OPEFB sample is associated with the bending vibrations of C–O of cellulose (Nazir *et al.*, 2013). The intensity of this peak is more pronounced in the sample of OPEFB-based cellulose.

The C=O stretching frequency of the carbonyl functional groups from hemicellulose and lignin fractions were observed in the OPEFB sample at 1720 cm^{-1} . Another peak that was present only in the spectrum of OPEFB is at 1238 cm^{-1} refers to the syringyl ring and C–O stretching of lignin and xylan (Chieng *et al.*, 2017). The complete disappearance of these peaks in the OPEFB-based cellulose sample indicates that the isolation process successfully eliminated or significantly decreased the presence of hemicellulose and lignin. The intensity of the peak located at 1613 cm^{-1} which is related to the C=C stretching of aromatic rings in lignin was also reduced in the sample of OPEFB-based cellulose. These observations are consistent with previous studies by Kaur *et al.* (2023) and Kundu *et al.* (2023) which also isolated cellulose from biomass.

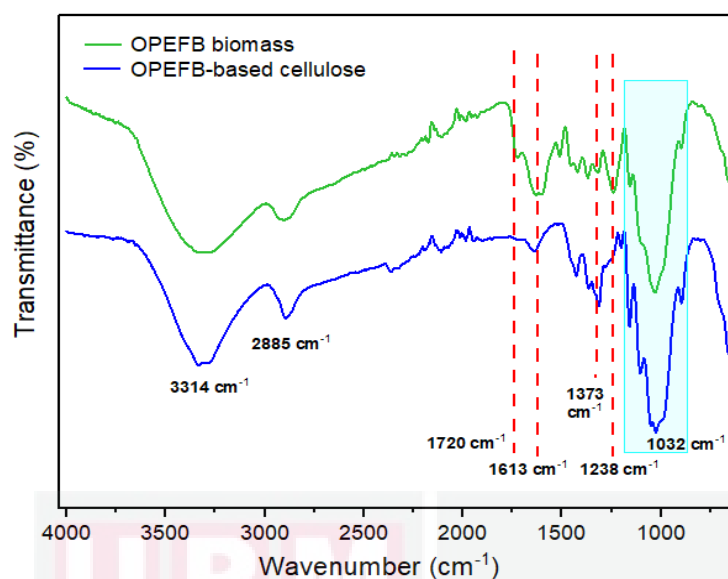


Figure 4.33: Comparison of FTIR analysis for OPEFB biomass and OPEFB-based cellulose

Figure 4.34 shows the XRD patterns of OPEFB-based cellulose and similar to FTIR analysis, a raw OPEFB sample is provided alongside for comparative purposes. This analysis was conducted to evaluate the phase purity and crystallinity of the OPEFB before and after the cellulose isolation process. The XRD pattern of the OPEFB sample was broad and did not show any sharp peaks. Only one peak appeared in this sample. This reveals that the sample had an amorphous structure which is similar to findings by Mirzaee *et al.* (2023). The appearance of additional peaks and a more noticeable peak at $2\theta = 22.5^\circ$ was ascribed to the elimination of lignin, which was verified by the FTIR findings. Furthermore, hemicellulose is known to be amorphous and the removal of amorphous compounds resulted in a more distinct appearance of crystalline peaks which caused an increase in crystalline index (CrI) for OPEFB-based cellulose. The CrI slightly increased to 76.43% compared to raw OPEFB (18.58%) and was higher than that reported in the literature for cellulose isolated from other sources. For example, Ndwandwa *et al.* (2023) obtained 63.82% and 72.10 % crystallinity of cellulose from bagasse and eucalyptus, 70.0% crystallinity of cellulose from rapeseed

straw by Mirzaee *et al.* (2023) and 64.48% crystallinity of cellulose from OPEFB by Norazli *et al.* (2023) but lower than Haafiz *et al.* (2013) which isolated cellulose with CrI of 87.0%.

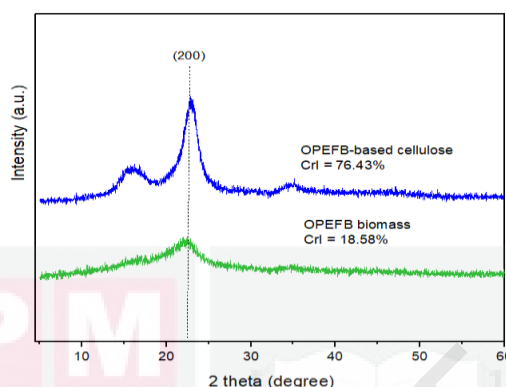


Figure 4.34: XRD analysis for OPEFB biomass and OPEFB-based cellulose

4.4.3 Evaluation on cellulose conversion in hydrolysis reaction

The evaluation of the cellulose obtained from the extraction process above were done by subjecting this material in hydrolysis reaction at 160 °C for 2 hours using 10% sulfonated carbon metal (15%FeNi/ACSO₃H) catalyst from previous objective. The yield of products generated from this cellulose were compared with products collected by using commercial cellulose. Table 4.10 presents the yield of glucose, HMF, FA and LA from OPEFB-based cellulose and commercial cellulose. The yield of LA from OPEFB-based cellulose is 8.98% (based on theoretical yield), slightly lower than the 9.73% yield from commercial cellulose. However, this difference within an acceptable range given the natural variability in cellulose sources and the properties of cellulose such as crystallinity degree. Furthermore, the difference between the two yields is small, indicating the level of purity of OPEFB-based cellulose. It is important to highlight that the total yields of LA from both starting materials are low as shown in

Table 4.10. This highlights the necessity for additional optimization and pretreatment of cellulose to improve the efficiency of the production of LA. The lower LA yield compared to other products may be attributed to various factors, including the complexity of the cellulose structure, making it challenging to access and convert this material into LA efficiently.

Table 4.10: Product yields from different celluloses

Starting materials	Yield (%) based on theoretical yield			
	Glucose	HMF	FA	LA
OPEFB-based cellulose	14.7	1.93	5.13	8.98
Commercial cellulose	15.3	0.57	7.34	9.73

4.4.4 Pretreatment by molten salt hydrates

In this study, different MSHs were used to pretreat OPEFB-based cellulose to enhance the production of LA. The effects of lithium bromide (LiBr), lithium chloride (LiCl) and zinc chloride (ZnCl_2) pretreatments were evaluated by analyzing the changes in cellulose properties, as determined through various analytical techniques including FTIR, XRD, SEM and XPS alongside evaluating the yield of LA produced in the hydrolysis reaction using sulfonated carbon metal catalyst.

4.4.4.1 Physical and Crystal Structure of Cellulose

Figure 4.35 presents the scanning electron microscope (SEM) images of OPEFB-based cellulose after pretreatment with different types of MSHs solutions. Non-pretreated cellulose exhibits a relatively compact and dense surface structure. After being pretreated with MSHs, the originally compact structure of cellulose was changed to a

wrinkled surface and swelled cellulose fibers. The fiber morphology analysis revealed that MSHs pretreatment effectively induced surface deconstruction of OPEFB-based cellulose, even when performed at room temperature only. Similar occurrences were demonstrated in the MSHs non-dissolving pretreatment of cellulose in the studies by Huang *et al.* (2022) and Zhang *et al.* (2023). More deconstruction occurred on the surface of the fibers pretreated by LiBr compared to other samples, resulting in a significant alteration of the cellulose surface. The notable difference in surface deconstruction shown in the LiBr-treated fibers compared to the other samples suggests that LiBr might be highly efficient in destructing the structure of cellulose fibers.

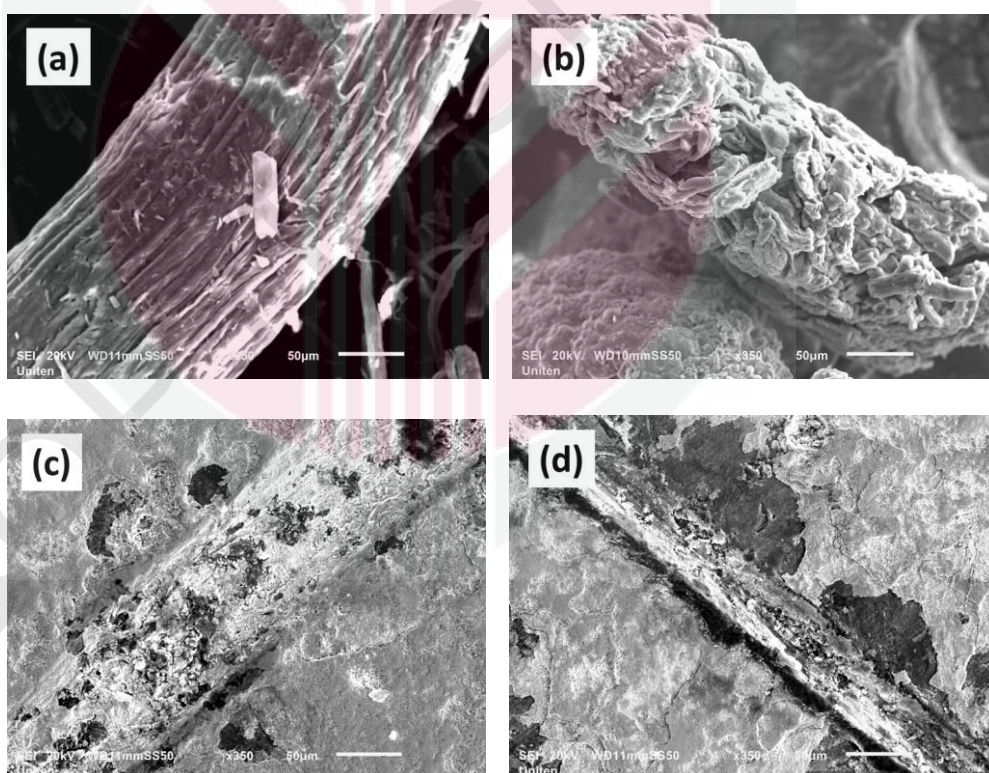


Figure 4.35: SEM images for OPEFB-based cellulose (a) non-pretreated (b) pretreated with LiBr (c) pretreated with LiCl and (d) pretreated with ZnCl_2

The XRD result in Figure 4.36 provides clear evidence of significant changes in the crystalline structure of the OPEFB-based cellulose sample after MSHs pretreatments. The decrease in the intensity of the crystallite peaks corresponding to the (110), (200), and (002) crystalline planes of cellulose I is a notable finding that indicates a swelling behavior and significant disruption in the crystalline structure of cellulose after pretreatments (Liu *et al.*, 2022). All MSHs-pretreated samples had a single broad amorphous peak in their XRD patterns, with the highest intensity peak at 22.6°. This result aligned with the previously documented highest point of standard amorphous cellulose in the study by Ma *et al.* (2022).

The changes in crystallinity indicate that MSHs pretreatment affects the ordered structure of cellulose chains, resulting in decreased crystallinity. The non-pretreated OPEFB-based cellulose has a crystallinity of 76.43%. Pretreatment using MSHs caused a significant reduction in crystallinity in all samples: LiBr-treated cellulose has 33.51%, ZnCl₂-treated cellulose has a crystallinity of 43.69% and LiCl-treated cellulose has 35.62%. This suggests a significant destruction in the crystalline structure, resulting in an amorphous structure. LiBr is remarkably effective in reducing crystallinity compared to other MSHs pretreatments. A study by Huang *et al.* (2022) observed an even more substantial decreasing in crystallinity from 79.1% to 19.0% after 30 minutes pretreatment with LiBr. Different cellulose sources can show differences in crystalline structure, which may react differently to pretreatment methods. Deng *et al.* (2023) and Zhang *et al.* (2023) noted a significant reduction in the crystallinity of hardwood dissolving pulp (HDP) from 72.3% to 42.3% and 83.23% to 36.56%, respectively, within the first 30 minutes of LiBr pretreatment. Reduced crystallinity can enhance the accessibility of cellulose molecules to catalysts or

enzymes (Burger *et al.*, 2020). Therefore, the efficiency of hydrolysis for cellulose conversion can be improved.

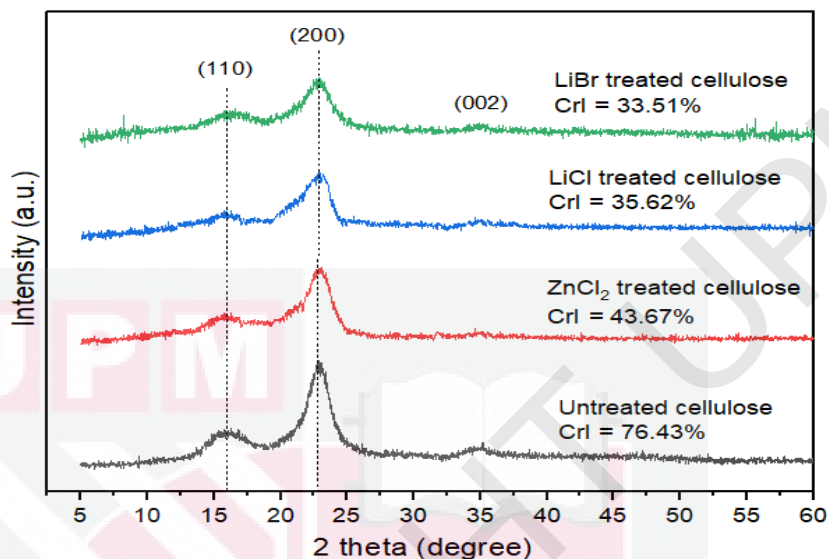


Figure 4.36: Comparison of XRD analysis for OPEFB-based cellulose pretreated by several molten salt hydrates

4.4.4.2 Chemical properties changes of cellulose

Figure 4.37 shows the FTIR spectra of OPEFB-based cellulose before and after non-dissolving pretreatment using different MSHs solutions. The result presents that OPEFB-based cellulose pretreated with MSHs maintained the original cellulose chain and the pretreatment did not significantly alter the FTIR spectra of the cellulose samples. None of the pretreatment cellulose fibers revealed a new absorption peak for a new functional group when compared to the non-pretreated OPEFB-based cellulose sample. Deng *et al.* (2023) suggested that cellulose did not undergo a derivatization reaction during pretreatment. However, the hydrogen bond rearrangement caused the C–O stretching band in cyclic alcohols (hydroxyl at C2 and C3 locations) to shift to a lower wavenumber, from 1025 to 1017 cm^{-1} . The shift in the infrared absorption peak

is reliant upon the bond energy, which in turn reflects the alteration in bond length and the change of the crystalline structure of cellulose (Zhang *et al.*, 2023). Furthermore, the C–O stretching of primary alcohols (the hydroxyl at the C6 position) at 1056 cm^{-1} was weakened, also suggesting alterations in the crystalline structure of cellulose after pretreatment. Moreover, after pretreatment, the C–O–H stretching vibration in ethers at 1110 cm^{-1} was weakened for all pretreated cellulose samples and the band of C–O–H pyranose ring skeletal vibrations shifted to lower wavenumber (from 1160 to 1158 cm^{-1}) for the samples pretreated with LiBr and ZnCl_2 , indicating a reduction in the overlapped part of the cellulose hydroxyl group (Chi *et al.*, 2019). The bands identified at 1644 , 3300 and 3400 cm^{-1} in the spectra were identified as being associated with intramolecular hydrogen bonding (Huang *et al.*, 2020).

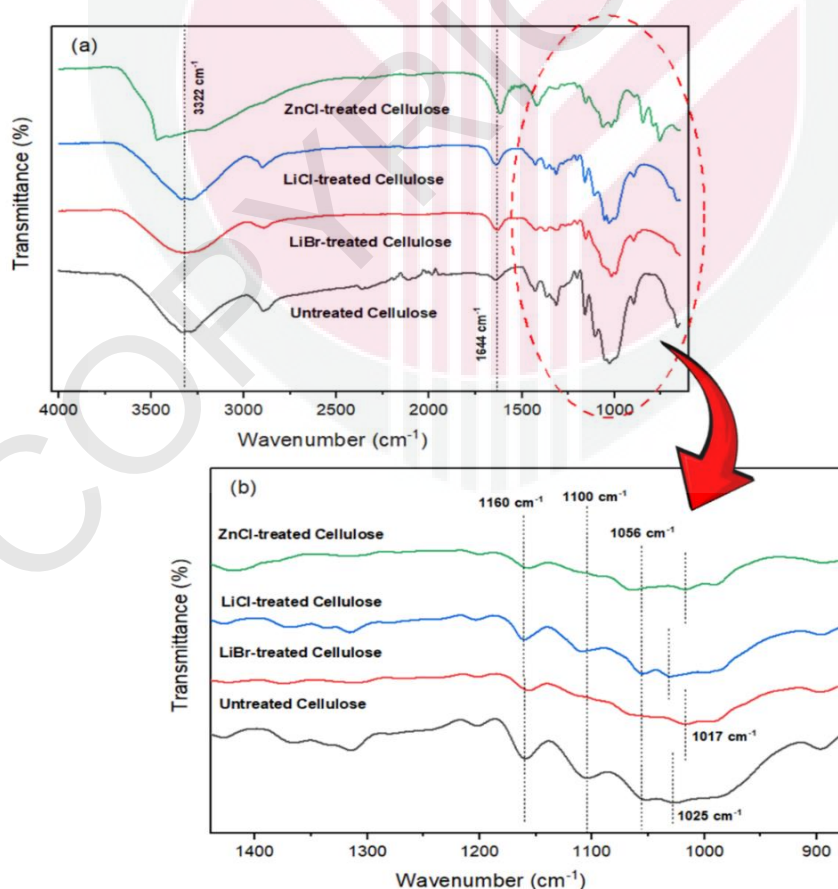


Figure 4.37: Comparison of FTIR analysis for OPEFB-based cellulose pretreated by several molten salt hydrates

The thermogravimetric (TGA) and derivative thermogravimetric (DTG) curves of OPEFB-based cellulose before and after pretreatment with LiBr samples are illustrated in Figure 4.38 (a) and 4.38 (b), respectively. Only the sample pretreated with LiBr was chosen because this sample produced the highest amount of LA which is discussed in the Section 4.4.4.3. The thermal degradation of all samples resulted in an initial weight loss within the temperature up to 100 °C, which could be attributed to different levels of moisture content and volatile compounds within the samples (Meraj *et al.*, 2023). The decomposition of hemicellulose happened within the temperatures 230 to 290 °C which can only be seen in the OPEFB biomass sample. Degradation of cellulose occurred within temperatures 290 to 370 °C. It was discovered that there is no significant difference in the initial decomposition temperatures between the OPEFB-based cellulose pretreated with LiBr and the non-pretreated sample. Nonetheless, a notable observation was made regarding the degradation behavior as the pretreated sample exhibited a more rapid degradation compared to the non-pretreated sample. It was assumed that the thermal stability of the pretreated sample was decreased which corresponded to the reduction of crystallinity (Deng *et al.*, 2023). Furthermore, the remaining amount of pretreated cellulose increased notably after thermal degradation compared to the non-pretreated OPEFB-based cellulose. This is because pretreated cellulose was easy to decompose and exhibited a tendency for producing thermally stable char (Köklükaya *et al.*, 2018). This most likely due to the presence of MSH (LiBr) in the sample. The result is also similar to the observations made in the study conducted by Zhang *et al.* (2023).

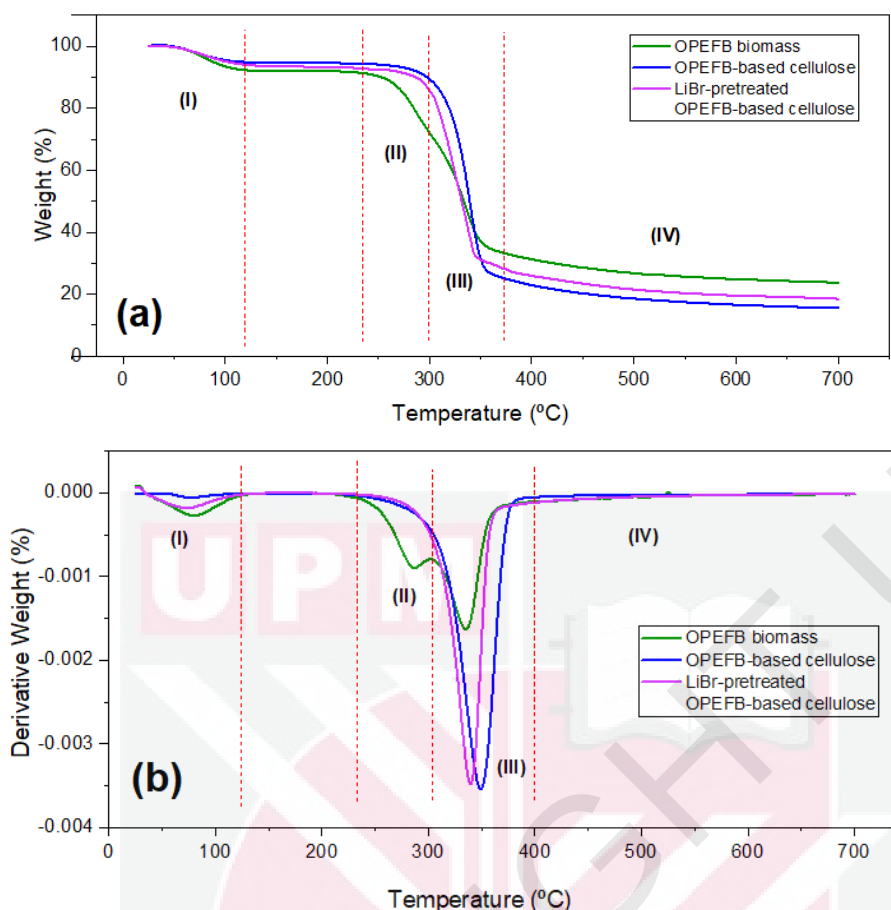


Figure 4.38: Comparison of TGA curve (a) and DTG curve (b) for OPEFB biomass, OPEFB-based cellulose and LiBr-pretreated OPEFB-based cellulose

Figure 4.39 shows XPS spectra for untreated and LiBr-treated OPEFB-based cellulose. The electron binding energy is related to the atomic groups or bound atoms. Both samples only exhibit O1s at 533 eV and C1s at 285 eV peaks as shown in Figure 4.39(a). There is no significant difference in the high-resolution O1s peak of both samples but the C1s peak demonstrates an obvious difference. Thus, the deconvolution method was applied to analyze the high-resolution spectra of cellulose samples before and after pretreatment with LiBr solution which can be viewed in Figure 4.39(b) and (c). A study by Huang *et al.* (2022) proposed that carbon atoms in cellulose may be categorized into three binding forms (C1s1, C1s2, and C1s3), each corresponding to a different energy spectrum peak in the XPS energy spectrum of C1s. The peak intensity

of C1s1 in the pretreated sample is slightly lower than untreated sample, possibly due to the elimination of a small quantity of non-cellulose elements in the sample, suggesting an increase in cellulose purity after pretreatment (Li *et al.*, 2020).

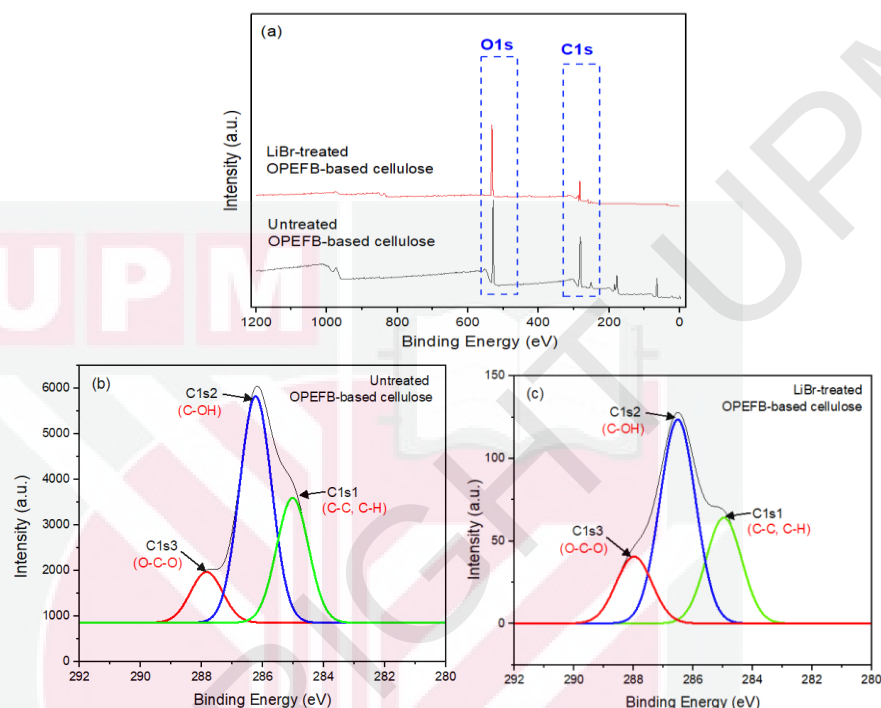


Figure 4.39: XPS analysis for untreated cellulose and LiBr-treated OPEFB cellulose

4.4.4.3 Accessibility Analysis of Cellulose

The findings from characterization studies such as FTIR, XRD, SEM, TGA and XPS demonstrated the changes in structure and chemical properties of OPEFB-based cellulose after pretreatment with different MSHs solutions. Hydrolysis studies were carried out further to examine the improved accessibility of cellulose after pretreatments. The results in Figure 4.40 are used to evaluate the accessibility of different pretreated OPEFB-based cellulose samples by comparing the yield of LA as the primary product, as well as the amount of HMF and glucose. The yield of LA

(based on theoretical) is significantly increased after pretreatment with LiBr (24.3%) and LiCl (22.52%), in contrast to untreated cellulose (8.98%). Both LiBr and LiCl pretreatments enhance cellulose accessibility to hydrolysis reaction resulting in increased LA production. However, pretreatment with ZnCl_2 produced low LA yield of 0.8%, indicating that this method may not effectively improve cellulose accessibility for the production of LA. This trend is similar to the production of FA. Furthermore, pretreatment with LiBr and LiCl significantly boosts the glucose yield to 45.3% and 49.0%, respectively, compared to only 11.3% from untreated cellulose. This demonstrates the effectiveness of LiBr and LiCl pretreatments in degrading cellulose into glucose, an important process in hydrolysis. As expected, the change in the cellulose crystalline structure and the lowering of crystallinity were advantageous to the hydrolysis of cellulose. Among the pretreatments evaluated, pretreatment using LiBr appears to be the most effective in enhancing conversion efficiency and cellulose accessibility as evidenced by the highest production of LA, FA, HMF, and glucose. Given the significant abundance of glucose collected, it indicated a considerable amount of glucose available for conversion. Hence, it is suggested to optimize the conditions to achieve the highest possible yield of LA by adjusting several parameters.

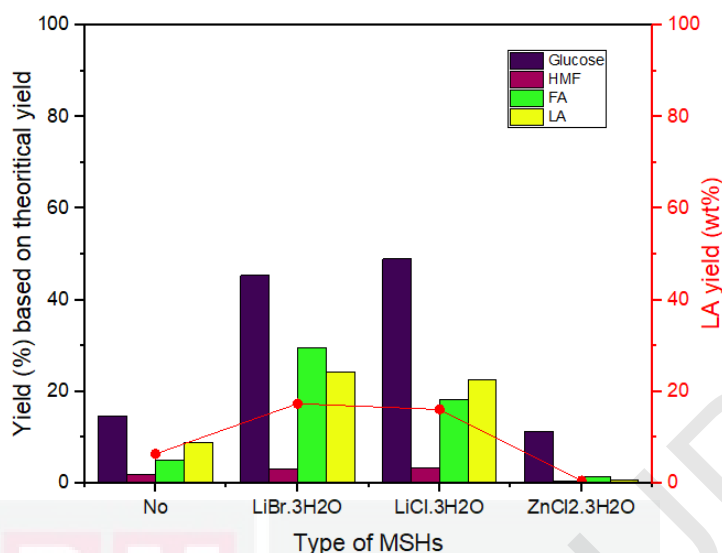


Figure 4.40: Comparison product yield (%) based on theoretical yield and LA yield (wt%) from cellulose pretreated by several MSHs. Reaction conditions: 1.0 g OPEFB-based cellulose, reaction temperature 160 °C, reaction time 2h, 10% catalyst dosage of 15%FeNi/ACSO₃H

4.4.4.4 Effect of Reaction Parameters

Subsequently, the conversion of pretreated cellulose to LA under different conditions was explored in detail to optimize the yield of LA. LiBr-pretreated cellulose was chosen as this sample produced the highest amount of LA and demonstrated the best structural and chemical changes.

The impact of reaction temperature on the catalytic conversion of LiBr pretreated OPEFB-based cellulose was tested, as demonstrated in Figure 4.41. As the temperature increases, the yield of LA (based on theoretical yield) also increases significantly. At 120 °C, the LA yield based on theoretical yield is 4.51% (3.23 wt.%), while it reaches 65.98% (47.24 wt.%) at 200 °C. This shows that higher temperatures promote the conversion of this cellulose to LA. It is not feasible to increase the temperature beyond 200 °C due to the temperature limitations of the reactor. Though the increase is not as

noticeable as it is for LA, the FA yield also increases with increasing temperatures similarly to LA. The HMF yield initially increases around 120 °C, suggesting that glucose is being converted to HMF. As the temperature rises, the HMF yield declines gradually which indicates that at elevated temperatures, HMF undergoes further conversion into LA or FA. As temperature increases, the amount of glucose produced drops, demonstrating that glucose is being transformed into HMF and then into LA or FA. The decrease in the production of glucose aligns with the increase in HMF and LA or FA production at high temperatures. This trend in the conversion process aligns with findings by Boonyakarn *et al.* (2019) who observed that at reaction temperatures ranging from 160 to 200°C, there was an initial rise in the yields of glucose and HMF with time, followed by a subsequent decline after reaching a certain point. Meanwhile, the LA yield continued to increase steadily over time. However, these findings contrast with those of a study by Cheng *et al.* (2022) which reported that at reaction temperatures more than 180 °C, the LA yield dropped to 35.6% despite achieving a cellulose conversion rate of 73.8%. It was assumed that, at very high reaction temperatures, intermediates in the reaction process are more likely to undergo polymerization resulting in the humins formation. Undesirable side reactions can greatly limit the generation of LA and other desired chemicals.

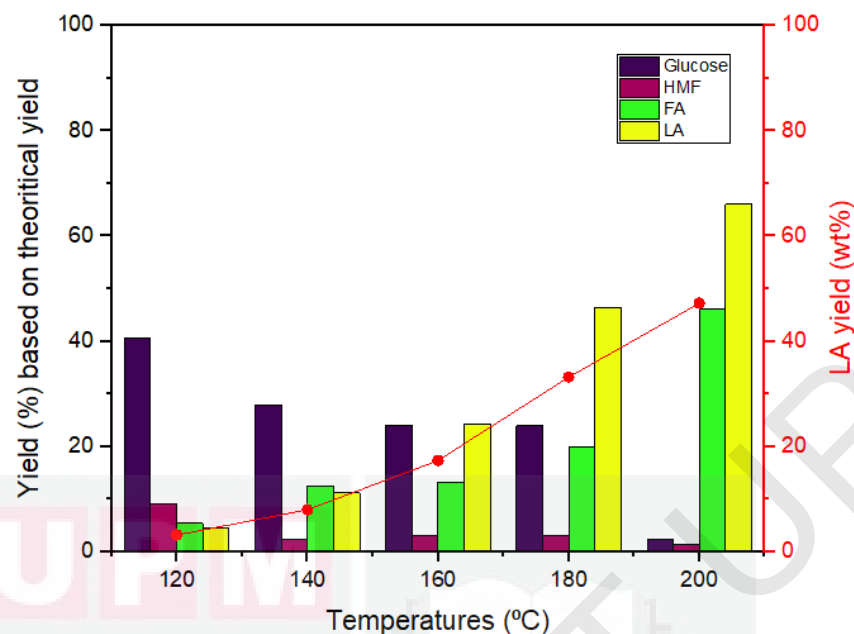


Figure 4.41: Products yield (%) based on theoretical yield and LA yield (wt%) from LiBr-pretreated cellulose at different temperatures. Reaction conditions: 1.0 g OPEFB-based cellulose, reaction time 2h, and 10% catalyst dosage of 15%FeNi/ACSO₃H

Figure 4.42 demonstrates the influence of catalyst loading from 1% to 20% on the production of important products such as LA, FA, HMF and glucose throughout the cellulose conversion process using OPEFB-based cellulose which was pretreated with LiBr. At lower catalyst loadings of 1% and 5%, there is a notable increase in the LA yield. This increase suggests that even a small quantity of catalyst promotes the conversion of cellulose into LA. The LA yield increases significantly when the catalyst loading rises to 10% and peaks at this concentration (65.98% of theoretical yield). This indicates that the catalytic efficiency is highest at a 10% loading, leading to the greatest conversion of cellulose to LA. However, beyond this loading, there may even be a minor decline between 15% and 20% loading of the catalyst. This trend may suggest that the catalyst loses its efficiency or that increasing catalyst concentrations cause side reactions or catalytic deactivation, which would limit the catalyst's ability to improve

LA production (Chen *et al.*, 2022). FA yield also significantly increases as catalyst loading increases, reaching its maximum at 10% loading (46.88%). The glucose and HMF yield shows minimal variation with changes in catalyst loading, as most of these products have already degraded into the next products. In summary, while higher catalyst loadings initially enhance the production of LA, there seems to be an optimal loading point (around 10%) beyond which further increases may not yield significant improvements or may even decrease the yield of LA.

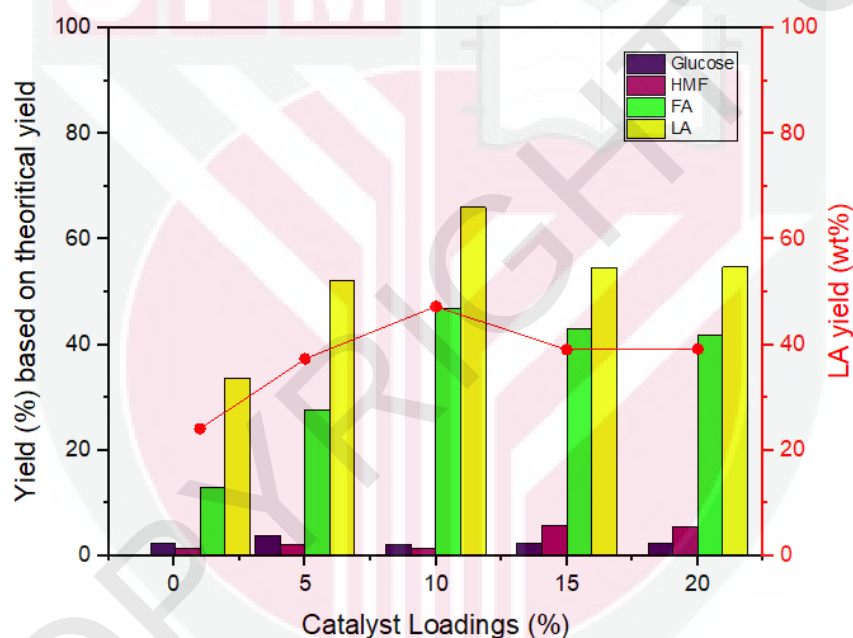


Figure 4.42: Products yield (%) based on theoretical yield and LA yield (wt%) from LiBr-pretreated cellulose using different loadings of 15%FeNi/ACSO₃H catalyst. Reaction conditions: 1.0 g OPEFB-based cellulose, reaction temperature 200 °C and reaction time 2 h

The effect of reaction time was investigated from 2 to 10 hours as demonstrated in Figure 4.43. The maximum amount of LA based on theoretical yield is collected with a response time of 4 hours (72.15%), followed by 6 hours (71.31%) and 8 hours (70.84%). After 10 hours, there is a notable drop in LA production of 44.91%. This

pattern suggests that there is a specific time frame in which the production of LA is at its highest level. The initial increase in LA yield over time is likely due to the gradual conversion of cellulose into LA, which is enhanced by extended exposure to catalytic conditions. However, the decrease in LA yield during extended reaction periods suggests the possibility of side reactions or catalyst deactivation, which limits the production of LA (Mthembu *et al.*, 2021). Similarly, FA yield shows a similar trend, with the highest yield achieved at 4 hours (49.10%), followed by a gradual decline at longer reaction times. The glucose and HMF yield, on the other hand, exhibits a steady decline when prolonged the reaction time, suggesting that glucose and HMF were progressively converted to subsequent products. A study by Chiappe *et al.* (2018) showed a corresponding decline in HMF from 1.4% to 0.4% upon going from 3 to 5 hours and longer reaction times, the LA yield decreased. In summary, the data indicates that a reaction period of 4 hours is optimal for achieving maximum yields of LA with LA yield peaking at 72.15% based on theoretical (51.66 wt.) After this period, additional reaction time does not considerably improve the yields of LA.

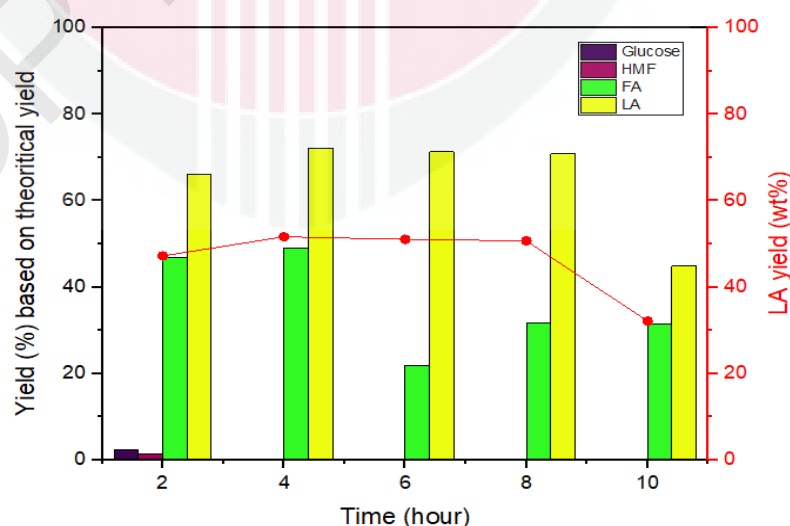


Figure 4.43: Products yield (%) based on theoretical yield and LA yield (wt%) from LiBr-pretreated cellulose at different times. Reaction conditions: 1.0 g OPEFB-based cellulose, reaction temperature 200 °C and 10% catalyst dosage of 15%FeNi/ACSO₃H

4.4.4.5 Evaluation of the reuse of lithium bromide molten salt hydrate

The recycling of the pretreatment solvent stands as an essential step within sustainable chemistry practices. In this study, using LiBr molten salt hydrate as a pretreatment solvent in OPEFB-based cellulose conversion reactions becomes more sustainable when the solvent may be reused. The OPEFB-based cellulose and salt hydrate solution were easily separated because cellulose is not soluble in the pretreatment solvent. Based on Figure 4.44, Runs 1 through 5 exhibit LA yields ranging from 70.78% to 72.15% (based on theoretical yield). The results demonstrated that LiBr molten salt hydrate maintained its effectiveness on the non-dissolving pretreatment of cellulose after the recovery process. The findings from Huang *et al.* (2022) also proved that the conversion values of cellulose were quite consistent for all the reuse experiments until 5 cycles. They also claimed that the recovery and reuse of LiBr molten salt hydrate can further lower the cost of the non-dissolving LiBr pretreatment. A study by Deng *et al.* (2023) discovered that the carboxyl content of transparent tempo oxidized cellulose nanofibril (TOCNF) generated by reusing LiBr molten salt hydrate 5 times in pretreatment could still achieve a similar under the same conditions of 2,2,6,6-Tetramethylpiperidine-1-oxyl radical (TEMPO) oxidation. This assessment on the reuse of LiBr molten salt hydrate through LA yield evaluation concluded that the molten salt hydrate offers a sustainable and economically feasible method in cellulose conversion reaction.

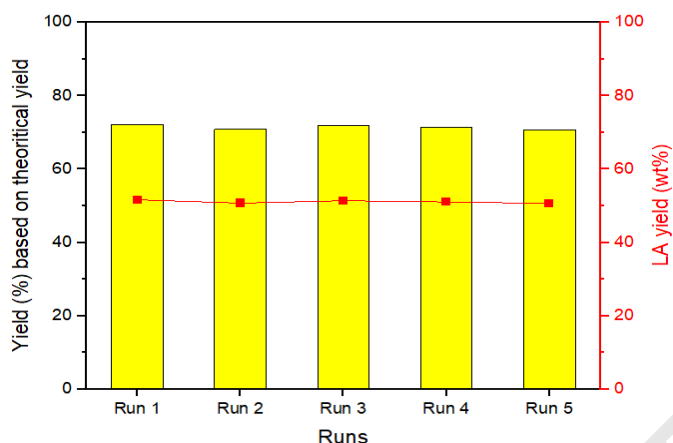


Figure 4.44: Reusability study of LiBr molten salt hydrates. Reaction conditions: 1.0 g OPEFB-based cellulose, reaction temperature 200 °C, reaction time 4 h, 10% catalyst dosage of 15%FeNi/ACSO₃H

4.4.5 Summary

The development of a sustainable and efficient pretreatment method is crucial for enhancing the hydrolysis reaction or functional modification of cellulose. The results indicated that MSHs have significantly improved the accessibility of cellulose and the efficiency of a hydrolysis reaction. Among the MSHs used for cellulose pretreatment, it is evident that LiBr induces the most significant alterations in functional cellulose properties. This observation is highlighted by its ability to produce the highest yield of LA (24.3% based on theoretical yield) in comparison to other MSHs. The crystallinity of all MSHs-pretreated cellulose was reduced and LiBr-treated cellulose had 33.51% of crystallinity. The study investigated the impact of various parameters on LA production, revealing that the optimal conditions for maximum LA yield from LiBr-pretreated OPEFB-based cellulose were achieved at 4 hours of reaction time using a 10% loading of sulfonated carbon metal catalyst at 200 °C. Under these conditions, the highest LA production reached 72.15% of theoretical yield with 51.66 wt.%, highlighting the significance of temperature, time and catalyst loading in influencing

the efficiency of LA synthesis from OPEFB-based cellulose. Furthermore, this efficient LiBr pretreatment technique can be conducted at room temperature without cellulose dissolution, enabling the recovery and reusability of the MSHs solvent.

The proposed approach will provide a novel option for converting abundant and cost-effective cellulosic biomass into LA. Oil palm empty fruit bunch (OPEFB) has significant potential as a raw material for synthesizing LA. Extraction of cellulose from OPEFB can yield 8.98% LA, based on the theoretical yield of cellulose, with the assistance of a sulfonated carbon metal catalyst (15% FeNi/ACSO₃H). The application of lithium bromide (LiBr) as a molten salt hydrate to pretreat the isolated cellulose further enhanced the LA yield to 24.3% based on theoretical yield. Through careful optimization of reaction parameters such as temperature, catalyst loading, and reaction time, the yield was increased to 78.12%.

4.5 Response Surface Optimization

A study was carried out to optimize the reaction conditions for converting OPEFB-based cellulose into LA enhance the LA yield. Response surface methodology (RSM) was applied to achieve this goal. The variables and operating range were determined based on the results of one variable at a time (OVAT) experiments conducted and were discussed in section 4.3.3.4. Three reaction parameters including reaction time, temperature and catalyst loading were varied using RSM. The presence of humins and the yield of FA were insignificant and not an important output to be predicted in this experimental design.

4.5.1 Model development and statistical analysis

The process parameters in the conversion of OPEFB-based cellulose into LA were investigated using a rotatable central composite design (CCD). Twenty experiments were conducted with the first 14 experiments organized in a factorial design while the remaining six experiments involved the replication of the central point for each stage present. Table 4.11 presents the variables and levels, the uncoded experimental design and the responses obtained from both the experimental and software sources. LA contents produced from experimental works were recorded as Response 1, calculated based on theoretical yield (%) or percentage of weight (wt.%).

Table 4.11: Experimental design matrix and results

Run	Factor 1 A: Temperature (°C)	Factor 2 B: Catalyst Loading (%)	Factor 3 C: Reaction Time (hours)	Response 1 LA Content	
				Based on theoretical yield (%)	Based on weight percentage (wt%)
1	168	13	2.4	45.94	32.89
2	168	7	2.4	27.00	19.33
3	192	7	6.6	65.89	47.18
4	180	15	4.5	60.40	43.25
5	180	10	8	36.93	26.44
6	168	7	6.6	35.07	25.11
7	168	13	6.6	33.17	23.75
8	180	10	4.5	53.31	38.17
9	180	10	4.5	50.55	36.19
10	180	5	4.5	30.48	21.82
11	192	7	2.4	48.17	34.49
12	200	10	4.5	78.12	55.93
13	160	10	4.5	42.24	30.24
14	192	13	6.6	54.78	39.22
15	180	10	4.5	50.54	36.19
16	180	10	1	32.61	23.35
17	180	10	4.5	49.41	35.38
18	180	10	4.5	45.34	32.46
19	180	10	4.5	47.22	33.81
20	192	13	2.4	62.84	44.99

Table 4.11 shows that the highest LA yield was obtained (55.93 wt.% or 78.12% based on theoretical yield) at a temperature of 200 °C using 10% catalyst loading for 4.5 hours. Meanwhile, the lowest yield of LA (19.33 wt.% or 27.00% based on theoretical yield) was obtained at 168 °C, reaction time of 2.4 hours using 7% catalyst loading. The highest amount of LA from this study is higher than the result by Chen *et al.* (2022) which also used solid acid as a heterogeneous catalyst for the conversion of cellulose. The highest LA from their study was 67.9% LA based on the theoretical yield at 180 °C for 3 hours. It was suggested that the yield of LA could be increased by increasing the temperature. However, the maximum yield of LA from this study was lower than the result by Wang *et al.* (2020) even though their conditions used were low. Their study managed to yield 94.0% LA based on theoretical yield at 175 °C for only 2 hours using a heterogeneous catalyst. Interestingly, their study was carried out in a biphasic system consisting of MSHs and methyl isobutyl ketone (MIBK). Adding an immiscible organic liquid such as MIBK to water enhances the production of HMF and LA (Mukherjee *et al.*, 2015).

The relationship between the independent factors and response variables was estimated using the regression analysis software known as Design Expert Software. A quadratic polynomial model was obtained to predict the LA yield. The best-fitting response surface model is shown below:

$$\begin{aligned} \text{LA Yield} = & + 49.39 + 10.99 A + 5.15 B + 0.8890 C - 1.65 AB + 1.76 AC - 5.72 BC \\ & + 3.82 A^2 - 1.39 B^2 - 5.17 C^2 \end{aligned}$$

Where A, B and C represent the reaction temperatures for the conversion, loadings of the sulfonated carbon metal catalyst and reaction time, respectively.

The suitability of the models was assessed by analysis of variance (ANOVA) and the data is shown in Table 4.12. This model had an F-value and p-value of 18.91 and less than 0.0001, respectively, indicating its significance. The probability of a "Model F value" occurring as a result of noise is only 0.01%. The suitability of each coefficient was determined by considering the p-values. A higher F-value and lower P-value suggest a greater significance of the corresponding variable (Gong *et al.*, 2019), thus, terms A, B, and C have a notable effect on the production of LA for this model. However, the software did not provide the exact p-values for all parameters; therefore, it is not possible to figure out the order of the most efficient conditions.

Table 4.12: Analysis of Variance (ANOVA) for response surface quadratic model for LA production

Source	Sum of squares	Degree of freedom	Mean square	F values	P values, Prob>F	Remarks
Model	3045.94	9	338.44	18.91	< 0.0001	significant
A-Temperature	1666.48	1	1666.48	93.09	< 0.0001	
B-Catalyst Loading	366.31	1	366.31	20.46	0.0011	
C-Time	10.91	1	10.91	0.6093	0.4531	
AB	22.71	1	22.71	1.27	0.2863	
AC	25.78	1	25.78	1.44	0.2578	
BC	271.68	1	271.68	15.18	0.0030	
A ²	211.91	1	211.91	11.84	0.0063	
B ²	28.28	1	28.28	1.58	0.2374	
C ²	388.27	1	388.27	21.69	0.0009	
Residual	179.02	10	17.90			not significant
Lack of Fit	139.87	5	27.97	3.57	0.0943	
Pure Error	39.15	5	7.83			
Cor Total	3224.96	19				

The lack of fit test was performed to evaluate the suitability of the model and the outcome reveals a statistically non-significant lack of fit, as indicated by an F-value of 3.57. This value ensured the model was good with low error (Asikin-Mijan *et al.*, 2017). A lack-of-fit F value this large has a 9.43% chance of occurring due to noise. The non-significant lack of fit implies that the model successfully predicted the reaction (Mthembu *et al.*, 2021)

Table 4.13 presents the statistical parameters derived from ANOVA. The coefficient of determination (R^2) can be interpreted as the fraction of the dependent variable's variability that is predicted by the model of statistics (Moodley and Kana, 2017). The result in Table 4.13 demonstrated that the models used for the response variables were highly adequate due to their high R^2 value ($R^2 > 0.94$) thus the model can elucidate 94.0% of the variations in the presented data. These statistics suggest that the proposed model had a good fit regarding the correlation between the input parameters and the response. The model accurately predicted the response value, as indicated by the reasonably close agreement between the predicted R^2 value of 0.6520 and the adjusted R^2 value of 0.8945 (with a difference of less than 0.25). The outcome also shows that the experimental values were within a reasonable range and that the co-efficiency of the variation (C.V = 8.91) was lower indicating a higher degree of precision (Lokman *et al.*, 2015). The value of adequate precision (18.3736) surpasses 4, indicating that the model can be effectively utilized for analyzing the design space (Zhou *et al.*, 2019).

Table 4.13: Statistical parameters derived from ANOVA

Variable	Values
Standard deviation	4.23
Mean	47.5
C.V. %	8.91
PRESS	1122.17
R-Squared	0.9445
Adjusted R-Squared	0.8945
Predicted R-Squared	0.6520
Adequate Precision	18.3736

The ability of the model to predict the value of LA yield is presented in Figure 4.45, where actual versus predicted values of response are assessed. The result revealed that the predicted values by the RSM were close to the actual experimental outcomes. The

responses to the normal probability plot of the residuals in Figure 4.46 supported the data, which means the errors are not analytically significant and are typically spread out along a straight line.

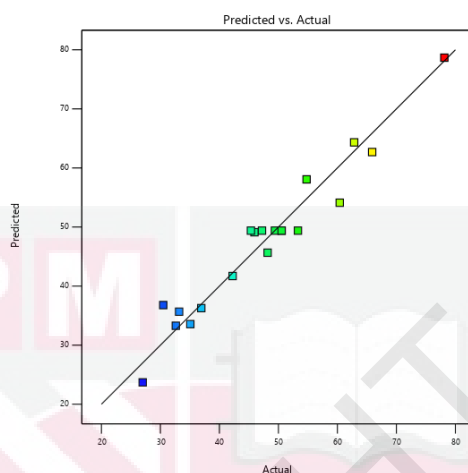


Figure 4.45: Predicted vs. experimental LA production

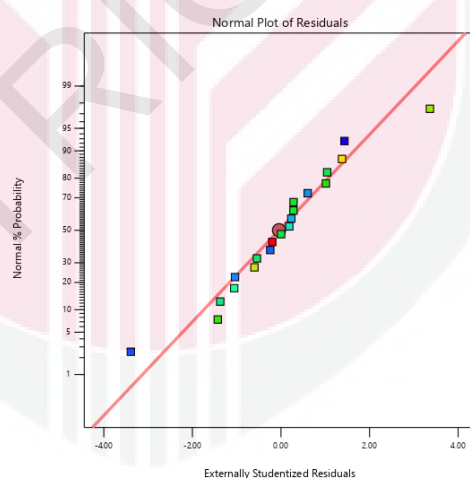


Figure 4.46: Normal probability plot of residuals

4.5.2 Effect of variables on LA production

Figure 4.47 presents the response surface plots and contour plots when varying the reaction time from 1 to 8 hours, the temperature between 160 and 200 °C and the

catalyst loadings between 5% and 15% (w/w). Each figure has three graphs, whereby one distinct variable is kept constant while the other two are varied based on the selected experimental values. Thus, the relationship between LA yield and the experimental levels of each variable and the interactions between the two remaining independent parameters can be clearly observed. All plots in Figure 4.47 demonstrate that the value of LA yield increases by increasing the temperature from 160 to 200 °C. Due to the constraints of the reactor conditions, it was impossible to produce LA beyond the temperature applied in this work.

The effect of the interaction between reaction time (1 to 8 hours) and temperature (160 to 200 °C) using catalyst loading at 10% (w/w) is presented in Figures 4.47(a) and 4.47(b). The trend of LA yield was similar when increasing the reaction time for both low and high temperatures. This trend is similar to the study by Lee *et al.* (2023) which demonstrated higher LA yields at longer reaction times and higher reaction temperatures. In this study, the yield of LA started to decrease at 6.5 hours. A study conducted by Peng *et al.* (2010) found that hydrolysis reaction required around 3 hours to produce LA completely.

The contour plots in Figures 4.47(c) and 4.47(d) illustrate the relationships between reaction temperature and catalyst loadings at 4.5 hours. The loadings of catalysts have less effect on the increasing or decreasing LA yield at low or high temperatures. At the lowest temperature (160 °C), the yield of LA was gradually increased when the catalyst loadings were increased from 5% to 15% (w/w). Meanwhile, at the highest temperature (200 °C), the amount of LA also gradually increased when the catalyst

loadings were inclined up to 8.75% (w/w) but started to decrease when increasing loadings more than 8.75% (w/w).

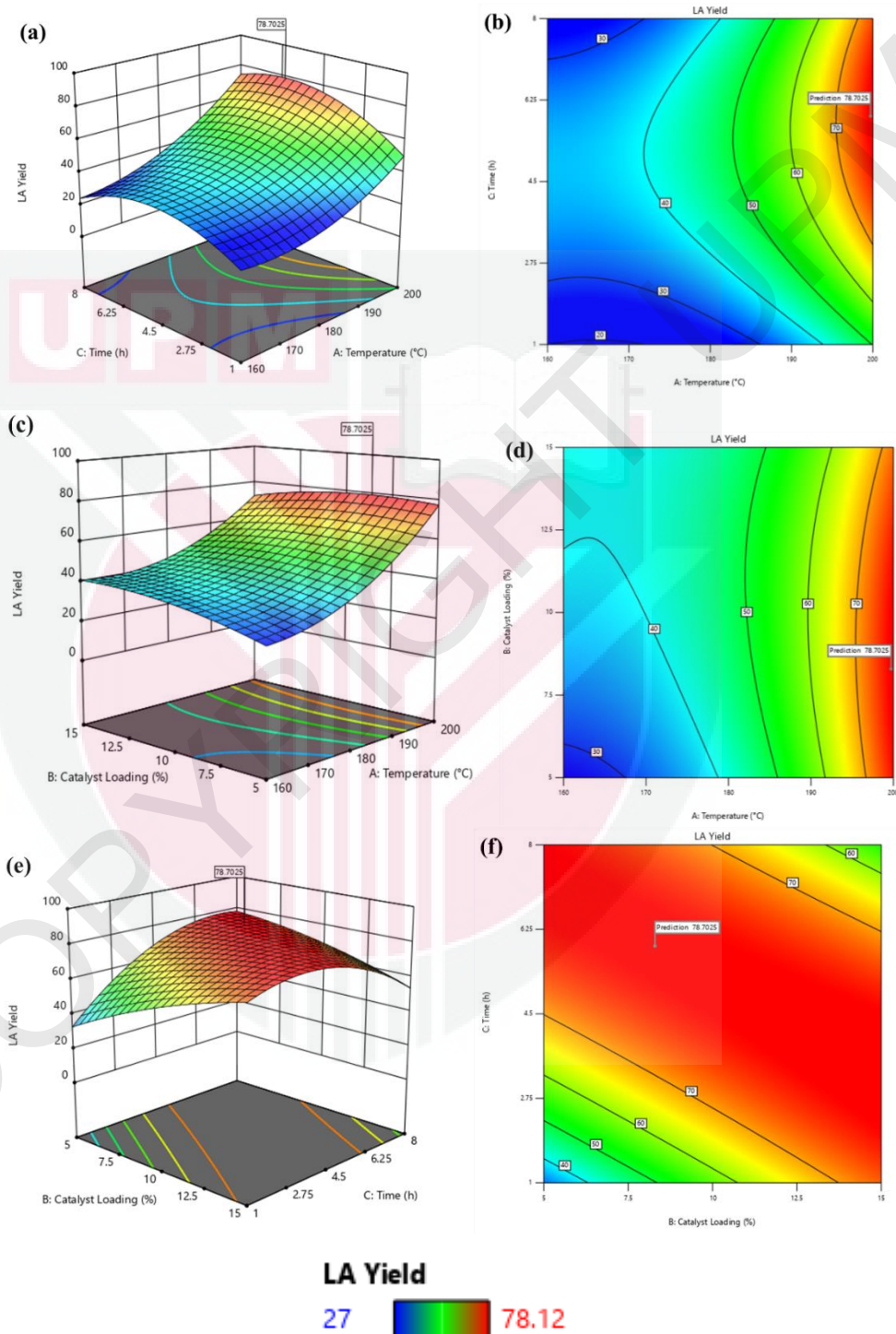


Figure 4.47: The response for LA yield (a) Surface plot and (b) Contour plot of temperature and reaction time; (c) Surface plot and (d) Contour plot of temperature and catalyst loading; (e) Surface plot and (f) Contour plot of reaction time and catalyst loading

The contour plots show that the highest value of LA could be produced at a temperature of 160 °C when the catalyst loadings were 5% to 15% (w/w) and the reaction time at 1 to 8 hours as shown in Figure 4.47(f) while Figure 4.47(e) presents the surface plots. When lower catalyst loading was used, the yield of LA increased when the reaction time was inclined from 1 hour to 8 hours. On the other hand, when more catalyst loading was used, the yield of LA first rose and then subsequently declined after 3 hours. Hence, a moderate amount of catalyst and reaction time are suitable for producing LA from OPEFB-based cellulose.

4.5.3 Optimization and validation

In order to achieve the maximum yield of LA, the optimal process conditions were discovered by applying Derringer's desirability approach for optimization (Ogedjo *et al.*, 2022). Based on the model's prediction, the highest yield of LA was measured at 78.70% (based on theoretical yield) which can be achieved by following the conditions outlined in Table 4.14 and Figure 4.48. An experimental validation was performed to verify the validation of the random data generated by RSM. The experimental validation was conducted three times. The experimental value of LA under this condition was 77.04% as shown in Table 4.14, resulting in a prediction error that was only 2.1% lower than the expected value. The close correlation between the expected and experimental values indicates the fit of the approach for optimizing and predicting the output of LA production. A high desirability value (1.000) was discovered, as shown in Figure 4.48.

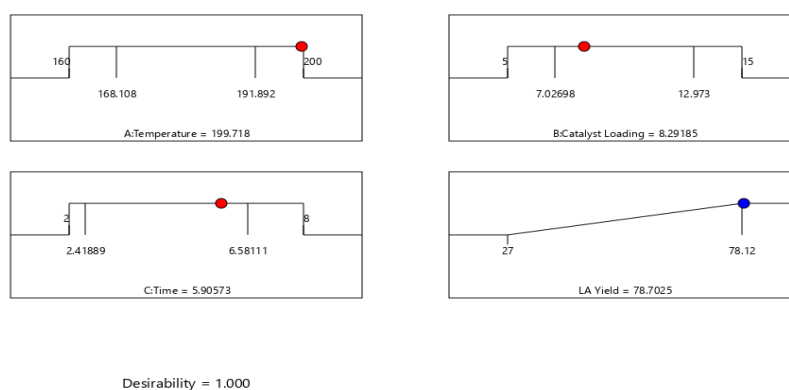


Figure 4.48: Desirability value and process conditions for optimal production of LA

Table 4.14: Model validation

Parameter/Response	
Temperature, A (°C)	199.72
Catalyst Loading, B (%)	8.29
Reaction time, C (hour)	5.91
LA yield (%) based on theoretical yield	
Predicted	78.70
Experimental	77.04

4.5.4 Summary

The conversion of OPEFB-based cellulose catalyzed by a sulfonated carbon metal catalyst was modelled using the conventional response surface methodology utilizing a central composite design. The highest LA yield was obtained (55.93wt% and 78.12% based on theoretical yield) at a temperature of 200 °C using 10% catalyst loading for 4.5 hours. Due to the limitations of the reactor, the temperature cannot be increased beyond its safety limits. Hence, the potential content of LA at high temperatures could not be determined. Nonetheless, the results suggest that the OPEFB-based cellulose can be used as a potential feedstock for the production of LA by direct hydrolysis using a heterogeneous catalyst.

4.6 Kinetic modelling and analysis

The aim of this study is to obtain the insights of the kinetics of reaction to convert OPEFB-based cellulose into LA. The experimental data obtained at optimum conditions from RSM study were employed to model the reaction kinetics. The experimental results were compared with the predicted values from the model to ensure that the generated model was accurate. To study the kinetics of reaction, the effect of time and temperature on LA production from OPEFB based cellulose was investigated. In the present work, the experiments were conducted at various temperatures up to 8 hours while the mass of raw materials and catalyst were kept constant.

4.6.1 Effect of temperatures on product yields

The rate of reaction and yield of glucose, HMF and LA varies with temperature from 170 °C to 200 °C as shown in Figure 4.49-4.51. The conversion of simple sugars like glucose and fructose to LA can be conducted at lower temperatures between 90-120°C was sufficient to start (Ismail *et al.*, 2019). However, in this study, the starting material is cellulose which is a polysaccharide and a more complex substance than sugars. Thus, higher temperatures are needed to perform the kinetic studies. Due to the reactor limitation, reaction at temperatures above 200 °C cannot be performed. After considering the fact that the FA to LA ratio remains nearly constant and equimolecular across all the runs, only the yield of LA was featured in this study. Similar to the study by Liang *et al.* (2017), the measurements of cellulose and humins concentration were also not considered due to technical difficulties. For examples, limitation on the

instrumental analysis (HPLC) to detect the amount of cellulose and humins (Martina et al., 2022)

Figure 4.49 shows the production of glucose from cellulose at different temperatures. With the increase of reaction temperature, it was found the rate of glucose decomposition increased sharply. Irreversible first-order kinetics was consistently observed in all temperatures. The formation of glucose started directly within less than 1 minute and immediately reached a maximum point before steadily decreasing to a final concentration at equilibrium. The steepest curve was observed at 200 °C, which indicates that it is the best temperature for glucose consumption which quickly started to reduce within 30 minutes. This contrasts with other temperatures that took a longer time to achieve higher equilibrium concentration for glucose.

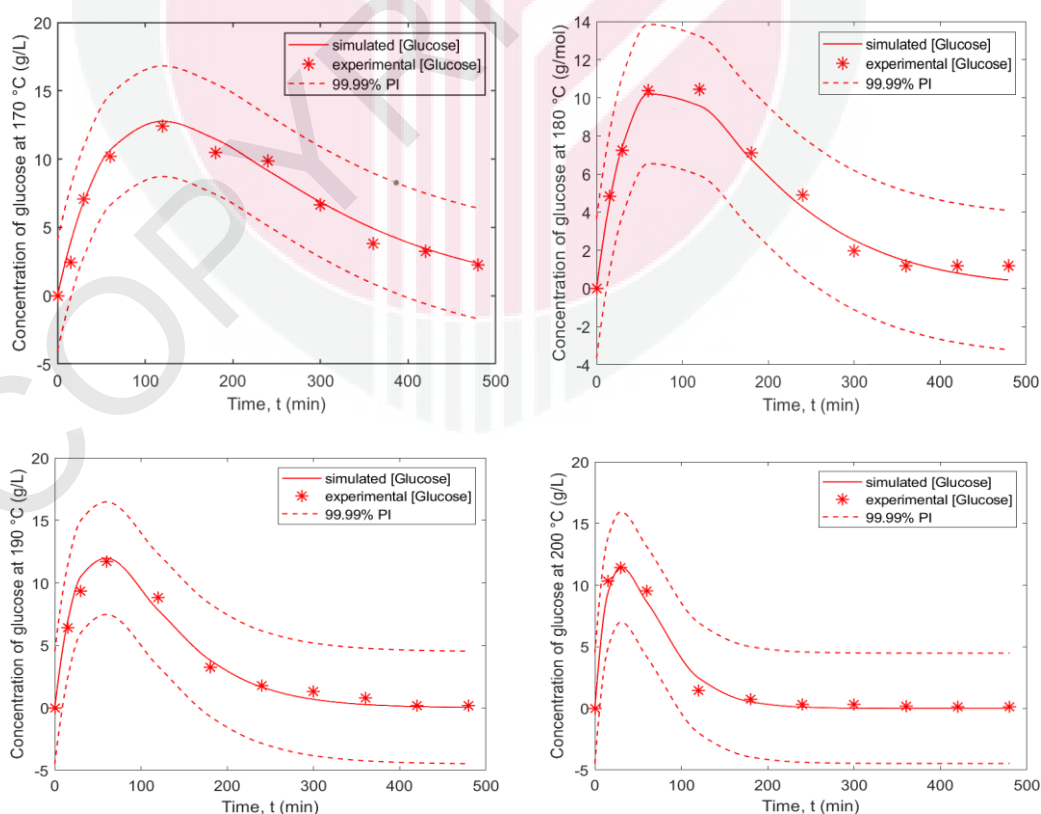


Figure 4.49: Experimental and modeled concentration-times profile for glucose at 170 °C, 180 °C, 190 °C and 200 °C

The concentrations of HMF based on experimental values and predicted values can be observed in Figure 4.50. The results show that the concentration of HMF reaches a maximum value and then decreases with reaction time in all hydrolysis reactions. Both the rate of formation and rate of decomposition of HMF increase quickly with temperature. The formation of HMF is highly dependent on the reaction temperature. This trend is similar to the findings obtained by Guo *et al.* (2021) which showed that increasing the temperature resulted in a higher maximum HMF yield from sugars, obtained in a shorter reaction time. The maximum HMF yield (0.11 g/L) was achieved at 200 °C in only 30 min. The decomposition of HMF occurs very fast because the concentrations of HMF produced are very low for all temperatures, indicating that HMF is rapidly consumed or degraded as soon as it is formed (Chang *et al.*, 2009). Additionally, it was discovered that HMF exhibited instability during this reaction, resulting in its rapid decomposition and subsequent formation of LA as a final product (Qing *et al.*, 2018). Hence, the HMF concentrations detected in the reaction were consistently low throughout the entire process. Higher reaction temperatures reduced HMF yields because HMF was rehydrated to LA and FA. As a result, the LA yield increased steadily as the reaction temperature increased as shown in Figure 4.51.

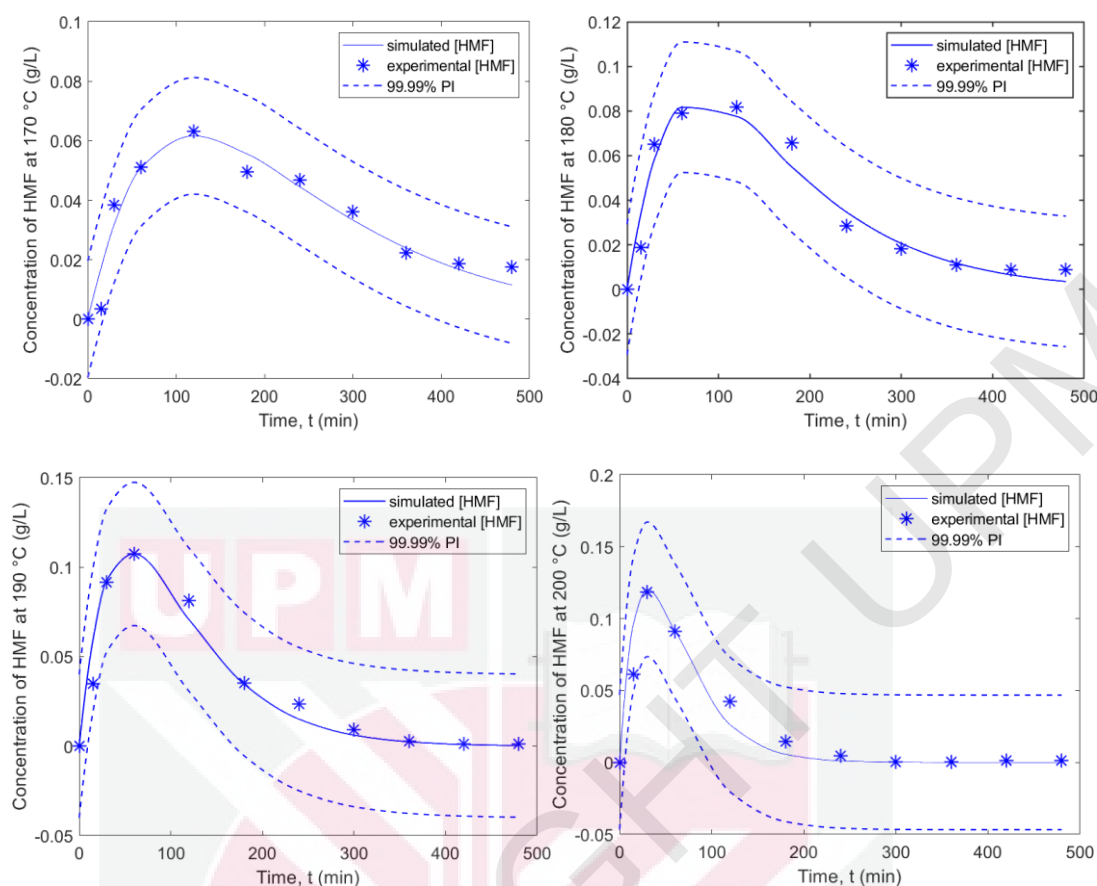


Figure 4.50: Experimental and modeled concentration-times profile for HMF at 170 °C, 180 °C, 190 °C and 200 °C

The product of HMF decomposition is LA (Chang *et al.*, 2009). Figure 4.51 shows the experimental and predicted values of LA concentration. The concentration of LA rapidly increased during the initial period and at a certain time, it reached a steady state. Prolonging the reaction did not increase the LA concentration. Hence, LA can be defined as the final product of the reaction under the experimental conditions (Chang *et al.*, 2009). The maximum LA productivity was reached after 4 h at 200 °C with a concentration higher than 16 g/L and this temperature generated the best results for the maximum value of LA. At high reaction temperature, atoms receive or donate electrons more easily and as a result, the chemical reaction rate increases (Ji *et al.*, 2019). The finding demonstrated that the reaction temperature has significantly

impacted the hydrolysis of cellulose into LA, which aligns with the findings of other researchers in their work (Li *et al.*, 2020).

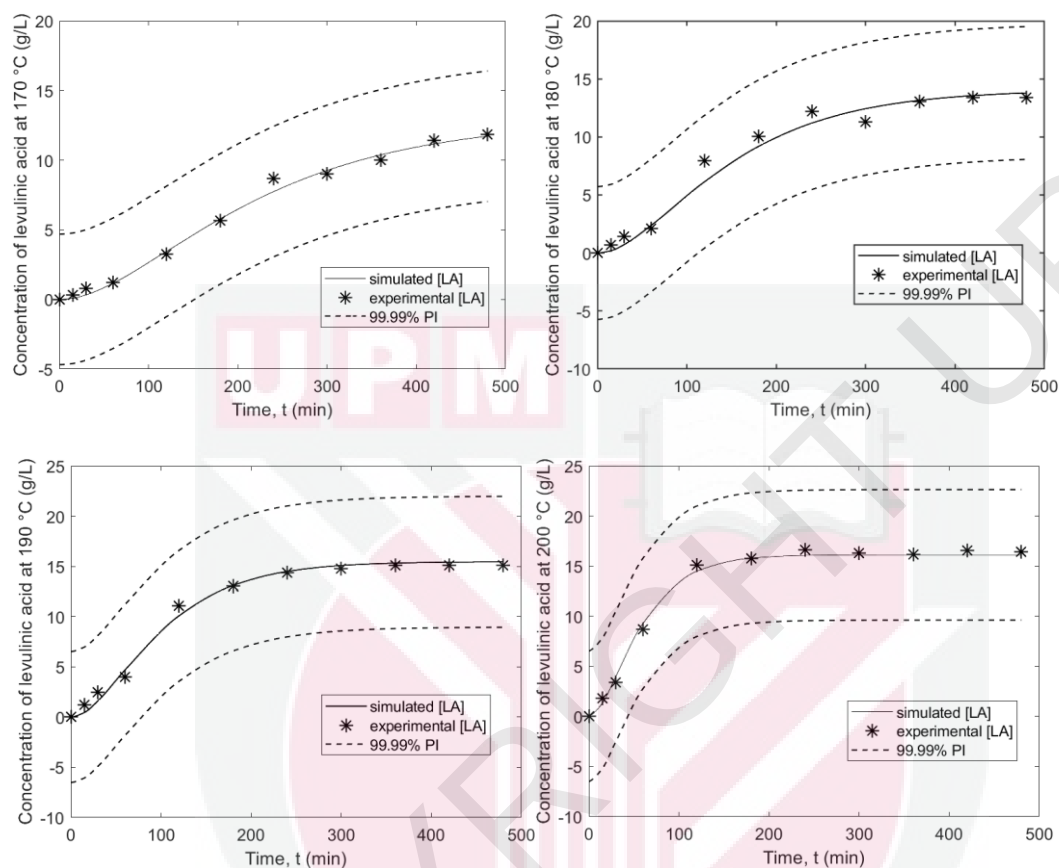


Figure 4.51: Experimental and modeled concentration-times profile for LA at 170 °C, 180 °C, 190 °C and 200 °C

4.6.2 Kinetic study of hydrolysis

This study introduces a novel kinetic model for the acid-catalyzed dehydration of OPEFB-based cellulose to LA. Our model specifically investigates the potential side reactions (production of humins) that have been overlooked in some of previous studies. The kinetics models developed in this study outperform those proposed by Nzediegwu *et al.* (2021) and Qing *et al.* (2018).

As discussed in Chapter 2 Section 2.10, PI, SE and RMSE were more accurate than those implemented in previous kinetics models such as SSE, CI, and R^2 . Hence, this model applied PI, SE and RMSE to achieve a more accurate fit. The prediction interval can be observed in Figure 4.49-4.51. Most of the simulated points are within 99.99% PI. The values for SE and RMSE for this study can be seen in Table 4.15. The statistical analysis showed that SE for all temperatures was in the range of 0.0060 to 1.9792 while RMSE was in the range 0.0055 to 0.8231. A smaller standard error indicates the samples are more representative of the whole population and lower RMSE values indicate better prediction methods (Nguyen *et al.*, 2020). The kinetic modelling fit experimental data well which suggest that the conversion of OPEFB-based cellulose into LA using sulfonated carbon catalyst was satisfactorily predicted by the kinetic model.

Table 4.15: Statistical analysis for this model

Reaction Steps	Standard Error, SE	Root Mean Square Error, RMSE
170 °C		
Cellulose → Glucose	1.2302	0.7019
Glucose → HMF	0.0060	0.0055
HMF → LA	1.4245	0.3683
180 °C		
Cellulose → Glucose	1.1097	0.4791
Glucose → HMF	0.0089	0.0067
HMF → LA	1.7390	0.8231
190 °C		
Cellulose → Glucose	1.3690	0.5766
Glucose → HMF	0.0122	0.0085
HMF → LA	1.9808	0.5355
200 °C		
Cellulose → Glucose	1.3601	0.5221
Glucose → HMF	0.0142	0.0119
HMF → LA	1.9792	0.4339

Figure 4.52 shows a parity plot using concentration values from experiment and predicted by model. The result shows that the predicted model is in good agreement with experiments for all cases and the relative error mostly within 15% indicating the model predictions for all products are very adequate.

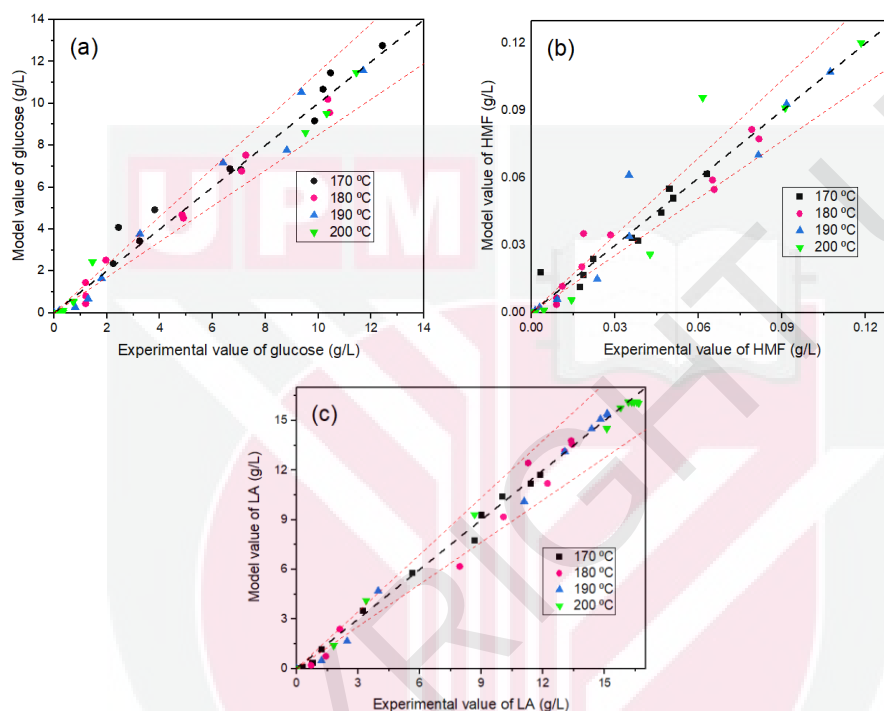


Figure 4.52: Parity plots of the experimental concentration and model concentration for glucose (a), HMF (b) and LA (c). Solid line is the parity line; points are data reserved for model assessment; and dashed lines are 15% error lines

Table 4.16 illustrates a clear pattern for k values derived from various temperatures based on the MATLAB simulation. Raising the temperature results in an increasing reaction rate coefficient leading to an increase in the reaction rate for both the desired reaction (the formation of LA) and the side products. The cellulose used in this study was pretreated with LiBr. Hence, the rate of conversion for cellulose is higher than glucose which is contradicted with some of previous studies. However, the values for both conversions were not too distinct.

At low temperatures (170 and 180 °C), the trend of k values was $k_2 < k_3 < k_1 < k_5 < k_4$. When the temperatures are higher (190 and 200 °C), the trend of k was $k_3 < k_2 < k_1 < k_5 < k_4$ which indicated k values for k_3 is lower than k_2 . This phenomenon was in line with previous studies by Mukherjee and Dumont (2016) and Nzediegwu and Dumont (2021). Both trends showed that at the lower temperatures, the formation rate of side products from glucose was faster than the formation of HMF from glucose. When increasing the temperature, the rate of HMF formation was faster than the formation of side products such as humins. It was anticipated that glucose would undergo isomerization into fructose at both low and high temperatures but at elevated temperatures, this isomerization process occurred more rapidly, subsequently facilitating a faster conversion into HMF (Taghavi *et al.*, 2022b).

For all temperatures, the value of k_2 was much smaller than that of k_4 , showing that the formation of HMF from glucose was much slower than the conversion of HMF to LA similar to the findings by Ringgani *et al.* (2022). As a result, the concentrations of HMF produced were low and appeared at short reaction times in all cases which can be seen in the Figure 4.50. This outcome is also consistent with previous studies reported by Rivas *et al.* (2013). The k_4 values were the highest, suggesting that the conversion HMF to LA was not the rate-determining step in the overall synthesis of LA from OPEFB-based cellulose. The formation of HMF from glucose was the rate-controlling in agreement with the result in previous studies (Zhao *et al.*, 2019). The significant value of k_5 at 200 °C verified the ease of humins formation which did not impede the LA production in this reaction. In summary, the results of the experiment suggested that the production of decomposition products held greater significance in

this particular study. The kinetic model based on the pseudo first-order kinetics demonstrated a strong correlation between experimental and prediction data.

Table 4.16: Kinetic rate constants (min^{-1}) for LA production from OPEFB-based cellulose

Reaction Steps	Kinetic parameter	Reaction rate constant (min^{-1})			
		170 °C	180 °C	190 °C	200 °C
Cellulose $\rightarrow$ Glucose	k_1	0.0089	0.0109	0.0184	0.0305
Glucose $\rightarrow$ HMF	k_2	0.0032	0.0066	0.0098	0.0199
Glucose $\rightarrow$ Side products	k_3	0.0050	0.0079	0.0092	0.0148
HMF $\rightarrow$ LA	k_4	0.6530	0.7589	0.9842	1.5989
HMF $\rightarrow$ Side products	k_5	0.0100	0.0589	0.1076	0.2960

4.6.3 Determination of thermodynamic parameters

The activation energy for the OPEFB-based cellulose hydrolysis reaction were determined for each reaction by applying the temperature coefficients and reaction rate to the Arrhenius equation (Ringgani *et al.*, 2022). Table 4.17 shows the highest activation energy of 156.84 kJ/mol was observed for the HMF to side products similar to the study by Nzediegwu and Dumont (2021). This is because, high temperatures produced more humins as side products (Ji *et al.*, 2019). Considering that the activation energy for the formation of HMF from glucose (102.45 kJ/mol) was higher than that of LA yielded from HMF (59.01 kJ/mol), it can be concluded that the high temperature promotes faster formation of LA and results in a relatively low HMF production (Lee *et al.*, 2022). Theoretical studies have demonstrated that lower activation energy values promote the feasibility of the conversion reaction by increasing the reaction rate (Tiong *et al.*, 2020). Similar to the finding by Nzediegwu and Dumont (2021), the activation energy for conversion of cellulose into glucose is lower than degradation of glucose into HMF, showing a lower degree of difficulty in cellulose degradation compared to glucose hydrolysis. This is possibly due to the cellulose used in this study already

being pretreated. The activation energy values for humins formation from degradation of glucose and HMF in this study were 59.38 and 156.84 kJ/mol, respectively. This finding demonstrated that the humins formation from glucose is relatively simple while it is more challenging to yield humins from HMF under the given reaction circumstances. This difficulty may also be attributed to the rapid conversion of HMF to LA as it is being produced (Zhao *et al.*, 2019). A comparison of activation energy can also be drawn with a study conducted by Tiong *et al.* (2018) and (Tiong *et al.*, 2020) as they also utilized oil palm biomass. However, their investigation lacks detailed values for activation energies pertaining to individual reactions, such as the conversion from biomass to glucose, glucose to HMF and HMF to LA. Instead, they solely reported the activation energy for the overall conversion of cellulose to LA. The activation energy for the conversion of oil palm biomass into LA in the study by Tiong *et al.* (2018) and Tiong *et al.* (2020) were 61.8 kJ/mol and 56.5 kJ/mol, respectively. The values are comparatively lower than the previous presented values via various catalytic means of LA production from others biomass. They suggested that the type of catalyst used in the reaction is important in order to improve the performance in LA production.

Table 4.17: Activation energy values (kJ/mol) for the synthesis of LA from OPEFB-based cellulose

Reaction Steps	Kinetic parameter	Activation energy (kJ/mol)			
		This study	Nzediegwu and Dumont (2021)	Ringgani <i>et al.</i> , (2022)	Lopes <i>et al.</i> , (2020a)
Cellulose → Glucose	k ₁	73.10	10.18	92.53	57.50
Glucose → HMF	k ₂	102.45	58.79	70.52	32.54
Glucose → Side products	k ₃	59.38	77.83	28.71	37.60
HMF → LA	k ₄	59.01	36.45	55.77	24.42
HMF → Side products	k ₅	156.84	136.25	94.86	n.a

In the present study, the thermodynamic features of LA production from OPEFB-based cellulose were also investigated. The thermodynamics variables entropy loss (ΔS), enthalpy change (ΔH) and Gibbs free energy change (ΔG) were utilized to explain the reaction behavior. Eyring plot of $\ln(k/T)$ versus $1/T$ in Figure 4.53 used to determine both ΔS and ΔH from the intercept and slope respectively. The thermodynamic parameters for LA formation are listed in Table 4.18. Positive values of ΔH in all reactions indicate that heat input is required to move the reactants to the transition state for product formation (Tiong *et al.*, 2020) The process is called as an endothermic reaction. The ΔH values from the the Eyring plots for all reactions were nearly similar but slightly lower than the activation energy values from the Arrhenius plots. The conversion of cellulose into LA is highly endothermic based on high ΔH values.

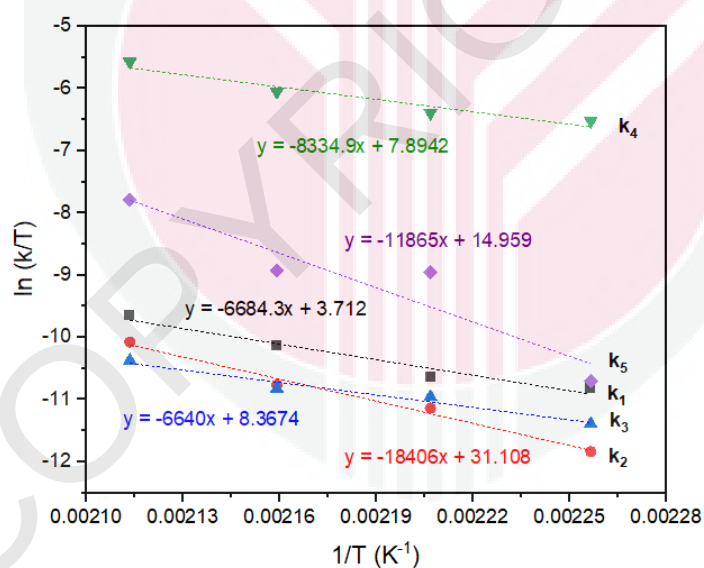


Figure 4.53: The Eyring plots of $\ln k/T$ versus $1/T$

A negative change in entropy (ΔS) indicates that the formation of the catalyst-substrate complex involves a significant decrease in entropy. This is due to the loss of translational and rotational degrees of freedom of the reactant and catalytic groups

(Tiong *et al.*, 2020). According to the fundamentals of thermodynamics, any product generated from a process with negative entropy is considered "stable" since negative entropy indicates increasing order within the system (Tizazu and Moholkar, 2018). Thus, we have classified glucose as a "stable product" based on thermodynamics without considering its chemical structure. It may be noted that glucose and HMF degradation also has negative entropy change, which means that it also leads to the stable product of HMF and LA. However, the glucose formation has more negative entropy than other products which signifies that glucose is a relatively more stable product than HMF and LA. The positive entropy during conversion of HMF into side products indicated the orderliness and stability of the side products from HMF were likely to be less than the desirable product (LA) (Yu *et al.*, 2021).

Lastly, all three of these formation reactions had positive ΔG values which indicated that these reactions were non-spontaneous (reactions that take place only when external energy is added) (Ramli and Amin, 2018). The ΔG values for glucose degradation are greater than hydrolysis of cellulose suggesting that glucose degradation is a less thermodynamically preferred process than production of glucose (on relative basis) (Tizazu and Moholkar, 2018). Similar to the absence of detailed activation energy values, the thermodynamic study by Tiong *et al.* (2020) also lacks specific values regarding individual reactions. Instead, the report only includes thermodynamic parameters for the overall oil palm biomass conversion into LA. However, their study also reported a non-spontaneous reaction shown by the positive values of ΔG (+115.11 kJ/mol), endothermic reaction indicated by the positive value of ΔH (53.0 kJ/mol) and ΔS value was -139.4 kJ/mol. The type of reaction in their study (Tiong *et al.*, 2020) was similar to this study.

Table 4.18: Thermodynamics parameters for the synthesis of LA from OPEFB-based cellulose at 200 °C

Reaction Steps	Kinetic parameter	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)
Cellulose $\rightarrow$ Glucose	k_1	69.30	-131.90	131.70
Glucose $\rightarrow$ HMF	k_2	98.65	-73.16	133.26
Glucose $\rightarrow$ Side products	k_3	55.57	-166.67	134.43
HMF $\rightarrow$ LA	k_4	55.20	-127.97	115.75
HMF $\rightarrow$ Side products	k_5	153.03	61.10	124.12

4.6.4 Summary

This study investigated the kinetic and thermodynamic studies of OPEFB-based cellulose conversion into LA via a sulfonated carbon metal catalytic system. The models proposed herein to predict aim the first-order irreversible reaction kinetics of OPEFB-based cellulose conversion into LA with high accuracy and low errors (SE and RMSE). A simulation for the reaction kinetics of LA synthesis was conducted using MATLAB R2023a (Simulink) by correlating with the experimental product distribution profiles. The constant values of the kinetic model were determined. The activation energies for the reactions of main products (glucose, HMF and LA) formation are evidently low at 59.01 – 73.10 kJ/mol. Besides, the hydrolysis reaction is endothermic, endergonic and non-spontaneous based on the value of positive value of ΔH , the negative value of ΔS and the positive value of ΔG . Therefore, the applied approach will offer a novel opportunity for converting abundant and cost-effective cellulosic biomass into LA.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The main aim of the study is assessing the potential of producing high yield of levulinic acid (LA) from OPEFB-based cellulose utilizing sulfonated carbon metal catalysts. By utilizing a comprehensive strategy involving catalytic screening, catalyst characterization, process parameter optimization and kinetics modeling, valuable insights have been obtained which contribute to the advancement of LA production from cellulose.

The study started with the catalyst screening of different loadings of Fe and Ni for the best yield of LA from cellulose and glucose. It was found that Fe.75Ni exhibited the most promising activity for LA production, yielding a maximum of 32.32% of theoretical (20.82 wt.%) from glucose and 10.51 % of theoretical (7.52 wt.%) from cellulose at 180 °C, 5 h and 0.15g catalyst loading. Subsequent impregnation of different ratio of Fe and Ni metals into sulfonated carbon catalyst led to further improvement in the catalytic activity for the LA synthesis. 15%FeNi/ACSO₃H catalyst produced the highest LA yield for both cellulose and glucose at 180 °C, 5 h and 0.15g catalyst loading. 16.76 % yield of LA based on theoretical (12.00 wt.% weight percentage) produced from this catalyst for cellulose. Meanwhile, glucose yielded 50.70% LA based on theoretical yield (32.65 wt.%) using the same catalyst. The

production of LA from cellulose was relatively low, indicating the need for cellulose modification or pretreatment to enhance the LA yield. The synthesized catalyst can be reused for a minimum of four reaction cycles with relatively good catalytic activity.

An extensive characterization of the physical and chemical properties of the catalysts was undertaken. Techniques such as TGA-DTG, N₂ adsorption-desorption analysis, FTIR, XRD, NH₃-TPD, XPS, and FESEM-EDX were employed, providing valuable insights into the catalyst's structural and chemical composition. Characterization studies examined the physical and chemical properties of the catalyst, confirming successful metal incorporation, sulfonation and increased acidity. These findings demonstrate the catalyst's suitability for catalyzing the hydrolysis reaction of glucose and cellulose.

Since the primary goal of this study was to produce LA from cellulose extracted from OPEFB, it is essential to utilize this material as a raw material in the subsequent reactions. Successful extraction of cellulose from OPEFB was achieved using the established technique involving dewaxing, NaOH treatment and bleaching with NaClO₂ solution. Notably, the study revealed the importance of developing efficient pretreatment methods for enhancing hydrolysis reactions via functional modification of cellulose. MSHs pretreatment, particularly with LiBr, significantly improved cellulose accessibility and hydrolysis efficiency. The yield of LA is significantly increased after pretreatment with LiBr (24.3%) and LiCl (22.52%), in contrast to the yield with untreated cellulose (8.98%). The reduction in crystallinity of all MSHs-pretreated cellulose samples, especially with LiBr treatment, was also observed, with LiBr-treated cellulose exhibiting 33.51% crystallinity.

The optimization study focused on identifying the optimal conditions for LA synthesis from LiBr-pretreated cellulose from OPEFB using Response Surface Methodology (RSM) revealing that the highest LA production (78.12% of theoretical and 51.66 wt.%) was achieved at 200 °C, 4.5 hours and 10% catalyst loading. These RSM conditions were validated with experimental results, highlighting the importance of temperature, time, and catalyst loading in influencing the efficiency of LA synthesis.

The work concluded with the development of a detailed kinetics model, which provided insight on the kinetics driving the conversion of OEFB-based cellulose into LA. The kinetics model accurately predicted first-order irreversible reaction kinetics by integrating experimental works and mathematical modelling. Its accuracy was confirmed by its correlation with experimental product distribution profiles, revealing important reaction parameters, such as the activation energy range of 59.01 – 102.45 kJ/mol required for LA synthesis for the production of important and desirable products which were glucose, HMF and LA. Advanced simulations using MATLAB R2023a (Simulink) offered deep insights into the thermodynamic factors that influence the hydrolysis reaction. The hydrolysis reaction is endothermic, endergonic and non-spontaneous. Therefore, the proposed approach will provide a novel option for converting abundant and cost-effective cellulosic biomass into LA.

5.2 Recommendations

For further research, it is recommended that the following areas to be explored:

1. While the study focused on cellulose from oil palm empty fruit bunches (OPEFB), future research could explore the use of other oil palm biomass

wastes such as OPMF, OPF, OPT and OPS. Investigating the feasibility of LA production from a diverse range of oil palm biomass wastes could provide valuable insights into the scalability and versatility of the process.

2. Prior research has demonstrated that while both Brønsted and Lewis acids serve as catalysts for the overall reaction, specific stages in the reaction process are more effectively catalyzed by varying types of acids. Due to the limitation in the part of product analysis, the isomerization step was excluded in this study. Therefore, further studies involving the evaluation of individual reaction steps including isomerization of glucose are crucial for a comprehensive understanding of the catalytic mechanisms of Brønsted and Lewis acids. These studies can provide insights into the specific roles played by each type of acid in different stages of the reaction, leading to the development of more efficient and selective catalytic processes.
3. Consider upgrading the reactor system to accommodate higher operating temperatures by installing a mechanical seal with higher specifications. This upgrade will enable the study of LA synthesis at temperatures beyond the current limit of 200 °C, providing insights into reaction kinetics and optimal conditions for higher temperature operation.
4. Optimization studies on the isolation process can be investigated in the future to improve the properties of cellulose from OPEFB, further enhancing the potential of this cellulose as a sustainable feedstock for valuable chemical synthesis.
5. Beyond the synthesis of LA, future research could also focus on the development of efficient downstream processing techniques for product purification and separation. Exploring innovative separation technologies, such as membrane filtration or adsorption processes, could help streamline the purification process and improve overall product quality and yield.

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APPENDICES

Appendix A

Sample calculation for preparation catalyst

$$\frac{\text{Metal loading, \%}}{100} \times \text{amount of catalyst needed} \\ \times \frac{\text{molecular weight metal chloride or nitrate}}{\text{molar mass metal}}$$

a) Catalyst: Fe₇₅Ni

Iron (Fe) loading = 25 wt. %

Molecular weight of FeCl₃·6H₂O = 270.30 g/mol

Atomic weight of Fe = 55.85 g/mol

$$\begin{aligned} \text{Amount of Iron (Fe) required, g} &= \frac{25 \%}{100} \times 5.0 \text{ g} \times \frac{270.30 \text{ g/mol}}{55.85 \text{ g/mol}} \\ &= 6.0496 \text{ g} \end{aligned}$$

Nickel (Ni) loading = 75 wt. %

Molecular weight of Ni(NO₃)₂·6H₂O = 290.81 g/mol

Atomic weight of Fe = 58.70 g/mol

$$\begin{aligned} \text{Amount of Nickel (Ni) required, g} &= \frac{75 \%}{100} \times 5.0 \text{ g} \times \frac{290.81 \text{ g/mol}}{58.70 \text{ g/mol}} \\ &= 18.5783 \text{ g} \end{aligned}$$

b) 15%FeNi/ACSO₃H

Fe-Ni = 15 wt. % (based on weight of support)

ACSO₃H (support) = 5.0 g

$$\begin{aligned} \text{Amount of Fe-Ni needed} &= \frac{15 \%}{100} \times 5.0 \text{ g} \\ &= 0.75 \text{ g} \end{aligned}$$

Appendix B
Actual experimental setup



Figure H.1: Experimental setup for hydrolysis reaction

Appendix C

HPLC mobile phase preparation

Mobile phase: Sulfuric Acid (H₂SO₄)

Convert Normality (N) to Molarity (M)

$$M = \text{Normality}/(n\text{-factor})$$

$$M = (0.05 \text{ N})/2 = 0.025 \text{ M}$$

To prepare 1L of 0.025M H₂SO₄ solution,

$$\text{Mass} = \text{molar mass} \times \text{Molarity} \times \text{Volume needed}$$

$$\text{Mass} = 98 \text{ g/mol} \times 0.025 \text{ M} \times 1000 \text{ mL} = 2.45 \text{ g}$$

$$\text{Volume} = \text{mass} \div \text{density}$$

$$\text{Volume} = 2.45 \text{ g} \div 1.84 \text{ g/mL} = 1.33 \text{ mL}$$

From 96% stock solution,

$$1.33\text{mL} \times 100/96 = 1.38\text{mL}$$

Appendix D

High Performance Liquid Chromatography (HPLC) Analysis

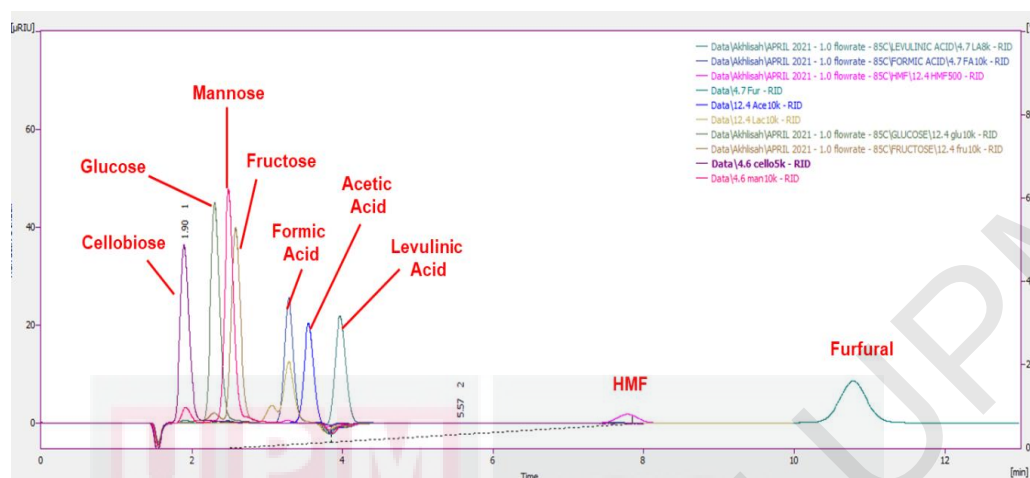


Figure H.2: Chromatography for all HPLC standards

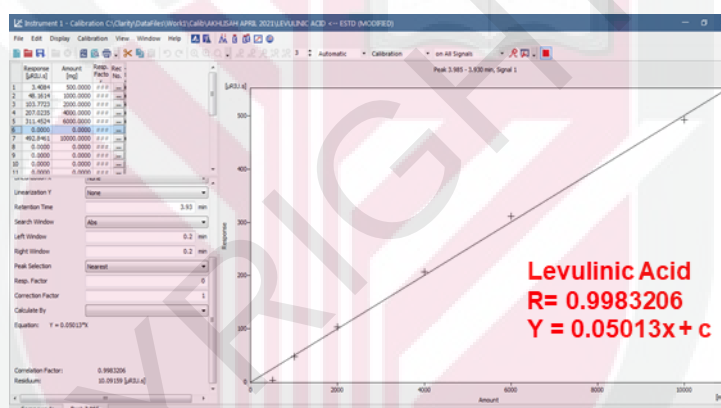


Figure H.3: Calibration curve for LA standards (500, 1000, 2000, 4000, 6000, 10000 ppm)

Example calculation for LA concentration

$$y = mx + c$$

$$y = 0.05013x + c$$

Since $c = 0$, $y = 0.24134 \text{ } \mu\text{RIU.s}$

$$0.24134 = 0.05013x + 0$$

$$y = 4.814 \text{ ppm or g/L}$$

Appendix E

Proximate Analysis Calculation

Acid Detergent Fiber (ADF): 56.76

Neutral Detergent Fiber (NDF): 77.43

Acid Detergent Lignin (ADL): 14.82

For cellulose,

$$\begin{aligned}\text{Cellulose (\%)} &= \text{ADF} - \text{ADL} \\ &= 56.76 - 14.82 \\ &= 41.94\%\end{aligned}$$

For hemicellulose,

$$\begin{aligned}\text{Hemicellulose (\%)} &= \text{NDF} - \text{ADF} \\ &= 77.43 - 56.76 \\ &= 20.67\%\end{aligned}$$

For lignin,

$$\begin{aligned}\text{Lignin (\%)} &= \text{ADL} \\ &= 14.82\%\end{aligned}$$

For extractives,

$$\begin{aligned}\text{Extractives (\%)} &= 100 - \text{NDF (\%)} \\ &= 100 - 77.43 \\ &= 22.57\%\end{aligned}$$

Appendix F

Sample calculation for molten salt hydrate solution

Preparation of $\text{LiBr} \cdot 3\text{H}_2\text{O}$

$$\begin{aligned}\text{Ratio} &= 1:3 \\ &= 0.2 \text{ mol}:0.6 \text{ mol}\end{aligned}$$

Molecular weight of $\text{LiBr} = 86.845 \text{ g/mol}$

Molecular weight of $\text{H}_2\text{O} = 18.015 \text{ g/mol}$

$$\begin{aligned}\text{LiBr}, \quad 0.2 \text{ mol} &= \frac{x}{86.845 \text{ g/mol}} \\ x &= 17.369 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{H}_2\text{O}, \quad 0.6 \text{ mol} &= \frac{x}{18.015 \text{ g/mol}} \\ x &= 10.81 \text{ g}\end{aligned}$$

Preparation of $\text{LiCl} \cdot 3\text{H}_2\text{O}$

$$\begin{aligned}\text{Ratio} &= 1:3 \\ &= 0.2 \text{ mol}:0.6 \text{ mol}\end{aligned}$$

Molecular weight of $\text{LiCl} = 42.394 \text{ g/mol}$

Molecular weight of $\text{H}_2\text{O} = 18.015 \text{ g/mol}$

$$\begin{aligned}\text{LiCl}, \quad 0.2 \text{ mol} &= \frac{x}{42.394 \text{ g/mol}} \\ x &= 8.48 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{H}_2\text{O}, \quad 0.6 \text{ mol} &= \frac{x}{18.015 \text{ g/mol}} \\ x &= 10.81 \text{ g}\end{aligned}$$

Preparation of $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$

$$\begin{aligned}\text{Ratio} &= 1:3 \\ &= 0.1 \text{ mol}:0.3 \text{ mol}\end{aligned}$$

Molecular weight of $\text{ZnCl}_2 = 136.30 \text{ g/mol}$

Molecular weight of $\text{H}_2\text{O} = 18.015 \text{ g/mol}$

$$\begin{aligned}\text{ZnCl}_2, \quad 0.1 \text{ mol} &= \frac{x}{136.30 \text{ g/mol}} \\ x &= 13.63 \text{ g}\end{aligned}$$

$$\begin{aligned}\text{H}_2\text{O}, \quad 0.3 \text{ mol} &= \frac{x}{18.015 \text{ g/mol}} \\ x &= 5.405 \text{ g}\end{aligned}$$

Appendix G

MATLAB Program for 170 °C

```

function levulinic_ode3_170
global k1 k2 k3 k4 k5
%Modified program with smooth curves, PI and SE
k1=0.008910;
k2=0.0032;
k3=0.005;
k4=0.6530;
k5=0.010;
t=[0;15;30;60;120;180;240;300;360;420;480];
C0=[33.33 0 0 0];
[t, C]=ode45(@ratelaw,t,C0);

lengtht=length(t);
samplingRateIncrease = 50;
newt= linspace(min(t), max(t), lengtht * samplingRateIncrease);
CA=[C(1:11)]; %CA=[C(1:11)];
CB=[C(12:22)]; %CB=[C(12:22)];
CC=[C(23:33)]; %CC=[C(23:33)];
CD=[C(34:44)]; %CD=[C(34:44)];
smoothedCA= pchip(t, CA, newt); %Nak smoothkan curve %smoothedCA= pchip(t,
CA, newt);
smoothedCB= pchip(t, CB, newt); %smoothedCB= pchip(t, CB, newt);
smoothedCC= pchip(t, CC, newt); %smoothedCC= pchip(t, CC, newt);
smoothedCD= pchip(t, CD, newt); %smoothedCD= pchip(t, CD, newt);

% Input mass fraction data and time steps based on the experimental works
% make sure ada 11 points (sbb ada 11 exp data)
C1_exp=[33.33; 0; 0; 0; 0; 0; 0; 0; 0; 0; 0]; %Letak 0 for all
C2_exp=[0; 2.4377; 7.0686; 10.1832; 12.4315; 10.4648; 9.8604; 6.6554; 3.8099;
3.2384; 2.2358];
C3_exp=[0; 0.0034; 0.0384; 0.0511; 0.0631; 0.0496; 0.0468; 0.0361; 0.0223;
0.0187; 0.0176];
C4_exp=[0; 0.3032; 0.7850; 1.2190; 3.2499; 5.6344; 8.6847; 9.0221; 10.0152;
11.4187; 11.8695];
C_exp=[C1_exp/100, C2_exp/100, C3_exp/100, C4_exp/100];
tspan=[0;15;30;60;120;180;240;300;360;420;480];
C0=[33.33 0 0 0];

%Statistical analysis
N=11;

```

%Sample mean

MA =

(C(1,1)+C(2,1)+C(3,1)+C(4,1)+C(5,1)+C(6,1)+C(7,1)+C(8,1)+C(9,1)+C(10,1)+C(11,1))/11;

MB =

(C(1,2)+C(2,2)+C(3,2)+C(4,2)+C(5,2)+C(6,2)+C(7,2)+C(8,2)+C(9,2)+C(10,2)+C(11,2))/11;

MC =

(C(1,3)+C(2,3)+C(3,3)+C(4,3)+C(5,3)+C(6,3)+C(7,3)+C(8,3)+C(9,3)+C(10,3)+C(11,3))/11;

MD =

(C(1,4)+C(2,4)+C(3,4)+C(4,4)+C(5,4)+C(6,4)+C(7,4)+C(8,4)+C(9,4)+C(10,4)+C(11,4))/11;

%Calculation of standard deviation for every product distribution curve

STDA=sqrt((1/(N-1))*([C(1,1)-MA]^2+[C(2,1)-MA]^2+[C(3,1)-MA]^2+[C(4,1)-MA]^2+[C(5,1)-MA]^2+[C(6,1)-MA]^2+[C(7,1)-MA]^2+[C(8,1)-MA]^2+[C(9,1)-MA]^2+[C(10,1)-MA]^2+[C(11,1)-MA]^2));

STDB=sqrt((1/(N-1))*([C(1,2)-MB]^2+[C(2,2)-MB]^2+[C(3,2)-MB]^2+[C(4,2)-MB]^2+[C(5,2)-MB]^2+[C(6,2)-MB]^2+[C(7,2)-MB]^2+[C(8,2)-MB]^2+[C(9,2)-MB]^2+[C(10,2)-MB]^2+[C(11,2)-MB]^2));

STDC=sqrt((1/(N-1))*([C(1,3)-MC]^2+[C(2,3)-MC]^2+[C(3,3)-MC]^2+[C(4,3)-MC]^2+[C(5,3)-MC]^2+[C(6,3)-MC]^2+[C(7,3)-MC]^2+[C(8,3)-MC]^2+[C(9,3)-MC]^2+[C(10,3)-MC]^2+[C(11,3)-MC]^2));

STDD=sqrt((1/(N-1))*([C(1,4)-MD]^2+[C(2,4)-MD]^2+[C(3,4)-MD]^2+[C(4,4)-MD]^2+[C(5,4)-MD]^2+[C(6,4)-MD]^2+[C(7,4)-MD]^2+[C(8,4)-MD]^2+[C(9,4)-MD]^2+[C(10,4)-MD]^2+[C(11,4)-MD]^2));

%standard error calculation

SEA=STDA/(sqrt(N))

SEB=STDB/(sqrt(N))

SEC=STDC/(sqrt(N))

SED=STDD/(sqrt(N))

TotalSE=SEB+SEC+SED

%standard error residual calculation

SEResidualA=sqrt((1/N)*([(C1_exp(1))-C(1,1)]^2+[(C1_exp(2))-C(2,1)]^2+[(C1_exp(3))-C(3,1)]^2+[(C1_exp(4))-C(4,1)]^2+[(C1_exp(5))-C(5,1)]^2+[(C1_exp(6))-C(6,1)]^2+[(C1_exp(7))-C(7,1)]^2+[(C1_exp(8))-C(8,1)]^2+[(C1_exp(9))-C(9,1)]^2+[(C1_exp(10))-C(10,1)]^2+[(C1_exp(11))-C(11,1)]^2));

SEResidualB=sqrt((1/N)*([(C2_exp(1))-C(1,2)]^2+[(C2_exp(2))-C(2,2)]^2+[(C2_exp(3))-C(3,2)]^2+[(C2_exp(4))-C(4,2)]^2+[(C2_exp(5))-C(5,2)]^2+[(C2_exp(6))-C(6,2)]^2+[(C2_exp(7))-C(7,2)]^2+[(C1_exp(8))-C(8,2)]^2+[(C2_exp(9))-C(9,2)]^2+[(C2_exp(10))-C(10,2)]^2+[(C2_exp(11))-C(11,2)]^2));

$C(8,2)]^2+[(C1_exp(9))-C(9,2)]^2+[(C1_exp(10))-C(10,2)]^2+[(C1_exp(11))-C(11,2)]^2));$

$SEResidualC=sqrt((1/N)*([(C3_exp(1))-C(1,3)]^2+[(C3_exp(2))-C(2,3)]^2+[(C3_exp(3))-C(3,3)]^2+[(C3_exp(4))-C(4,3)]^2+[(C3_exp(5))-C(5,3)]^2+[(C3_exp(6))-C(6,3)]^2+[(C3_exp(7))-C(7,3)]^2+[(C1_exp(8))-C(8,3)]^2+[(C1_exp(9))-C(9,3)]^2+[(C1_exp(10))-C(10,3)]^2+[(C1_exp(11))-C(11,3)]^2));$

$SEResidualD=sqrt((1/N)*([(C4_exp(1))-C(1,4)]^2+[(C4_exp(2))-C(2,4)]^2+[(C4_exp(3))-C(3,4)]^2+[(C4_exp(4))-C(4,4)]^2+[(C4_exp(5))-C(5,4)]^2+[(C4_exp(6))-C(6,4)]^2+[(C4_exp(7))-C(7,4)]^2+[(C1_exp(8))-C(8,4)]^2+[(C1_exp(9))-C(9,4)]^2+[(C1_exp(10))-C(10,4)]^2+[(C1_exp(11))-C(11,4)]^2));$

SEResidualA

SEResidualB

SEResidualC

SEResidualD

%SSE Calculation

$SSEA=([C(1,1)-(C1_exp(1))]^2+[C(2,1)-(C1_exp(2))]^2+[C(3,1)-(C1_exp(3))]^2+[C(4,1)-(C1_exp(4))]^2+[C(5,1)-(C1_exp(5))]^2+[C(6,1)-(C1_exp(6))]^2+[C(7,1)-(C1_exp(7))]^2+[C(8,1)-(C1_exp(8))]^2+[C(9,1)-(C1_exp(9))]^2+[C(10,1)-(C1_exp(10))]^2+[C(11,1)-(C1_exp(11))]^2);$

$SSEB=([C(1,2)-(C2_exp(1))]^2+[C(2,2)-(C2_exp(2))]^2+[C(3,2)-(C2_exp(3))]^2+[C(4,2)-(C2_exp(4))]^2+[C(5,2)-(C2_exp(5))]^2+[C(6,2)-(C2_exp(6))]^2+[C(7,2)-(C2_exp(7))]^2+[C(8,2)-(C2_exp(8))]^2+[C(9,2)-(C2_exp(9))]^2+[C(10,2)-(C2_exp(10))]^2+[C(11,2)-(C2_exp(11))]^2);$

$SSEC=([C(1,3)-(C3_exp(1))]^2+[C(2,3)-(C3_exp(2))]^2+[C(3,3)-(C3_exp(3))]^2+[C(4,3)-(C3_exp(4))]^2+[C(5,3)-(C3_exp(5))]^2+[C(6,3)-(C3_exp(6))]^2+[C(7,3)-(C3_exp(7))]^2+[C(8,3)-(C3_exp(8))]^2+[C(9,3)-(C3_exp(9))]^2+[C(10,3)-(C3_exp(10))]^2+[C(11,3)-(C3_exp(11))]^2);$

$SSSED=([C(1,4)-(C4_exp(1))]^2+[C(2,4)-(C4_exp(2))]^2+[C(3,4)-(C4_exp(3))]^2+[C(4,4)-(C4_exp(4))]^2+[C(5,4)-(C4_exp(5))]^2+[C(6,4)-(C4_exp(6))]^2+[C(7,4)-(C4_exp(7))]^2+[C(8,4)-(C4_exp(8))]^2+[C(9,4)-(C4_exp(9))]^2+[C(10,4)-(C4_exp(10))]^2+[C(11,4)-(C4_exp(11))]^2);$

SSEA

SSEB

SSEC

SSSED

TotalSSE=SSEB+SSEC+SSSED

%RMSE calculation

$RMSEA = \sqrt{((1/N)) * ([C(1,1)-(C1_exp(1))]^2 + [C(2,1)-(C1_exp(2))]^2 + [C(3,1)-(C1_exp(3))]^2 + [C(4,1)-(C1_exp(4))]^2 + [C(5,1)-(C1_exp(5))]^2 + [C(6,1)-(C1_exp(6))]^2 + [C(7,1)-(C1_exp(7))]^2 + [C(8,1)-(C1_exp(8))]^2 + [C(9,1)-(C1_exp(9))]^2 + [C(10,1)-(C1_exp(10))]^2 + [C(11,1)-(C1_exp(11))]^2)}$;
 $RMSEB = \sqrt{((1/N)) * ([C(1,2)-(C2_exp(1))]^2 + [C(2,2)-(C2_exp(2))]^2 + [C(3,2)-(C2_exp(3))]^2 + [C(4,2)-(C2_exp(4))]^2 + [C(5,2)-(C2_exp(5))]^2 + [C(6,2)-(C2_exp(6))]^2 + [C(7,2)-(C2_exp(7))]^2 + [C(8,2)-(C2_exp(8))]^2 + [C(9,2)-(C2_exp(9))]^2 + [C(10,2)-(C2_exp(10))]^2 + [C(11,2)-(C2_exp(11))]^2)}$;
 $RMSEC = \sqrt{((1/N)) * ([C(1,3)-(C3_exp(1))]^2 + [C(2,3)-(C3_exp(2))]^2 + [C(3,3)-(C3_exp(3))]^2 + [C(4,3)-(C3_exp(4))]^2 + [C(5,3)-(C3_exp(5))]^2 + [C(6,3)-(C3_exp(6))]^2 + [C(7,3)-(C3_exp(7))]^2 + [C(8,3)-(C3_exp(8))]^2 + [C(9,3)-(C3_exp(9))]^2 + [C(10,3)-(C3_exp(10))]^2 + [C(11,3)-(C3_exp(11))]^2)}$;
 $RMSED = \sqrt{((1/N)) * ([C(1,4)-(C4_exp(1))]^2 + [C(2,4)-(C4_exp(2))]^2 + [C(3,4)-(C4_exp(3))]^2 + [C(4,4)-(C4_exp(4))]^2 + [C(5,4)-(C4_exp(5))]^2 + [C(6,4)-(C4_exp(6))]^2 + [C(7,4)-(C4_exp(7))]^2 + [C(8,4)-(C4_exp(8))]^2 + [C(9,4)-(C4_exp(9))]^2 + [C(10,4)-(C4_exp(10))]^2 + [C(11,4)-(C4_exp(11))]^2)}$;

RMSEA
 RMSEB
 RMSEC
 RMSED

% 99.99 prediction interval, z score=3.29; 99% prediction interval, z=2.58; 95% prediction interval, z=1.96
 z=3.29;

$PIA_upper = [(C(1,1)+z*SEA);(C(2,1)+z*SEA);(C(3,1)+z*SEA);(C(4,1)+z*SEA);(C(5,1)+z*SEA);(C(6,1)+z*SEA);(C(7,1)+z*SEA);(C(8,1)+z*SEA);(C(9,1)+z*SEA);(C(10,1)+z*SEA);(C(11,1)+z*SEA)]$;

$PIA_lower = [(C(1,1)-z*SEA);(C(2,1)-z*SEA);(C(3,1)-z*SEA);(C(4,1)-z*SEA);(C(5,1)-z*SEA);(C(6,1)-z*SEA);(C(7,1)-z*SEA);(C(8,1)-z*SEA);(C(9,1)-z*SEA);(C(10,1)-z*SEA);(C(11,1)-z*SEA)]$;

$PIB_upper = [(C(1,2)+z*SEB);(C(2,2)+z*SEB);(C(3,2)+z*SEB);(C(4,2)+z*SEB);(C(5,2)+z*SEB);(C(6,2)+z*SEB);(C(7,2)+z*SEB);(C(8,2)+z*SEB);(C(9,2)+z*SEB);(C(10,2)+z*SEB);(C(11,2)+z*SEB)]$;

$PIB_lower = [(C(1,2)-z*SEB);(C(2,2)-z*SEB);(C(3,2)-z*SEB);(C(4,2)-z*SEB);(C(5,2)-z*SEB);(C(6,2)-z*SEB);(C(7,2)-z*SEB);(C(8,2)-z*SEB);(C(9,2)-z*SEB);(C(10,2)-z*SEB);(C(11,2)-z*SEB)]$;

$PIC_upper = [(C(1,3)+z*SEC);(C(2,3)+z*SEC);(C(3,3)+z*SEC);(C(4,3)+z*SEC);(C(5,3)+z*SEC);(C(6,3)+z*SEC);(C(7,3)+z*SEC);(C(8,3)+z*SEC);(C(9,3)+z*SEC);(C(10,3)+z*SEC);(C(11,3)+z*SEC)]$;

$PIC_lower = [(C(1,3)-z*SEC);(C(2,3)-z*SEC);(C(3,3)-z*SEC);(C(4,3)-z*SEC);(C(5,3)-z*SEC);(C(6,3)-z*SEC);(C(7,3)-z*SEC);(C(8,3)-z*SEC);(C(9,3)-z*SEC);(C(10,3)-z*SEC);(C(11,3)-z*SEC)]$;

```
PID_upper=[(C(1,4)+z*SED);(C(2,4)+z*SED);(C(3,4)+z*SED);(C(4,4)+z*SED);(C
(5,4)+z*SED);(C(6,4)+z*SED);(C(7,4)+z*SED);(C(8,4)+z*SED);(C(9,4)+z*SED);(
C(10,4)+z*SED);(C(11,4)+z*SED)];
PID_lower=[(C(1,4)-z*SED);(C(2,4)-z*SED);(C(3,4)-z*SED);(C(4,4)-
z*SED);(C(5,4)-z*SED);(C(6,4)-z*SED);(C(7,4)-z*SED);(C(8,4)-z*SED);(C(9,4)-
z*SED);(C(10,4)-z*SED);(C(11,4)-z*SED)];
```

%Smooth Prediction Interval: upper and lower lines

```
PIA.upper=[PIA_upper(1:11)];
PIA.lower=[PIA_lower(1:11)];
PIB.upper=[PIB_upper(1:11)];
PIB.lower=[PIB_lower(1:11)];
PIC.upper=[PIC_upper(1:11)];
PIC.lower=[PIC_lower(1:11)];
PID.upper=[PID_upper(1:11)];
PID.lower=[PID_lower(1:11)];
smoothedPIA.upper= pchip(t, PIA.upper, newt);
smoothedPIA.lower= pchip(t, PIA.lower, newt);
smoothedPIB.upper= pchip(t, PIB.upper, newt);
smoothedPIB.lower= pchip(t, PIB.lower, newt);
smoothedPIC.upper= pchip(t, PIC.upper, newt);
smoothedPIC.lower= pchip(t, PIC.lower, newt);
smoothedPID.upper= pchip(t, PID.upper, newt);
smoothedPID.lower= pchip(t, PID.lower, newt);
```

figure (1)

```
plot(newt,smoothedCA,'b',tspan, (C1_exp),'*b',newt, smoothedPIA.upper,':b',newt,
smoothedPIA.lower,':b');
xlabel('Time, t (min)');
ylabel('Concentration of cellulose at 170 °C (g/L)'); %tukar kpd conc of cellulose
%tukar temp %dlm kurungan (g/L)
legend('simulated CA','experimental CA','99.99% PI'); %Tukar Xtmp kpd CA
```

figure (2)

```
plot(newt,smoothedCB,'r',tspan, (C2_exp),'*r',newt, smoothedPIB.upper,':r',newt,
smoothedPIB.lower,':r');
xlabel('Time, t (min)');
ylabel('Concentration of glucose at 170 °C (g/L)');
legend('simulated [Glucose]','experimental [Glucose]','99.99% PI');
```

figure (3)

```
plot(newt,smoothedCC,'b',tspan, (C3_exp),'*b',newt, smoothedPIC.upper,':b',newt,
smoothedPIC.lower,':b');
xlabel('Time, t (min)');
```

```
ylabel('Concentration of HMF at 170 °C (g/L)');
legend('simulated [HMF]', 'experimental [HMF]', '99.99% PI');
```

figure (4)

```
plot(newt,smoothedCD,'k',tspan, (C4_exp),'*k',newt, smoothedPID.upper,':k',newt,
smoothedPID.lower,':k');
xlabel('Time, t (min)');
ylabel('Concentration of levulinic acid at 170 °C (g/L)');
legend('simulated [LA]', 'experimental [LA]', '99.99% PI');
```

```
function dCdt=ratelaw(t,C)
dCdt=[-k1*C(1);
k1*C(1)-(k2+k3)*C(2);
k2*C(2)-(k4+k5)*C(3);
k4*C(3)];
```

```
end
```

```
end
```

```
%levulinic_ode3_170
```

LIST OF PUBLICATIONS

Journal Publications

- Akhlisah, Z. N.**, Yunus, R., Abidin, Z. Z., Lim, B. Y., & Kania, D. (2021). Pretreatment methods for an effective conversion of oil palm biomass into sugars and high-value chemicals. *Biomass and Bioenergy*, 144, 105901 (*Published*)
- Akhlisah, Z.N.**, Yunus, R., Azlina, W.W., Abidin, Z.Z., Taufiq-Yap, Y.H. and Rashid, U. (2024) Comparative Analysis of Alkaline Pretreatment Methods for Levulinic Acid Production from Oil Palm Biomass Waste. (*Published*)
- Zulkipli, N.A.**, Ghani, W.A.W.A.K., Yunus, R., Hin, T.Y.Y. and Rashid, U., 2024. Preparation and Characterization of Oil Palm Empty Fruit Bunch-Based Cellulose for Levulinic Acid Production. *Malaysian Journal of Science and Advanced Technology*, pp.374-382. (*Published*)
- Sjahro, N., Yunus, R., Abdullah, L. C., Rashid, S. A., Asis, A. J., & **Akhlisah, Z. N.** (2021). Recent advances in the application of cellulose derivatives for removal of contaminants from aquatic environments. *Cellulose*, 28(12), 7521-7557 (*Published*)
- Misenan, M.S.M., Farabi, M.A., **Akhlisah, Z.N.** and Khair, A.S.A., 2025. Enhancing polymer electrolytes with carbon nanotube fillers: A promising frontier. *Next Materials*, 7, p.100365. (*Published*)
- Z.N. Akhlisah**, R. Yunus, W.A.K. Wan Azlina, Y.H. Taufiq-Yap, U. Rashid, G Abdulkareem-Alsultan, N. Asikin-Mijan (2024) Synthesis of Levulinic Acid from Cellulose Using Iron and Nickel Catalysts (*Submitted*)
- Z.N. Akhlisah**, R. Yunus, W.A.K. Wan Azlina, Y.H. Taufiq-Yap, U. Rashid, G Abdulkareem-Alsultan, N. Asikin-Mijan (2024) Synthesis of Levulinic Acid from Cellulose Using Sulfonated Carbon Metal Catalysts (*Submitted*)
- Z.N. Akhlisah**, W.A.K. Wan Azlina, R. Yunus, Y.H. Taufiq-Yap, N. Sjahro, R.S.R.M. Hafriz, S.H. Habib (2024) Improvement of Cellulose Via Non-Dissolving Pretreatment with $\text{LiBr} \cdot 3\text{H}_2\text{O}$ for Levulinic Acid Production (*Submitted*)

Conference

- SEARCA Scholar and Alumni Conference 2024, 25-26 April 2024 at SEARCA, College, Los Baños, Laguna, Philippines.
- The 2nd International Conference on Agricultural, Nutraceutical, and Food Science (ICANFS) 2024, 23 October 2024, Magelang, Central Java, Indonesia.
- 8th Science and Technology Graduates Colloquium, 5 November 2024, Universiti Sains Islam Malaysia, Nilai, Negeri Sembilan, Malaysia.