ORGANOSOLV PRETREATMENT ON
OIL PALM EMPTY FRUIT BUNCH: A CASE STUDY
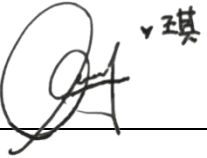
CELINE WONG SU CHEE

A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering

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May 2021

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

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ABSTRACT

Organosolv pretreatment has high potential in sustainable energy development by transforming lignocellulosic biomass into biofuels. Meanwhile, various studies have limited attempts in exploring different solvents and catalysts used in pretreatment, while inconclusive approaches still existed in the study of synergistic effects between process factors. Consequently, the objective of this research is to comparatively study and analyse organosolv pretreatment on OPEFB under various parameters, including different types of solvents, catalysts, and process factors (concentration, temperature, time). These parameters were explored for their effects on delignification, cellulose recovery/yield, and sugar yield. Besides, this research also studied the physical and chemical characterization of pretreated OPEFB including changes in structural and morphological, degree of crystallinity, functional group, and thermal stability, through the analysis of SEM, XRD, FTIR, and TGA. Furthermore, the interactive effects between sulphuric acid concentration (0.5 – 2.0 %), reaction temperature (160 – 200 °C), and residence time (30 – 90 min) on Glucose (GLU) recovery and Ethanol Organosolv Lignin (EOL) recovery were analyzed from the Central Composite Design (CCD) model built via Design-Expert software. The findings of this research showed that High Boiling Point (HBP) or Low Boiling Point (LBP) alcohols provided higher pretreatment efficiency compared to other solvents. This similar concept was applied to acid catalyst compared with base catalyst. Other than that, an increase in concentration, temperature, and time contributed positive impacts on the pretreatment efficiency until a certain high limit, wherein the exceeded limit led to adverse impact due to inhibitory product formation, sugar decomposition, and lignin recondensation. For characterisation study, more cracks and porous structures with lower crystallinity index were investigated due to the removal of lignin, hemicellulose, and inorganic elements. Other than that, the outcome of modelling showed that SA concentration provided the greatest influence on both GLU and EOL recoveries compared with reaction temperature and residence time. The optimum process conditions (1.97 % SA; 172 °C; 68 min) predicted a GLU recovery rate of 99.07 %, which was in good agreement with a 100 % GLU recovery rate obtained by Goh, et al. (2011).

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LIST OF SYMBOLS / ABBREVIATIONS

I_{002}	Maximum intensity of the (002) lattice diffraction at $2\theta=22°$
I_{AM}	Minimum intensity of diffraction at $2\theta=18°$
AA	Acetic Acid
AFEX	Ammonia fibre explosion
BT	Billion tonnes
C	Carbon
C=C	Carbon-carbon bonding
C=O	Carbonyl bonding
CCD	Central composite design
$C_2H_4O_3$	Peracetic acid
C_2H_5OH	Ethanol
$C_2H_6O_2$	Ethylene glycol
C_3H_6O	Acetone
$Ca(OH)_2$	Calcium hydroxide
C-H	Carbon-hydrogen bonding
CH_2	Methylene
CH_2-OH	Hydroxymethyl group
CH_3COOH	Acetic acid
C-O-C	Ether bonding
EFB	Empty fruit bunch
EOL	Ethanol organosolv lignin
FA	Formic Acid
FELCRA	Federal Land Consolidation and Rehabilitation Authority
FELDA	Federal Land Development Authority
FFB	Fresh fruit bunch
FTIR	Fourier Transform Infrared Reflectance Spectroscopy
G	Guaiacyl unit
GHG	Greenhouse gases
GLU	Glucose
H	p-hydroxyphenyl unit
H_2O_2	Hydrogen peroxide

H_2SO_4	Sulphuric acid
H_3PO_4	Phosphoric acid
HBP	High Boiling Point
HCl	Hydrochloric acid
HMF	5-hydroxymethylfurfural
KL	Klason lignin
KOH	Potassium hydroxide
LBP	Low Boiling Point
LCB	Lignocelluloses biomass
LHW	Liquid Hot Water
$MgCl_2$	Magnesium chloride
MMT	Million metric tonnes
NaOH	Sodium hydroxide
NH_4	Ammonium
O	Oxygen
O-H	Hydrogen bonding
OH	Hydroxyl group
OPEFB	Oil palm empty fruit bunch
RISDA	Rubber Industry Smallholders Development Authority
S	Syringyl unit
SA	Sulphuric acid
S/L	Solid to liquid ratio
SEM	Scanning Electron Microscopy
TCI	Total crystallinity index
TGA	Thermogravimetric Analyser
TWh	Terawatt-hours
XRD	X-Ray Diffractometer
α	Alpha-linkages
β	Beta-linkages

CHAPTER 1

INTRODUCTION

1.1 General Introduction

1.1.1 Overview of Primary Energy

Energy exposure has become significant support for human welfare, economic growth, and poverty reduction. Almost all energy is derived directly from natural sources, while it can classify into fossil-based fuels (oil, coal, natural gas), renewable sources (solar, wind, hydropower), and nuclear energy. These primary energies can convert into energy currency and secondary fuel for various applications in industrial, residential, and commercial sectors. Over the past five decades, crude oil has been the main energy source with the largest share of global consumption, followed by coal and natural gas, as shown in Figure 1.1. Globally, there are about 13355 million litres of oil consumed daily. It is expected to increase by 18.443 billion liters in the year 2030. In short, non-renewable fossil fuel has dominated the global energy system by approximately 95 %, whereas the consumptions for renewable sources are relatively low. (Hanania and Donev, 2020).
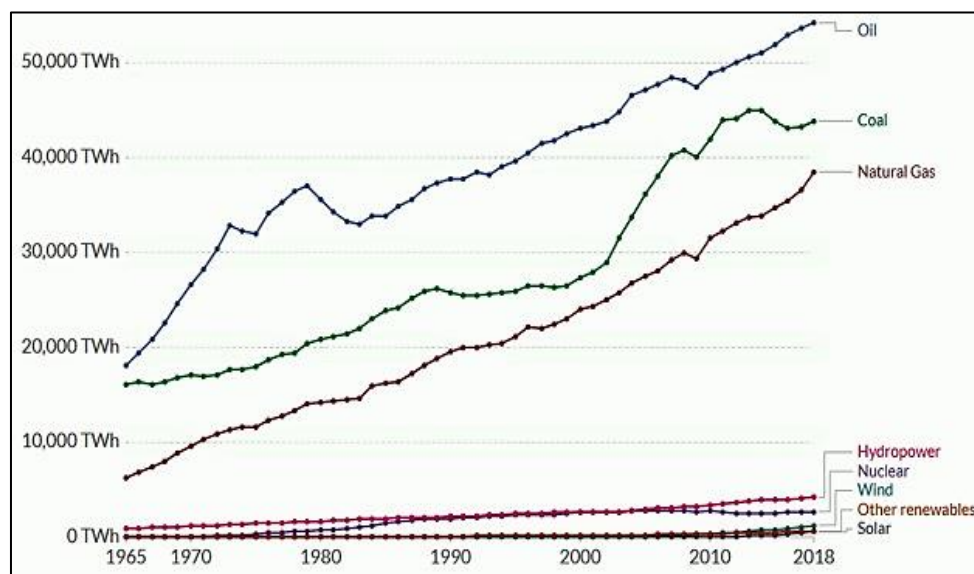
Figure 1.1: Annual Global Energy Consumption, by Sources (1965 – 2018), Measured in Terawatt-hours -TWh (Ritchie and Roser, 2014).

Figure 1.2 shows that in 1965, North America and Eurasia jointly consumed 35,383 TWh. This value has indicated over 80 % of global energy consumption. Besides, the Asia-Pacific region experienced the most significant growth. During this period (1965-2018), overall energy consumption increased by more than 12 times. The Asia-Pacific region became the largest regional consumer which was attributed to the highest total energy intake of 63,682 TWh in the year 2015, compared with the Middle East, Latin America and Africa that were consumed less energy (Ritchie and Roser, 2014).
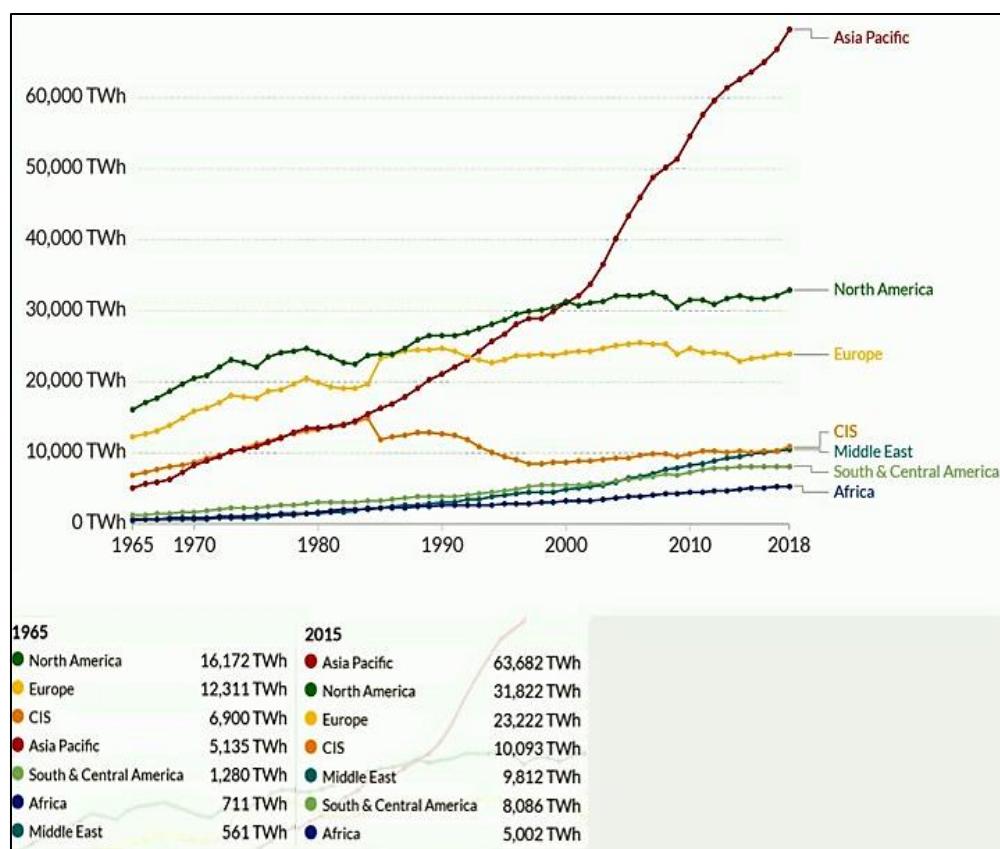
Figure 1.2: Annual Global Energy Consumption, by World Region (1965 – 2018), Measured in Terawatt-hours -TWh (Ritchie and Roser, 2014).

1.1.2   Impacts of Global Energy Consumption

The 20th century witnessed rapid economic expansion and high population growth, resulting in a substantial rise in the demand for fossil fuels and energy consumption. As a result, fossil resources continue to degrade, causing an energy crisis. In turn, higher energy prices will be levied and will bring further economic burdens to society, including the decline in product supply and

demand (Hollaway, 2013). The huge global energy demand may have exceeded the production of renewable energy. Therefore, the demand for fossil fuels is expected to rise over the subsequent ten years.

Regarding the higher demand and the large consumption of fossil fuels, more greenhouse gases (GHG) will be released during the combustion process, and not limited to the wastewater generated by mining activities. These problems have led to many adverse environmental impacts, such as ocean acidification, land destruction, climate change, air and water pollution (Denchak, 2018). As illustrated in Figure 1.3, there was a significant rise in global total carbon emissions from 2 billion tonnes in 1900 increased to about 36 million tonnes in 2016. In 2017, China was the largest contributor with 9.7 billion tons of carbon emissions, followed by the United States and Europe with 5.31 tons and 3.5 billion tons, respectively (Ritchie and Roser, 2017).
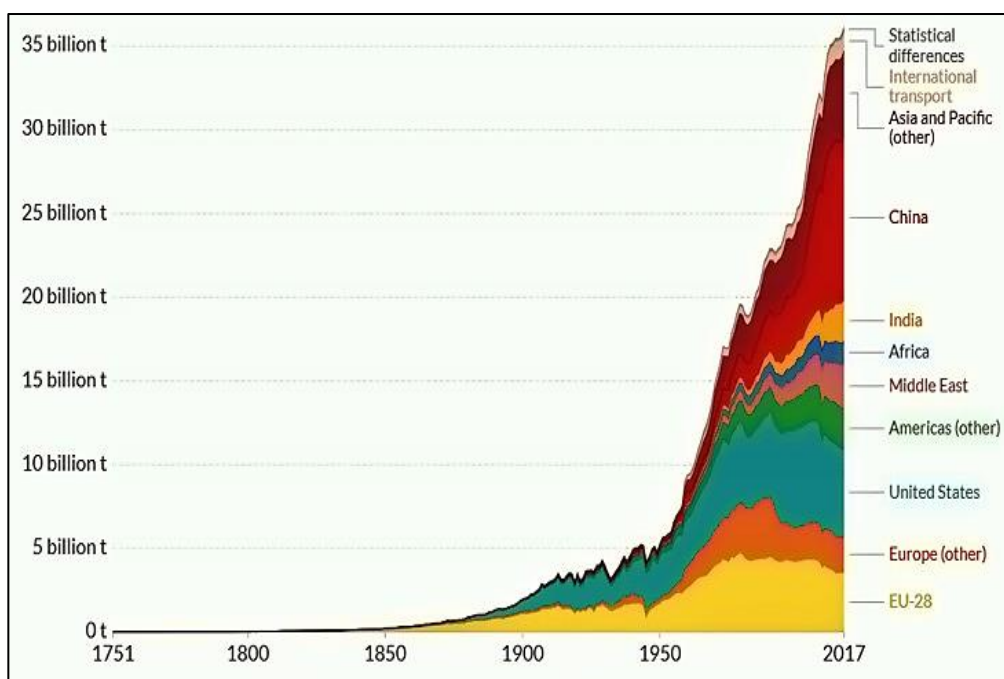
Figure 1.3: Annual Carbon Dioxide Emission, by World Region (1751 – 2017), Measured in Billion Tonnes -BT (Ritchie and Roser, 2017).

1.1.3   Lignocellulosic Biomass for Sustainable Energy System

Due to limited natural resources and increasing attention to environmental pollution, sustainable energy development has been significant in the research field. In recent years, biomass has become a potential green energy source

among other renewable energy sources. It combines the value of waste management and energy production, thereby enhancing the prospects of biomass for biorefineries. Biomass comprises a diversified group of materials including forestry or agricultural wastes, organic waste from municipal and industrial sectors (Galbe and Wallberg, 2019). Since biomass is cheap and abundant, it has great potential to be used and explored for the unlimited and constantly replenished energy supply.

Furthermore, this project focuses on lignocellulosic biomass (LCB) which contributes approximately up to 50 billion dry tons globally per year, indicating 50 % of global biomass production (Zhao, Cheng, and Liu, 2009). LCB is a waste material of plant origin. Its main components can be 50-60 % polysaccharides (cellulose and hemicellulose) and 20-30 % aromatic polymers (lignin). It also comprises fatty acids, extractives, ash, and others to a lesser extent. The high proportion of complex carbohydrates makes LCB an important source of reducing sugar to produce biofuels. In this project, the oil palm empty fruit bunch is the prominent LCB to be studied.

1.1.4 Palm Oil Production and Consumption

The global market has emphasized palm oils' sustainable growth, in which 32 % of the worldwide fats and oils production obtain from palm oil. This has resulted in palm oil becoming the prominent edible oil suppressing soybean oil, as presented in Figure 1.4 (Shahbandeh, 2020). In 1999, Malaysia was the world's largest palm oil manufacturer and exporter, providing 10.55 million tons of global palm oil production. Indonesia and Malaysia are the first two largest manufacturers, and they account for approximately 85 – 90 % of global palm oil production.

In 2011, global crude palm oil production reached 48.99 million metric tonnes (MMT) per annum, mainly contributed by Southeast Asia as follows: Indonesia (23.9 MMT), Malaysia (18 MMT), and Thailand (1.45 MMT) (Geng, 2013). Moreover, it was predicted that Malaysia achieved an average annual palm oil production of 15.4 million tonnes during the forecast period (2016 - 2020) (Abdullah and Sulaiman, 2013). An estimated 72 % of crude palm oil was consumed by the most substantial proportion in India (46 %), followed by

Europe (22 %) and Malaysia (11 %). The remaining 21 % was consumed to a smaller extent by other countries (Rahayu, Wirjodirdjo and Hadi, 2019).
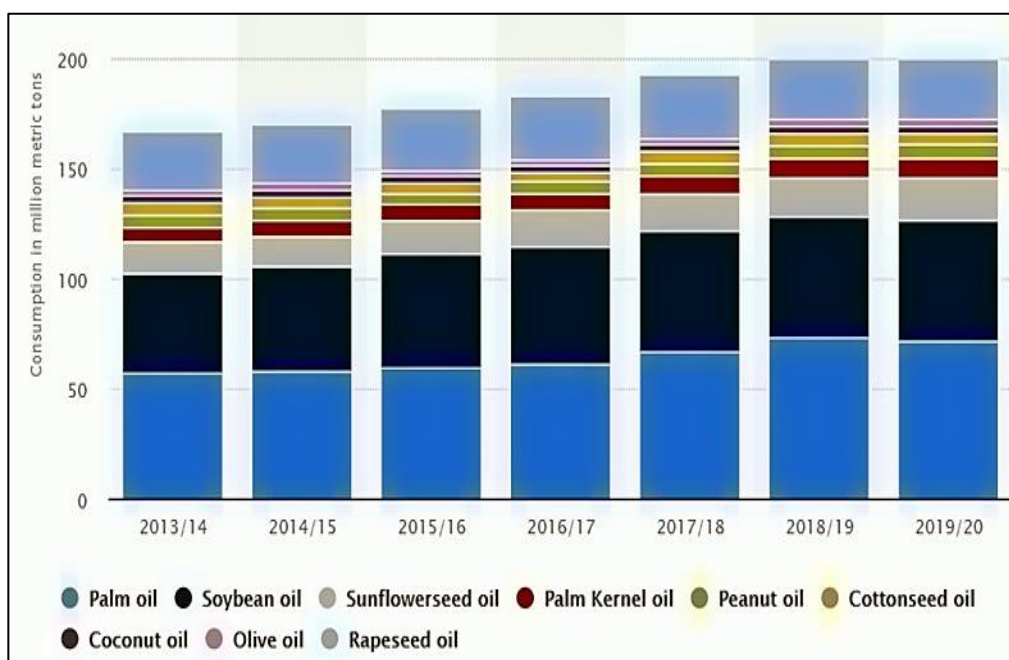
Figure 1.4: Consumption of Edible Oil Worldwide from 2013/14 to 2019/20, by Oil Type, Measured in Million Metric Tons (Shahbandeh, 2020).

1.1.5   Oil Palm Land Use

The rising in palm oil production attributes to its better production efficiency compared to other oil sources. Generally, 1 ton of oil can be produced from the land: oil palm (0.26 hectares), rapeseed (1.5 hectares), and soybeans (2.2 hectares) (Palm Oil Research, 2017). This shows that the productivity of oil palm is ten times higher than soybeans, which supports a stable supply of edible oil. Besides, Palm Oil Research (2017) pointed out that the global agricultural land used for oil palm cultivation was accounted for 5.48 % (780,000 hectares). By 1999, of the 10.2 million hectares of agricultural land in Malaysia, the use of arable land for oil palm had reached 3.31 million hectares. Of these, 62 % were located in Peninsular Malaysia, while 28 % were located in Sabah and 10 % were located in Sarawak (Abdullah and Sulaiman, 2013). By 2017, Malaysia's oil palm plantations had reached 5.81 million hectares (Tahir, et al., 2019).

1.1.6   Lignocellulosic Products/Wastes From Oil Palm Industries

Throughout the entire upstream to the downstream production process, the oil palm agricultural industry generates a large amount of lignocellulosic solid waste. In terms of dry weight, an estimated 83 million tonnes of oil palm biomass waste was generated in 2012, and by 2020, the waste was expected to incline to 100 million tonnes. Specifically, it can be acknowledged that 23% of fresh fruit bunch was palm oil mill residues in EFB, as shown in Table 1.1. Referring to Table 1.2, the waste volume of EFB in 2007 had estimated to be 18 million tonnes, which was higher compared with other production wastes except for oil palm fronds.

Table 1.1: Breakdown of Products/Wastes from Each Fresh Fruit Bunch (FFB) (Abdullah and Sulaiman, 2013).

Oil palm lignocellulosic products/wastes	Weight percentage to oil palm fresh fruit bunch – FFB (dry basis)
Palm Oil	21
Palm Kernel	7
Fibre	15
Shell	6
Empty fruit bunches (EFB)	23
POME	28
Total	100

Table 1.2: Analysis of Palm Oil Production Wastes in 2007 (Abdullah and Sulaiman, 2013).

Wastes	Quantity (Kilo-tonnes)
Oil Palm Fronds	46,837
Empty Fruit Bunches (EFB)	18,022
Palm Pressed Fibres	11,059
Oil Palm Trunks	10,827
Palm Kernel Shell	4,506

1.1.7 Oil Palm Empty Fruit Bunch

OPEFB is one of the typical large-scale biomass waste generated in the entire palm oil supply chain, and Malaysia may accumulate about 16 million tons of OPEFB per year (Han and Kim, 2018). In theory, each ton of crude palm oil produced can generate 1.42 to 1.88 tons of OPEFB. However, OPEFB has not been optimally adopted and is usually limited to very few downstream uses. Its high moisture content may lower the combustion temperature, resulting in reduced energy efficiency and limiting its use as boiler fuel. Alternatively, OPEFB can be incinerated and recycled as fertilizers for oil palm cultivation, not limited to mulching materials that function to prevent soil abrasion, as shown in Figure 1.5 (a). Even so, the incineration process will release gases with particulate into the atmosphere and cause air pollution (Tahir, et al., 2019). Concerning the environmental problems, the Department of Environment (DOE) in Malaysia has discouraged the incineration or open burning of OPEFB.

Eventually, OPEFB will be disposed of as waste and accumulated in an open environment, as presented in Figure 1.5 (b). The indiscriminate dumping of OPEFB has led to the rapid growth of disease-causing pests on these accumulated wastes. As a result, OPEFB will be rotted away unutilized, along with methane gas and odour emissions that may affect health (Tahir, et al., 2019). In addition to the disposal difficulties in terms of extensive landfills, the high operating cost for treatment has further aggravated this problem. In short, OPEFB must be fully exploited for environmental conservation and energy sustainability.

(a)   (b)

Figure 1.5: (a) EFB as Mulch Material in Plantation Area (b) EFB Dumping around Oil Palm Industries (Rahayu, Wirjodirdjo and Hadi, 2019).

1.1.8 OPEFB as Biorefineries Feedstock

OPEFB is lignocellulosic biomass with a high polysaccharide content, as described previously in Section 1.1.3. This content can be used to produce second-generation biofuels, thereby replacing non-renewable fossil resources. Its non-edible properties provide no disruption over global food security. Hence, it can be used as an alternative raw material to replace edible sugarcane and corn in biofuel production. Biofuels derived from biogenic-origin OPEFB encourage the carbon neutrality concept, thus significantly less greenhouse gas emission compare to fossil products. All these facts have rendered OPEFB a more promising energy source for biorefineries.

However, the rigid and compact lignocellulose structure has built up the spatial network between polysaccharides and lignin. This network forms a protective barrier, imparting recalcitrance property to lignocellulose, which limits its structure deconstruction and cellulose accessibility for sugar conversion. Furthermore, both direct and indirect factors can affect the accessibility of biomass cellulose, such as surface area accessibility, chemical compositions (lignin, hemicellulose, and acetyl groups), cellulose structure (cellulose crystallinity, polymerization degree), and biomass structure (particle size, pore size, volume) (Zhao, Zhang and Liu, 2012). Therefore, numerous pretreatment methods are mandatory as crucial strategies to depolymerize lignocellulose, thus enhance cellulose accessibility by altering the physical and chemical properties of LCB.

1.1.9 Overview of Pretreatment

Classification of pretreatment methods are shown as follows: physical, chemical, physicochemical, and biological. The physical pretreatment functions with the concept of elevated temperature and irradiation, or both particle size and cellulose crystallinity reduction. The downsides of this pretreatment may be that higher energy consumption and the generation of fine particles may negatively affect its subsequent processes. Besides, chemical pretreatment is applicable with either acid, alkali, and organic solvent, to list a few. Concentrated acid solvents are not favourable due to their corrosiveness and high cost, while alkaline solvents are only meaningful for treating low lignin biomass. However, chemical pretreatment is still widely used on an industrial scale.

Physicochemical pretreatment allows a combination of physical and chemical concepts. For biomass with high lignin content, the effect of this pretreatment is usually poor, owing to less fraction of solubilization. Other than that, biological pretreatment makes use of microorganisms that encourage low energy consumption and non-toxic by-product generation. However, this method is time-consuming and has a low hydrolysis rate, so it is not suitable for industrial-scale use (Kumar and Sharma, 2017).

All the above-mentioned pretreatment methods have similarities, which are mainly used to disrupt the lignocellulosic matrix to a significant extent. This disruption reduces the recalcitrance of lignocellulosic biomass by degrading and removing the lignin content, resulting in a reduction of cellulose crystallinity. Thus, a higher digestibility of lignocelluloses and an easement of the hydrolysis process can be achieved, allowing polysaccharides to be efficiently converted into fermentable sugars to produce biofuel. The effectiveness of pretreatment can be proven by little or no carbohydrates degradation, inhibition of by-products formation, limited waste generation, and concern for low reactants and energy consumption (Mardawati, et al., 2018).

1.1.10 Organosolv Pretreatment

Organosolv pretreatment is one of the promising chemical method that can be used to pretreat lignocellulosic biomass with high lignin content. It is usually carried out at high temperatures and high pressure. Besides, it is more feasible for biorefineries of lignocellulosic biomass, due to its full-scale application of biomass components with a high purity fractionation of the three main components, including glucan, dry lignin, and aqueous hemicellulose stream (Zhao, Cheng and Liu, 2009).

In this pretreatment, ethanol is frequently utilized as an organic solvent. It is inexpensive, miscible with water, and allows efficient lignin dissolution. The ethanol solvent is easy to reuse and recover through the evaporation or distillation process. Organic solvents such as methanol, ethylene glycol, and acetone can also be used in this pretreatment. Other than that, non-catalytic organic solvent pretreatment usually obtains a relatively low delignification rate (≤60 %) (Mondylaksita, et al., 2020). Therefore, acid or alkali is added as a catalyst to accelerate the delignification and solubilization rate of hemicellulose.

Sulphuric acid is the typical catalyst used in this pretreatment, owing to its high efficiency and reactivity thus allowing an increase in the hydrolysis of holocellulose. Acetic acid, magnesium chloride, and sodium hydroxide, to list a few, can also be used as pretreatment catalysts (Zhao, Cheng and Liu, 2009).

There are still several shortcomings of this pretreatment, such as inconvenient washing procedures, and strict control of process operations are required to avoid leakage of the digestion tank of highly volatile and flammable solvents thus prevent fire and explosion hazards. In addition, energy-consuming processes (solvent recovery and recycling) are crucial in this pretreatment, in order to prevent the residual solvents from inhibiting the microorganism growth, hydrolysis, and fermentation process. Organic solvents are always expensive but the cost-saving from recovered solvent can compensate for the high operational cost (Zhao, Cheng and Liu, 2009).

1.2   Importance of the Study

The sustainable energy system has always been a potential research area, which supports a transformation toward green growth and a highly developed bio-based economy. Recently, OPEFB has become a potential renewable energy source for the production of alternative carbon-based fuels. These fuels promote the concept of carbon neutrality and ensure a reliable energy supply to replace finite energy. The high proportion of complex carbohydrates in OPEFB can be obtained by chemical hydrolysis, so it can be further catalytically converted into biofuel. However, the high lignin content reduces the efficiency of hydrolysis and leads to a decrease in sugar yield. Consequently, pretreatment is required before the hydrolysis process to cleave the composite structure of lignocellulose, followed by lignin removal and ensure better accessibility of carbohydrates. This research will emphasize a comprehensive study of organosolv pretreatment on OPEFB and the effects of influential pretreatment parameters. With the aids of this study, the sugar yield can be enhanced for energy recovery thus improving energy security and efficiency, reducing carbon intensity and environmental damage.

Parallel to the rapid generation of OPEFB wastes from the palm oil mill process, this study is crucial to get rid of the massive wastage issue and disposal difficulties of OPEFB through the management of it into biofuel, rather than

indiscriminate dumping or incinerate it. Through this complete valorization of OPEFB for energy applications, the circular economy is promoted and environmental pollution is minimized and mitigated. Considering the advanced planning and research before actual application, a complete optimisation model is of great significance for more effective and accurate result prediction. This can reduce resource, time, and cost consumption, which may be attributed to unnecessary trial and error for optimal pretreatment results. With the support of optimisation modelling, it is worth noting to analyse the synergies of pretreatment parameters on the pretreatment efficiency.

1.3 Problem Statement

A variety of organosolv strategies have been applied to the pretreatment on OPEFB, not limited to other potential biomass such as sugarcane bagasse, corn stover, wheat, or rice straw. However, so far, very limited studies have been attempted to analyse the impacts of different solvents and catalysts on the organosolv pretreatment efficiency. Most studies only emphasize one solvent with or without catalyst in the pretreatment, without further compiling and evaluating the comprehensive study between different types of solvents and catalysts. Therefore, it is of great significance to determine whether the types of solvents and catalysts will affect the delignification, cellulose recovery/yield, and sugar yield in organosolv pretreatment on OPEFB. Also, the pretreatment effects of other parameters including concentration, temperature, and time are considered as well.

Other than that, characterisation methods such as SEM, XRD, FTIR, and TGA are usually used in research to evaluate the physical and chemical properties of OPEFB. Yet, its physical and chemical characteristics are still not revealed distinctly in the literature. The characterisation of OPEFB largely depends on the pretreatment parameters, and the interaction should be further determined between these variables. Regarding optimisation modelling, most investigations only specify the effects of parameters distinctly, thus given limited reviews and inconclusive approaches for the synergistic effects of parameters on organosolv pretreatment efficiency. It is thus, of interest, to extensively analyse the interactions of parameters via modelling and pre-planning for the optimum pretreatment conditions on OPEFB.

1.4 Aim and Objectives

This research project aims to analyse the development of organosolv pretreatment on oil palm empty fruit bunch (OPEFB), in conjunction with the following objectives:

(i) To analyse and compare different types of organosolv pretreatments on OPEFB.

(ii) To compare the effect of different solvents and catalysts on organosolv pretreatment efficiency.

(iii) To investigate the selected parameters affecting delignification, cellulose recovery/yield, sugar yield in organosolv pretreatment and characterisation of OPEFB.

(iv) To analyse synergistic effects and optimum conditions among the selected parameters on ethanol organosolv lignin (EOL) recovery and glucose (GLU) recovery via optimisation modelling.

1.5 Scope and Limitation of the Study

Based on the aforementioned goals, it is necessary to develop and establish a scope to specify the range of studies performed, owing to limited information access and time constraint. Different types of organic solvents and catalysts impact on organosolv pretreatment efficiency are discussed, in which the former will be highlighted in four categories (LBP alcohol, HBP alcohol, organic acid, ketone), while the latter is of two categories (acid and base). Besides, three selected pretreatment parameters such as concentration, temperature, and time are concerned with delignification, cellulose recovery/ yield, sugar yield, and characterisation study. The scope of the characterisation study are listed as follows: structural and morphological, degree of crystallinity, functional group, and thermal stability.

Other than that, one journal will be selected as a reference for building the optimisation model. The response surface contour plots and any relevant information from the developed model are used to analyse the interaction between the parameters and thus further validate the findings. All possible aspects that may affect the results should be considered and included in the development of the model regardless of the complexity, leading to a good validation of the results obtained. However, there are always uncertainties and

various assumptions throughout the modelling process, depending on the biomass used, pretreatment conditions, and other limitations. Therefore, this may restrict and limit the reliability of the developed model, leading to uncertain predictions of results.

1.6 Contribution of Study

The outcome of this research assists the experts in the sustainable energy field to adopt suitable types of solvents and catalysts along with relevant operating conditions to ensure highly efficient organosolv pretreatment on OPEFB. This research also serves as the key transformation to green growth, ensuring a better prospectives of lifestyle while conserving our Mother Earth.

1.7 Outlines of Report

In Chapter 1, the general introduction has provided the background of primary energy and also seeks the potential of OPEFB as a biorefinery feedstock. Also, various pretreatment methods are briefly introduced as well. Chapter 2 has further revealed the chemical composition of OPEFB. This chapter has mainly highlighted the organosolv pretreatment. The impacts of the selected pretreatment parameters against pretreatment efficiency and characterisation have been discussed, not limiting to their interaction. Besides, the in-depth procedures of this research are explained in Chapter 3, including the review and extraction of information from various related journals, articles, and e-books. It is also provided the steps for the preparation and building of the optimisation model. Other than that, Chapter 4 has summarized and discussed numerous studies in response to the effects of the selected parameters on organosolv pretreatment efficiency and OPEFB's characterisation. Response Surface Methodology (RSM) developed from the built model has generated the analysis of parameters' interactions and thus further validate with the supported journal. Throughout this study, the main findings associated with the objectives met are pointed out in Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1   OPEFB as Lignocellulosic Biomass

Lignocellulosic biomass (LCB) is a highly renewable, abundant, and economical natural resource. A major portion of the global biomass refers to as LCB, of which about 64 % can be obtained from non-tree plant species (Das, Das and Dash, 2020). In this context, oil palm empty fruit bunch (OPEFB) with natural renewability is studied. Its abundance of biomass generated from the palm oil extraction mill process is usually being disposed of as waste.

Malaysia has always been the world's most important palm oil manufacturer, with a production volume of 19.52 million metric tons achieved by 2018. Besides, there is a strong development in oil palm plantation and palm oil industries, through various government associations that can be classified into FELDA, RISDA, and FELCRA, while not limiting to private estates such as IOI plantations, Sime Darby, Guthrie, and Genting Plantations. In the year 2014, the total oil palm plantation area reached 5.39 million hectares and 62 % of which came from private estates. Figure 2.1 presents the ownership of the oil palm plantation in Malaysia (Faizi, et al., 2016).
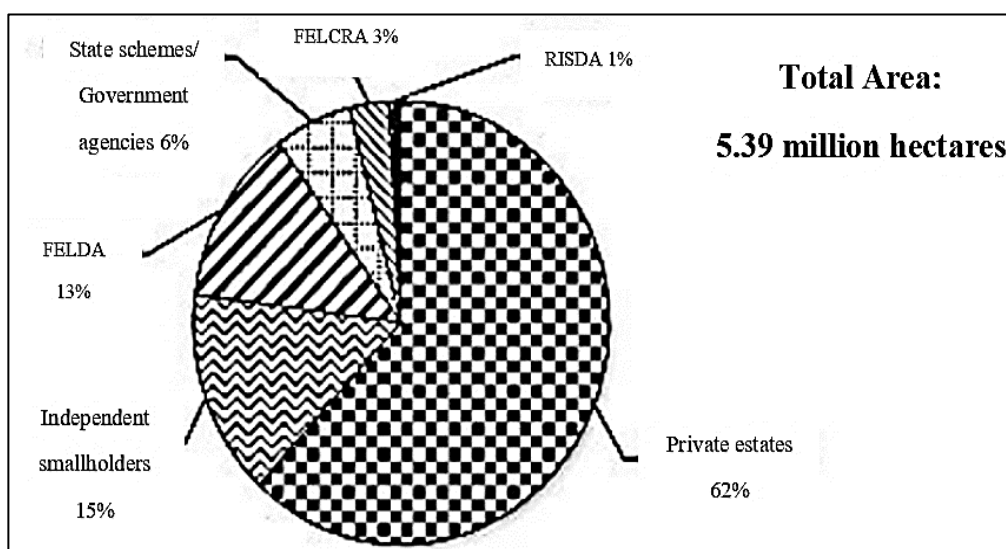
Figure 2.1: Oil Palm Plantation Ownership in Malaysia (Faizi, et al., 2016).

Among excessive waste generated during the mill processing of palm oil, OPEFB has the highest weight percentage, accounting for 20-23 % of fresh fruit bunches (FFB). In Malaysia, the amount of OPEFB can reach about 16 million tons annually, which is a typical massive waste. Furthermore, OPEFB is generally restricted to downstream use (boiler fuel), and conversion to fertilizer through incineration is discouraged. Hence, it is eventually dumped under an open environment, leading to negative environmental impacts including airborne pollution from the decomposition of OPEFB, disease spreading, and odour emission. Water pollution may also be due to the infiltration of the remaining remnant oil into the soil and groundwater. The simple breakdown part of FFB is shown in Figure 2.2 below.
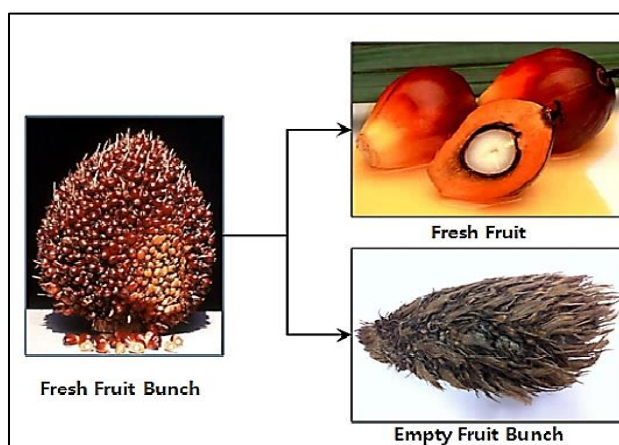
Figure 2.2: The Breakdowns of Fresh Fruit Bunch.

The abundance, environmentally friendly, and inexpensive perspectives of OPEFB, along with its high carbohydrate content (glucan, xylan, arabinan) of about 57.9 %, all together make it a vast potential biorefineries feedstock. Moreover, OPEFB does not compromise food security due to its non-edible properties (Rahayu, Wirjodirdjo and Hadi, 2019). Biofuels derived from OPEFB have carbon-neutral properties and it promotes sulphur-free biorefineries as well, which solve the problem of environmental pollution. OPEFB is a fairly strong and tough natural fibre with a lignin composition of about 35 %, taking into account the strong resistance to degradation. However, its lignin content, structure, morphology, and crystallinity can be altered with

the aid of pretreatment process thus given a greater access to cellulose content and provide a higher sugar conversion rate in biofuel production.

2.2 Component Structure of Lignocellulosic Biomass

All lignocellulosic biomass (LCB) generally consists of three primary biopolymers, which are cellulose $(C_6H_{10}O_5)_m$, hemicellulose $(C_5H_8O_4)_n$, and lignin $(C_9H_{10}O_3 (OCH_3)_{0.9-1.7})_o$ [lignin-C $(C_{15}H_{14}O_4)_w$; lignin-H $(C_{22}H_{28}O_9)_x$; lignin-O $(C_{20}H_{22}O_{10})_y$] (Shirkavand, et al., 2016). These biopolymers are directly formed by the photosynthesis of plants and mainly present in plant cell walls (Chen, 2015). Based on the type of biomass, they are arranged in complex, non-uniform 3D structures to varying degrees (Isikgor and Becer, 2015). Besides, they have been highly sealed, meshed with each other, and chemically bonded through covalent and noncovalent crosslinks. This results in a rigid and inflexible hetero-matrix that contributes to the recalcitrance properties of LCB. Moreover, LCB is also composed of other minor constituents including proteins, extractive acids, tannins, and secondary metabolites (Zhang, et al., 2019). Figure 2.3 illustrates the overall structure of plant cell walls and the distribution of biopolymers (Mathews, Pawlak and Grunden, 2015).
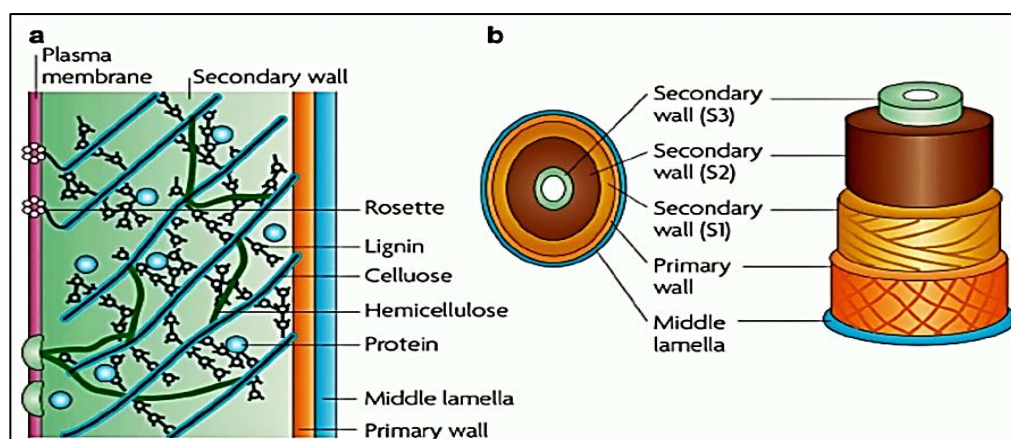
Figure 2.3: (a) Distribution of Lignocellulosic Components in Plant Cell Wall (b) Structural Organization of Cell Wall (Mathews, Pawlak and Grunden, 2015).

2.2.1 Cellulose Structure

Cellulose is considered to be the most abundant and main polysaccharide component in lignocellulosic biomass. It is composed of β-D-glucopyranosyl

units (glucose monomers). They are called linear homopolymers that link together by β- (1,4) -glycosidic bonds, forming disaccharide cellobiose. This cellobiose is referred to as the building block and repeating unit in the cellulose chain. Besides, each repeating unit contains three hydroxyl groups, which have different acidity and reactivity in the cellulose chain. The primary hydroxyl groups are located at the C-6 positions, and the secondary hydroxyl groups are located at the C-2 and C-3 positions.

Moreover, cellulose is composed of elongated rod-shaped crystalline microfibre bundles that are associated with ordered crystalline regions and disordered amorphous regions along their length. These regions are tightly bound by a wide network of intra- and intermolecular hydrogen bonds, which form highly crystalline and strong cellulose microfibres that are resistant to biodegradation. Furthermore, the average degree of polymerization (number of glucose units) of cellulose reaches at least 9,000 to 10,000. Meanwhile, it may reach up to 15,000, thus contributing to its high molecular weight. Due to the hydroxyl (-OH) surface, hydrophilic cellulose microfibres can form hydrogen bonds with water. However, it can often be solvable in solutions with very low or high pH concentrations (Baruah, et al., 2018). Figure 2.4 depicts a schematic diagram of the cellulose structure.
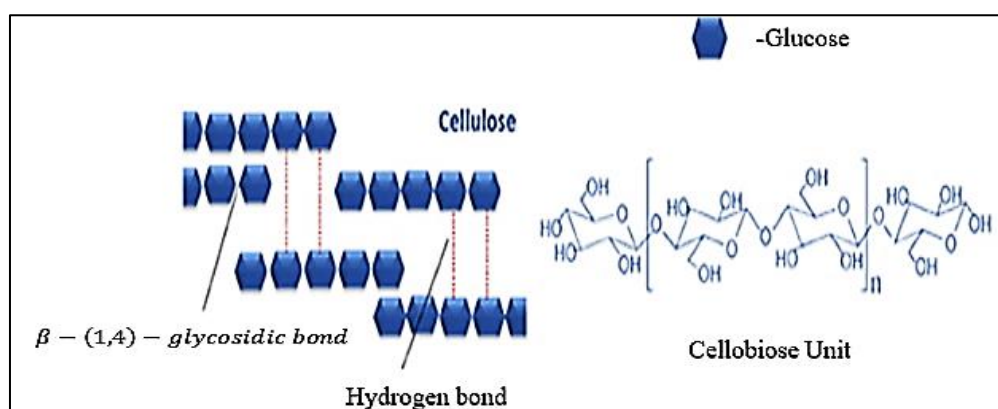
Figure 2.4: Schematic Chemical Structure of Cellulose Component in Plant Cell Wall (Baruah, et al., 2018).

2.2.2 Hemicellulose Structure

Hemicellulose is the second largest proportion of polysaccharides present in the primary and secondary plant cell walls of lignocellulosic biomass. Similar to

cellulose, it is composed of sugars and is considered a heteropolysaccharide due to the variety of sugars it contains (Pecha and Garcia-Perez, 2015). Its random and amorphous structure is considered to be complex, such that it is mainly composed of the following short-chain polysaccharides: pentose (β-d-xylose, α-1-arabinose), hexose (β-d -glucose, β- α-l-rhamnose, α-l-fucose, d-mannose, α-d-galactose), and Glycolytic acid (α-d-4-O-methyl-glucose acid, α-d-glucose fermentation acid, α-d-galacturonic acid).

Besides, there are complex bond networks in the hemicellulose chain, such that the connection between monosaccharide groups by β-(1,4)- or β-(1,3)-glycosidic bonds, along with lignin cross-linkage. Van der Waals force is associated with the oxygen-hydrogen bond connection, which plays a positive role in its close connection with cellulose (Chen, 2015). Moreover, the content of xylan in hardwood hemicellulose is high, while softwood hemicellulose is mainly composed of glucomannan, galactoglucomannan, and arabinoxylan (Shirkavand, et al., 2016). Hemicellulose chains can be multi-branched instead of straight chains (Pecha and Garcia-Perez, 2015). Generally, the degree of polymerization of hemicellulose is lower than that of cellulose, about 100 to 200 on average. This fact leads to its naturally low molecular weight. Due to its high solubility and non-crystalline nature, it is more susceptible to chemical degradation than cellulose (Bajpai, 2018). A schematic diagram of the structure of hemicellulose is presented in Figure 2.5.
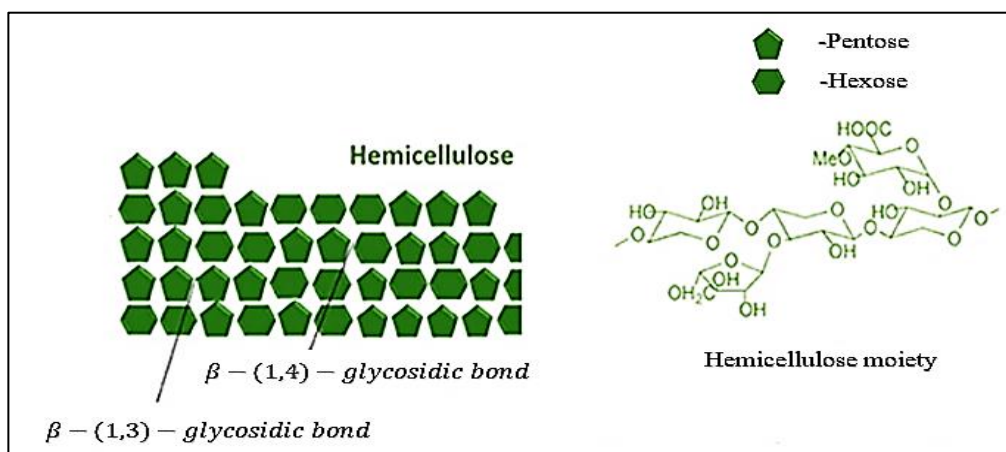
Figure 2.5: Schematic Chemical Structure of Hemicellulose Component in Plant Cell Wall (Baruah, et al., 2018).

2.2.3 Lignin Structure

Lignin is an amorphous and extensively branched phenolic polymer with high molecular weight and insolubility. Compared with cellulose and hemicellulose, it has the lowest composition in LCB. It is a hetero-polymer consist of three main phenylpropanoid monomers, which are p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units. The monomer units vary in the methoxylation degree of the aromatic ring at the three different positions, including ortho-, meta- and para-positions. Besides, these monomer units can be derived from respective aromatic alcohol precursors, called monolignols, including p-coumarin, coniferyl, and sinapyl alcohol (Welker, et al., 2015). Relatively few ferulic acid and coumaric acid units also can be identified in lignin.

Three monolignols randomly aggregate in a highly cross-linked three-dimensional structure. They have different ratios between angiosperms and gymnosperms, depend on the plant sources as well. Furthermore, gymnosperms (softwood) compose of major G units in lignin, while both G and S units have existed in dicotyledonous angiosperms (hardwoods). Monocotyledonous consist of overall H, G, and S units. Also, there are various types of carbon-carbon bonds (C-C bonds: 5–5, β-β) and aryl-ether bonds (C-O-C bond: β-O-4, α-O-4) between these non-fermentable phenylpropane units (H, G, S units). These connecting networks give lignin high rigidity and can act as a protective sealant for cellulose and hemicellulose. (Lu, et al., 2017). The advantages of these bonds and several hydroxyl groups promote cross-linking with other polymers, such as polysaccharides (cellulose, hemicellulose) and proteins (Moore, 2011). Figure 2.6 shows a schematic diagram of the structure of lignin.
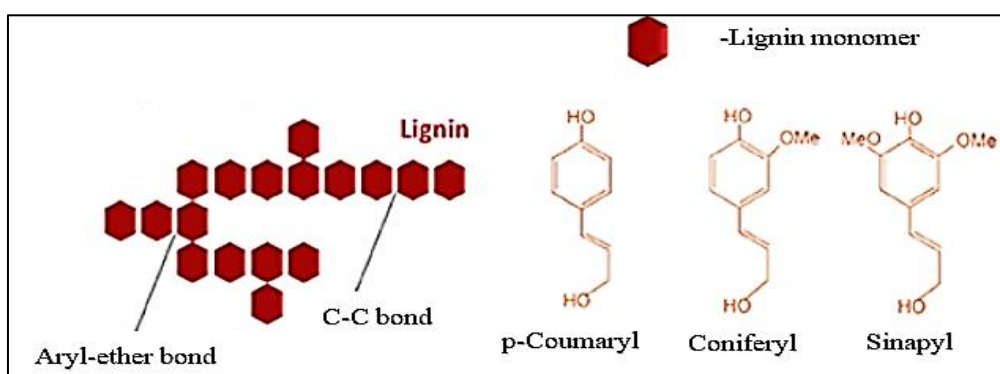
Figure 2.6: Schematic Chemical Structure of Lignin Component in Plant Cell Wall (Baruah, et al., 2018).

2.2.4   Summary

Among the significant constituents, the content and distribution of lignin with hydrophobic properties are the main factors that cause physical obstruction. The highly crystalline cellulose structure is embedded in a highly lignified heterogeneous and complex polymers matrix (Guerriero, et al., 2015). This barrier poses difficulties in surface penetration for carbohydrate polymer (holocellulosic fragments) that can convert into sugar for biofuel production.

2.3   Chemical Composition of Lignocellulosic Biomass

Generally, the chemical composition range of the three main biopolymers in lignocellulosic biomass (LCB) can be subdivided on a dry basis: 40 - 60 wt% cellulose, 20 - 40 wt% hemicellulose, and 10 - 25 wt% lignin. However, these constituents can vary according to LCB type, species, genetic variability, source (hardwood, softwood, or grass), and environmental conditions. Other influencing factors may be the harvest period, the method used, and the storage conditions (Welker, et al., 2015). The composition range of OPEFB is listed as follows: 37.3 – 46.5 wt% cellulose, 25.3 – 33.8 wt% hemicellulose, and 27.6 – 32.5 wt% lignin. The remaining percentage is composed of other minor components including protein and organic acids (Sudiyani, et al., 2013).

Rosli, et al. (2017) has studied that the principal components of structural carbohydrates (cellulose and hemicellulose) in natural OPEFB are accounted for about 57.9 %, which can subdivide into 34.6 % glucan, 20.3 % xylan, and 3.1 % arabinan. The structural component of lignin is about 35 %, including acid-soluble and acid-insoluble lignin. The remaining 0.4 % is composed of non-structural components (ash and extract). Besides, the moisture content in natural OPEFB is estimated to be 9.51 %. Table 2.1 lists the chemical composition of all structural and non-structural components in natural OPEFB.

Table 2.1: Chemical Composition of Native Oil Palm Empty Fruit Bunch (Rosli, et al., 2017).

Constituents	Composition of Native OPEFB (%)
1. Structural Constituent	
Carbohydrates	57.9 ±2.46
Glucan	34.6 ±2.39
Xylan	20.3 ±0.05
Arabinan	3.10 ±0.02
Total Lignin	35.0 ±2.18
Acid Insoluble Lignin	28.00±1.94
Acid Soluble Lignin	7.07±0.74
2. Non-Structural Constituent	
Ash	0.40 ±0.01
Total Extractives	NR (Not Relevant)
3. Moisture Content	9.51±1.46
Total Composition	102.81

2.4 Overview Pretreatment to Lignocellulosic Biomass

Preliminary treatment is necessary to improve the digestibility of the lignocellulose composite structure by removing lignin. Pretreatment can dissolve lignin and hemicellulose fragments, thereby reducing the crystallinity and polymerization degree of cellulose. The surface area and porosity of the biomass will also increase. The changed characteristics allow an increase in the rate and extent of the subsequent enzymatic hydrolysis process, leading to better sugar recovery (Tsabitah, Omar and Ismail, 2014).

Besides, pretreatment methods can be categorized into physical (grinding, milling), biological (fungi and bacteria), chemical (acid, alkaline, ionic liquids, and organosolv), and physicochemical (AFEX, steam explosion, liquid hot water) (Baruah, et al., 2018). Different pretreatment methods provide their peculiar capabilities in biomass degradation. The preference for a convenient pretreatment process depends on the type of biomass with diversified chemical compositions (Dahadha, et al., 2017). Furthermore, all

pretreatment methods can achieve the removal of lignin and the recovery of carbohydrates as soluble sugars. However, chemical pretreatment has proven to be the most reliable, effective, and cost-effective method. It does allow the deconstruction of lignocellulosic biomass with low pretreatment intensity. By combining several pretreatment methods to form multi-stage pretreatment, delignification and pretreatment yield can be further improved.

2.4.1 Physical Pretreatment

Physical pretreatment highlights the particle size reduction, and it is environmentally friendly in terms of less poison generation (Shirkavand, et al., 2016). However, compared to softwood, it is less efficient and requires high energy to process hardwood (Rajendran, et al., 2017). As studied by Ariffin, et al. (2008), there is no significant sugar increase in the physical pretreated OPEFB fibres (1 – 2 mm). The increased sugar yield of 0.15 g/L may due to the strong lignin content that further limits the enzymatic attack during fermentation.

2.4.2 Biological Pretreatment

Biological pretreatment is an environmentally friendly technology, it requires low energy consumption and does not promote the formation of inhibitors. Generally, cells or enzymes from plants, soil, and agricultural waste (such as white rot fungi) are used in two extracellular enzyme systems: the hydrolysis system and the lignin decomposition system. The former system functions to degrade cellulose and hemicellulose. The latter is used for lignin depolymerization (Wagner, et al., 2018). The most significant drawback is that the enzyme used can be expensive, and its long pretreatment duration is undesirable for industrial-scale operations. As described in the study by Arbaain, et al. (2019), biological pretreatment without adding nutrients to the unwashed OPEFB achieved the maximum delignification and sugar yield of 53.8 % and 230.4 mg/g, respectively, within 14 days.

2.4.3 Physicochemical Pretreatment

2.4.3.1 Steam Explosion

Steam explosion treats the biomass under high-pressure saturated steam and high operating temperature. The method uses the principle of rapid pressure release, which causes the biomass to explode into split fibres. Besides, this method has provided benefits in terms of high energy efficiency, no recycling expenses, fewer chemicals used, as well as low environmental effects (Pielhop, et al., 2016). However, the formation of inhibitors will occur under extreme steam explosion conditions (Vivekanand, et al., 2013). Medina, et al. (2016) showed in their research that the glucan content of OPEFB treated under steam explosion increased by 34.69 %, and the hemicellulose removal rate reached 68.12 %. A higher enzymatic digestibility to 33 % has attained and given 4.2 g/L of glucose yield.

2.4.3.2 Ammonia Fibre Explosion

Ammonia Fibre Explosion (AFEX) applies a similar principle as steam explosion, but it involves liquid ammonia. This pretreatment method can be optimised by diversifying the parameters related to temperature, blowdown pressure, ammonia, and water load (El-Ahmady, Deraz and Khalil, 2014). Moreover, the disadvantage is its high preference for processing biomass with low lignin content. The applied ammonia has high volatility which leads to adverse environmental impacts and it requires high operating costs as well. Ling and Hassan (2013) studied the pretreatment of empty fruit bundle fibre (EFBF) with ammonia water in a reflux system and by soaking, thus found that a better amount of xylose and glucose at about 242.91 mg/g and 320.49 mg/g were generated.

2.4.3.3 Liquid Hot Water

Exceptions are made for liquid hot water (LWH) compared to steam explosion and AFEX, such as the use of water in treatment instead of steam, and does not require rapid pressure release. It is performed under controlled pH conditions to avoid the formation of inhibitors and sugar degradation (Li, et al., 2014). Furthermore, no catalysts and chemicals are required, and the formation of

toxicity is negligible. Although the water solvents used are abundant and cheap, it still consumes a lot of energy when processing large amounts of water. In a previous study, Risanto, et al. (2018) found that LHW pretreatment produced lower reducing sugars of 11.86 g /100 g biomass, compared to acid pretreatment.

2.4.4 Chemical Pretreatment

2.4.4.1 Alkaline

Various alkaline reagents (NaOH, KOH, Ca(OH)2, NH4) can be used for alkaline pretreatment. It has been found that sodium hydroxide (NaOH) is the most effective alkaline pretreatment solvent (Kim, Lee and Kim, 2016). However, there are some limitations such that this method is preferably used for pretreatment against low lignin biomass content. As studied by Duangwang and Sangwichien (2012), alkaline pretreatment with sodium hydroxide on OPEFB under optimal conditions achieved a maximum cellulose value of 68.8% and a high glucose yield of 19.96 g/L.

2.4.4.2 Acid

Acid pretreatment can be used with organic and inorganic acids, including sulphuric acid, phosphoric acid, and formic acid. A high sugar conversion rate can achieve in a concentrated acid pretreatment. However, this method can lead to several drawbacks, including the generation of undesirable inhibitory compounds (furfural, phenolic acid, and aldehyde), which may cause toxicity (Jönsson and Martín, 2016). Due to the high toxicity and corrosiveness of the concentrated acid used, this may require high operating and maintenance costs. In short, dilute acid is preferable for pretreatment owing to its cheaper value while also environmentally friendly (Zheng, et al., 2014; Kumar and Sharma, 2017). A study by Risanto, et al. (2018) revealed that the highest reducing sugar obtained in sulphuric acid pretreatment on OPEFB was 50.48 g/100 g biomass.

2.4.4.3 Ionic Liquid

The cations and anions in the ionic liquid pretreatment are mainly used to break the intramolecular and intermolecular hydrogen bonds in cellulose (Yoo, Pu and Ragauskas, 2017). Most ionic liquids are considered green solvents because they are non-volatile, non-toxic, recyclable, reusable, negligible vapor pressure,

thermal stable, and high chemical stability. Significantly, the nature of ions can adjust based on the ionic liquid's properties (Chen, et al., 2017). Yet, major drawbacks can refer to the high cost of ionic liquid, not limiting their toxicity against microorganisms and enzymes. An ionic liquid pretreatment with triethylamine hydrogen sulphate [TEA][HSO4] under the research of Nurdin, et al. (2020) pointed out that the delignification rate was about 80%. In addition to the above-mentioned pretreatment methods, organosolv pretreatment has been emphasized as a promising chemical pretreatment method that will be studied in depth for this research.

2.5   Mechanism for Organosolv Pretreatment

Organosolv pretreatment is a promising technique that employs a wide range of organic solvents or aqueous solutions including ethanol, methanol, organic acid, ethylene glycol, glycerol, and acetone. These organic solvents can easily recover through the distillation process and recycled for second applications. They will help break the internal bond between hemicellulose and lignin, leading to the delignification and solubilization of hemicellulose. As a result, the pore volume and surface area of cellulose will increase, thereby improve the accessibility of enzymatic hydrolysis and saccharification of the cellulose fraction, with almost no degradation (Zhang, Pei and Wang, 2016). Other than that, the addition of catalysts including mineral acid [sulphuric acid], alkaline [sodium hydroxide], and salt can lower the pretreatment temperature or significantly increase the lignin removal rate (Borand and Karaosmanoğlu, 2018). According to the chemical process of organosolv pretreatment, the reaction mechanism involved can be listed as below:

(1) Solvolysis (rate-limiting step) involved the breakup of the ether linkages of α and β-aryl from lignin and the disruption of 4-O-methyl glucuronic acid ester bonds from lignin-hemicellulose compounds.

(2) Cleavage of β-glycosidic bonds in both hemicellulose and cellulose, based on the process conditions.

(3) Acid-catalysed degradation of monosaccharides into 5-hydroxymethyl furfural and furfural.

(4) Condensation reactions between reactive aldehydes and lignin.

Moreover, the α-aryl ether bond is easily hydrolysed and is almost easily broken under acidic conditions. On the contrary, β-aryl ether bonds have higher hydrolytic cleavage resistance and stability, thus its preference to be broken down is subjected under highly acidic conditions. The cleavage of these ether linkages is crucial for lignin degradation. Furthermore, the addition of acid catalysts during the pretreatment process will not have much impact on these mechanisms (Chin, et al., 2020). In short, the aforementioned mechanisms are crucial for the aromatics and polysaccharides of lignocellulose to be broken down. The following solvation and solubilization of lignin fragments will involve the extraction of lignin into a solvent and form a final liquid mixture (Borand and Karaosmanoğlu, 2018).

2.5.1   Organosolv Pretreatment Among Peer

Organosolv pretreatment has higher dominance over the other pretreatment methods, owing to its good isolation of lignin as a solid material and carbohydrate as syrup. In addition to the high cellulose recovery rate for biofuel production, it also can extract almost unaltered and qualified organosolv lignin as an economic co-product, which can be used for coating and construction application (Wei Kit Chin, et al., 2020). In other words, lacking efficiency in other pretreatment methods for lignin recovery and purity has contributed to undesired lignin by-products. Besides, organosolv pretreatment consumes lesser water, energy, and reagent thus reducing the capital cost. Since this pretreatment is sulphur-free, the impact on the environment is much lower.

In terms of drawbacks, the solvent recovery and recycling process in organosolv pretreatment can be energy-intensive. However, they are necessary to compromise the high cost of organic solvents. Due to the high flammability and volatility of organic solvents that can cause fire and explosion hazards, the entire pretreatment requires extensive and strict control conditions (Borand and Karaosmanoğlu, 2018). Furthermore, pretreated solids require a complex washing procedure, which involves a primary organic solvent washing and subsequent water washing. This washing can prevent the dissolved lignin from precipitation (Zhao, Cheng and Liu, 2009).

2.5.2   Types of Solvents for Organosolv Pretreatment

A variety of prominent solvents can be applied in organosolv pretreatment, including low or high boiling point alcohols, organic acids, ketones, and other solvents. In this context, it may not be necessary to add a catalyst because the organic acids released from the biomass itself will also destroy the lignin-carbohydrate complex (Zhao, Cheng, and Liu, 2009). However, this is optional because the catalyst addition can enhance delignification and xylan degradation.

2.5.2.1   Low Boiling Point (LBP) Alcohol

LBP alcohols such as ethanol and methanol are easy to recover due to the close difference in boiling point with water. Besides, they can reduce pulping liquor's viscosity, while allowing for the rapid diffusion and penetration of chemicals into the biomass structure. Besides, delignification rate and glucose recovery yield are significantly improved under mild pretreatment conditions, with or without catalyst, as follows: concentration (50 – 60 wt%), ratio of solvent to water (1 -3 wt%), high reaction temperature (170 – 220 °C), and short residence time (30 – 120 minutes). Due to the high volatility of the solvent, higher operating pressure is required to ensure the solvent keeps in a liquid state for effective pretreatment (Wei Kit Chin, et al., 2020). The high-pressure condition may cause higher safety risks as well as higher capital costs.

2.5.2.2   High Boiling Point (HBP) Alcohol

HBP alcohols including ethylene glycol and glycerol are usually hindered for industrial application due to their high cost. Unlike LBP alcohols, they can be applied at atmospheric pressure and allow low energy consumption at higher operating temperatures. Moreover, glycerol is mostly used for pretreatment as it is non-toxic, readily available, completely recyclable, and reusable. Regarding the optimum pretreatment conditions, a higher solvent to water ratio is required during pretreatment compared to LBP alcohols. However, an extreme solvent concentration of 90 wt% will restrict the delignification performance, owing to its high viscosity limit the dispersion of particles. Due to the low Hildebrand solubility δ value of HBP alcohols in lignin, high delignification efficiency is usually unattainable (Wei Kit Chin, et al., 2020). Hence, HBP alcohols could provide greater efficiency for the recovery of glucose yield than lignin yield.

Also, catalysts will be required for a better cleavage rate of lignin structure. Furthermore, higher temperature and longer residence time are preferred but may vary based on the HBP alcohols used and the pressure conditions.

2.5.2.3 Organic Acid

Acetic acid and formic acid are the most commonly used organic acids for the pretreatment, while their similar δ value with lignin has allowed for efficient delignification. Generally, the solvent concentration exceeds 60 wt%, high temperature (135-200°C), and short duration (30-120 minutes) can achieve the best organic acid pretreatment. With the aid of acid catalysts, lower temperatures below 110°C can achieve acceptable delignification. Other than that, the main obstacle of this pretreatment is that cellulose will react with the solvent to acetylate or formylate. This will cause the inhibitory effect of cellulose on enzymatic interactions, resulting in a lower enzymatic digestion yield corresponding to a lower ethanol yield. Nevertheless, alkaline post-pretreatment with CaO or Ca(OH)$_2$ can tackle this problem by removing acetyl groups from the biomass pulp, thereby ensuring that the digestibility of cellulose is well restored (Chen, et al., 2015).

2.5.2.4 Ketone

Acetone is a well-known ketone that can be used in organosolv pretreatment, with or without a catalyst. It has a similar δ value to lignin, given a good solubility for lignin, thus high efficiency in delignification and enzyme digestibility. Besides, it allows the precipitation of amorphous-based cellulose and hemicellulose, followed by the separation of solid saccharides from the solvent. Moreover, acetone pretreatment can provide a high yield of xylose, negligible side reactions with sugars and lignin, and less furfural formation. Although acetone is found to be costly, it is more efficacious in treating hardwood lignin than softwood lignin that consists of stronger 5-5' linkages. However, this pretreatment is disadvantageous under atmospheric pressure. The optimum pretreatment efficiency can be achieved with lower solvent concentration, high operating pressure, high temperature (140 – 180 °C), and a shorter pulping time (30 – 120 mins) (Wei Kit Chin, et al., 2020). In addition to

the common solvents mentioned above, other pretreatment solvents can be phenol, dioxane, ethylenediamine, and N-methyl morpholine-N-oxide.

2.5.3   Catalysed Organosolv Pretreatment

Park, et al. (2010) conducted a comparative study for the pretreatment with solvent control and catalyst control. For solvent control, higher digestibility can achieve under more stringent pretreatment conditions. Unless the catalyst concentration is higher, else the digestibility of catalyst control is low compared to solvent control. However, neither of the two independent controls can achieve as effectively as the organosolv method. This fact highlights the importance of synergies between solvents and catalysts to the pretreatment efficiency.

Acid and base catalysts function to enhance the rate and extent of hemicellulose hydrolysis and the break down of lignin-lignin bonds (α-aryl and β-aryl ether linkages). Generally, sulphuric acid, hydrochloric acid, and phosphoric acid are favorable mineral acids against organic acid (formic acid, acetic acid, oxalic acid) in organosolv pretreatment (Zhao, Cheng and Liu, 2009; Sun and Cheng, 2002). From the research by Mardawati, et al. (2018), sulphuric acid is the most likely acid catalyst used in the pretreatment due to its high efficiency and strong reactivity in cleaving the lignin-carbohydrate and lignin-lignin bonds. Due to its toxicity and corrosiveness, additional safety facilities are needed to monitor these issues, leading to high equipment costs. Other than that, sodium hydroxide is a strong base with strong solubility and can be used for pretreatment. Higher loading of it is required for effectual delignification, compared to acid catalysts. However, the base catalyst will cause the problem of salt generation in the reactor.

Martin, et al. (2011) has studied the impact of the catalyst type (acid, base, no catalyst) on glycerol organosolv pretreatment. Sulphuric acid: H_2SO_4 providing a greater lignin yield, but a lower cellulose recovery than sodium hydroxide: NaOH or no catalyst. A similar result is justified with the study conducted by Park, et al. (2010), in which H_2SO_4 used for ethanol organosolv pretreatment was more efficacious towards higher lignin yield compared to NaOH, but lower in carbohydrate yield. Whereas, NaOH has high digestibility but a low solid recovery rate. Compared with NaOH which requires higher energy consumption, H_2SO_4 is more favorable for organosolv pretreatment.

2.6 Pretreatment Factors

The organosolv pretreatment efficiency may be affected by the following factors: the types of solvents and catalysts used, concentrations, reaction temperatures, and residence times. These parameters form a complex interaction with each other upon the organosolv pretreatment, which makes them an interesting attempt to be analysed by various studies and researches.

2.6.1 Effect of Organic Solvent Type and Concentration

The effects of ethanol concentrations (35 %, 55 %, 75 %) on the total sugar yield obtained in organic solvent pretreatment were studied by Nurfahmi, et al. (2016), as shown in Figure 2.7. It was figured out that the sugar yield prone to be increased with 35% and 55% ethanol concentration. A higher ethanol concentration will enhance the ether chain cleavage of hemicellulose and lignin molecules. Hence, there is more conversion of cellulose and hemicellulose contents into sugar. However, the sugar conversion showed a noticeable decrement at 75 % vol ethanol concentration. A heavy concentration higher than 60 % vol caused inhibitory effects and led to polysaccharides decomposition.
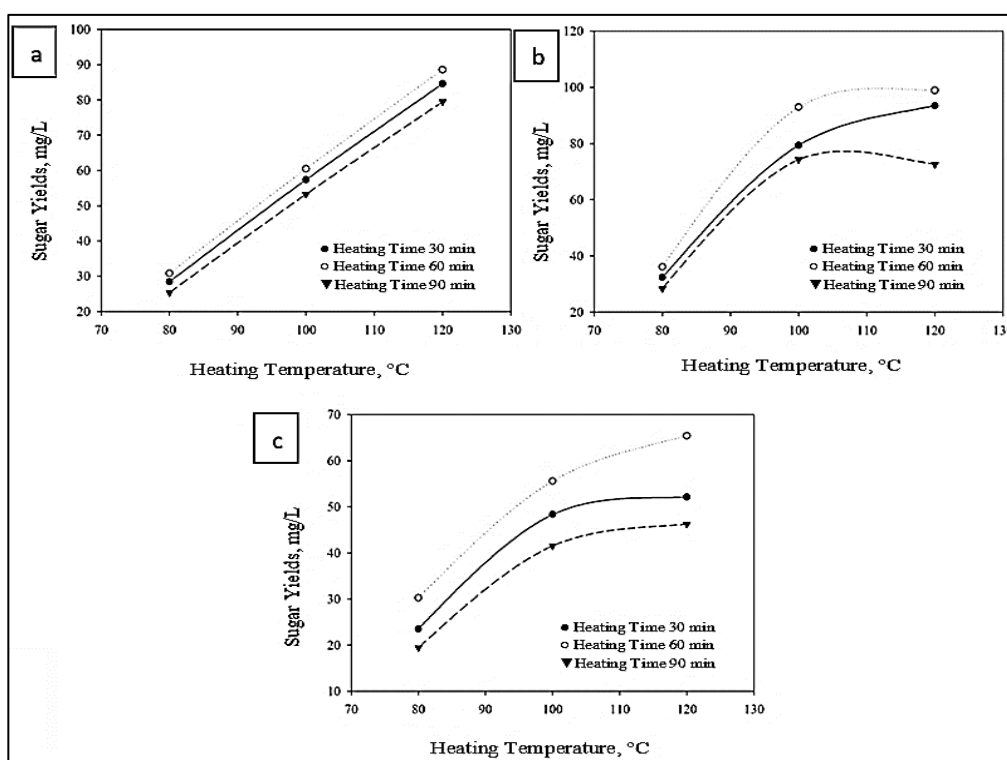
Figure 2.7: Effect of (a) 35% vol (b) 55% vol (c) 75% vol Ethanol Concentration on Sugar Yield (Nurfahmi, et al., 2016).

Besides, Hidayati, Zuidar and Satyajaya (2017) studied the pretreatment effect of the ratio of acetic acid to formic acid. Higher concentrations of formic acid above 10% did not only dissolve lignin but also hydrolyse glycosidic bonds. The maximum pretreatment was achieved using a ratio of 85% acetic acid to 15% formic acid, resulting in the contents of 75 % cellulose, 7.78 % hemicellulose, and 1.61 % lignin. With the support of the research by Harahap, et al. (2020), compared with 5 % acetic acid pretreatment, a higher concentration of 15 % acetic acid pretreatment at 125°C for 60 minutes provided the optimum reducing sugar yield of 40%.

2.6.2   Effect of Catalyst Type and Concentration

The study by Mondylaksita, et al. (2020) revealed that ethanol organosolv pretreatment using acetic acid (32 w/w%) and sulphuric acid (0.13 w/w%) showed no significant difference in their effect against lignin purity and recovery, as shown in Figure 2.8. When the same concentration (0.13 w/w%) of sulphuric acid and acetic acid was used, sulphuric acid obtained the best pretreatment performance in which the purity and recovery of lignin were significantly higher at 68.25% and 48.00%, respectively.
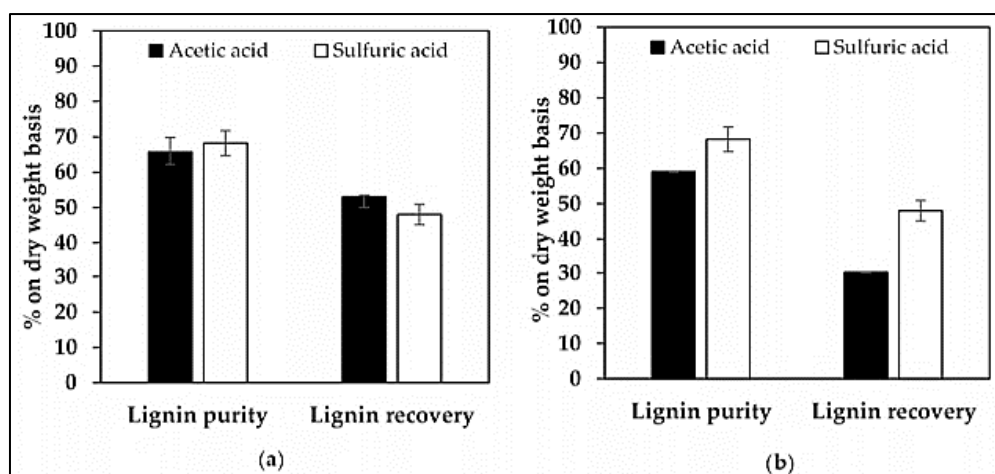
Figure 2.8: Effect of (a) Catalyst under Different Concentrations (b) Catalyst under Same Concentration (0.13 w/w%) (Mondylaksita, et al., 2020).

Ibrahim, et al. (2019) pointed out in their research that 0.2% NaOH catalysed pretreatment on EFB fibre has reduced the cellulose content of the fibre, while also decreased the hemicellulose and lignin content by 7% and 35%,

respectively. The hydroxide anion has cleaved the aryl-ether bond in the lignin, causing the lignin to fragment and dissolve, thereby a higher cellulose dissolution was achieved. Besides, this study also reported that the cellulose and lignin contents of pretreated fibres catalysed with acetic acid were reduced by 29% and 30%, respectively. This reduction showed higher efficiency of an acid catalyst in removing hemicellulose, while the removal of lignin was more effective by a base catalyst.

Other than that, Choopakar, et al. (2018) conducted a comparative study of the organosolv pretreatment with distilled water, waste glycerol, acidic glycerol, and alkaline glycerol. The results showed that hemicellulose content did not seem to improve under acidic glycerol pretreatment. A decrease in pH caused lignin precipitation, thereby limited the access of high holocellulose yield. The optimum pretreatment was achieved with alkaline glycerol under 5 % loading for 15 minutes, in which the holocellulose content was increased to 97.98 % whereas the lignin content was reduced to 9.17 %.

2.6.3 Effect of Reaction Temperature

The reaction temperature is considered to be the main parameter in organosolv pretreatment. According to the two similar studies reported by Meilany, Kresnowati and Setiadi (2018) and Meilany, et al. (2020), the rising temperature at 10% solid loading with 60 minutes' pretreatment process on OPEFB has caused an increase in glucose recovery. As shown in Figure 2.9, the maximum recovery of xylose was obtained at 165°C, whereas the maximum recovery of glucose has not yet been reached. When the temperature has exceeded 165°C, the xylose recovery rate was decreased significantly. This response proved that hemicellulose was more sensitive to heat than cellulose. In other words, hemicellulose is easy to degrade and solubilize under high temperatures. Generally, hemicellulose is allowed to maintain thermal stability between 180 °C and 340 °C, but it will be greatly degraded above 340 °C.
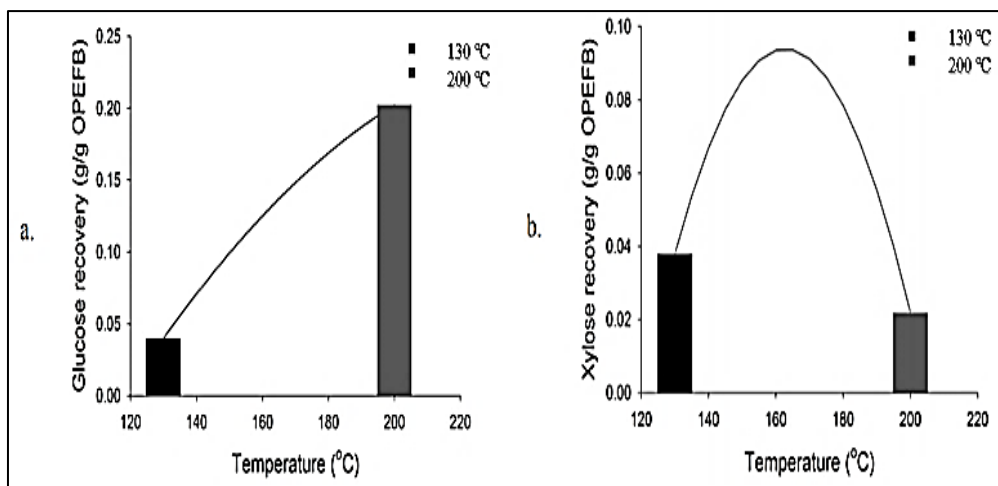
Figure 2.9: Temperature Effects on Sugar Recovery (a) Glucose (b) Xylose (Meilany, Kresnowati and Setiadi, 2018).

Furthermore, Mondylaksita, et al. (2020) investigated the influence of different temperatures (180 °C, 210 °C, 220 °C) on the organosolv pretreatment of OPEFB for 120 minutes. The rigid correlation between temperature and solubility of lignin is consistent. Based on Figure 2.10, a lower temperature caused a lower lignin recovery owing to insufficient pretreatment. When the temperature rose from 180 °C to 220 °C, the purity and recovery rate of lignin were significantly improved. A higher temperature has allowed a higher reaction rate for delignification. However, there was no further change above 220 °C, in which an excessively high temperature may cause the formation of inhibitory products that limit pretreatment efficiency.
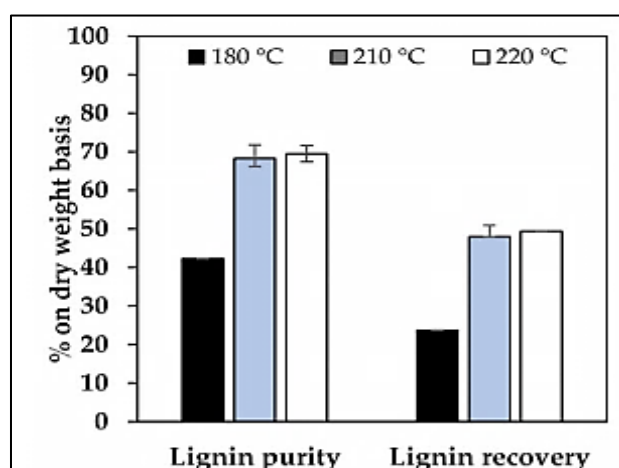
Figure 2.10: Effect of Temperature on Lignin Purity and Lignin Recovery for Organosolv Pretreatment (Mondylaksita, et al., 2020).

2.6.4   Effect of Residence Time

A study investigated by Nurfahmi, et al. (2016) showed the comparison of total sugar yields of ethanol pretreated OPEFB at different reaction times (30, 60, 90 minutes). It was found that 60 minutes and 90 minutes of reaction times obtained the highest and lowest total sugar yields, respectively. The intermediate to long pretreatment duration is likely to dissolve a portion of hemicellulose, as well as increase the solubility of lignin that allows a greater delignification rate.

Besides, Meilany, Kresnowati and Setiadi (2018) studied the pretreatment time effect on sugar recovery, along with solid content of 10% and a heating temperature of 130 °C. The results showed that a longer pretreatment time from 30 minutes to 60 minutes has caused a slight increase in sugar recovery. When the pretreatment time was further extended to 90 minutes, the xylose recovery rate became less obvious. The prolonged pretreatment time will lead to the formation of furfural and pseudo-lignin (insoluble lignin resulted from hemicellulose decomposition). This potentially reduces the delignification and solubilization of biomass, thus resulting in reduced sugar recovery. According to Figure 2.11, time has a greater impact on glucose recovery than xylose recovery, owing to the steeper slope obtained. By referring to Figure 2.11 and Figure 2.9, it can be acknowledged that time has a smaller impact on the glucose and xylose recoveries compared to the temperature which showed more significant impacts.
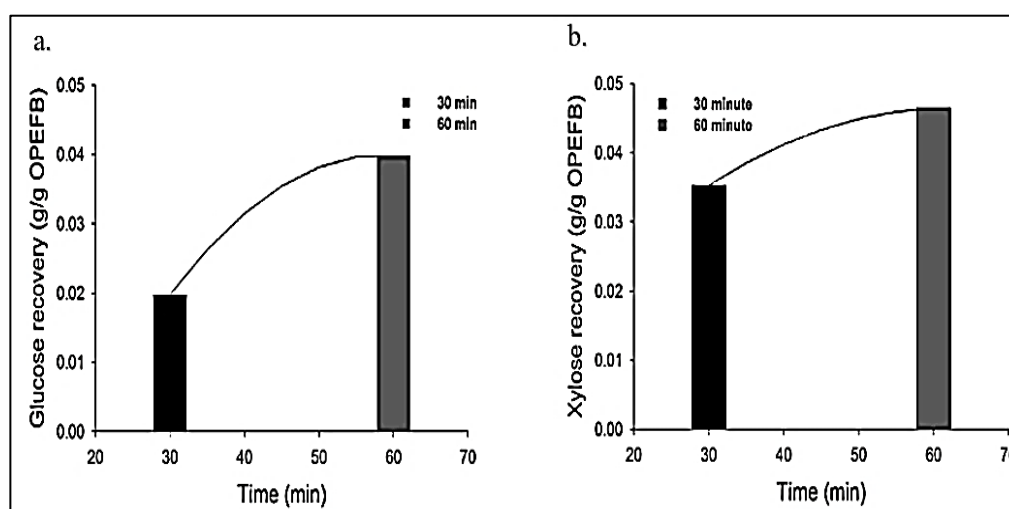
Figure 2.11: Pretreatment Time Effects on Sugar Recovery (a) Glucose (b) Xylose (Meilany, Kresnowati and Setiadi, 2018).

2.7   Characterisation Analysis

OPEFB will subject to chemical and physical changes after pretreatment. The organic solvents and chemical substances used in the pretreatment are the main factors causing these changes. Besides, the physical properties and surface morphology of pretreated fibres are studied using a scanning electron microscope (SEM). Further characterisation of the functional groups can be carried out by Fourier transmission infrared reflectance spectroscopy (FTIR). Furthermore, the crystallinity index of OPEFB fibre can be obtained by X-ray diffraction (XRD) analysis. Thermogravimetric analysis (TGA) is to determine the thermal stability of microcrystalline cellulose. In short, a comprehensive characterisation analysis of pretreated OPEFB can be performed via SEM, XRD, FTIR, and TGA.

2.7.1   Structural and Morphological Changes

The native OPEFB shows an unexposed area of rigid crystals embedded around by amorphous hemicellulose and lignin, together with solid circular elemental particles, as presented in Figure 2.12. There is a formation of a matrix layer or protective layer that covers the dense fibril surface and prevents water loss. Besides, OPEFB is composed of a thicker cell wall, which gives it a higher rigidity index and roughness. In addition to the irregular massive deposition of cellulose, hemicellulose, and lignin on the outer surface, OPEFB also contains a high constituent of inorganic elements, such as silica and metal ions (Na, Mg, K, Ca, Al). Numerous silica bodies are attached to the uniformly spread circular craters over the fibre strands' surface. Figure 2.13 (a) and (b) shows the SEM images of native OPEFB fibre at various magnifications (Rosli, et al., 2017).
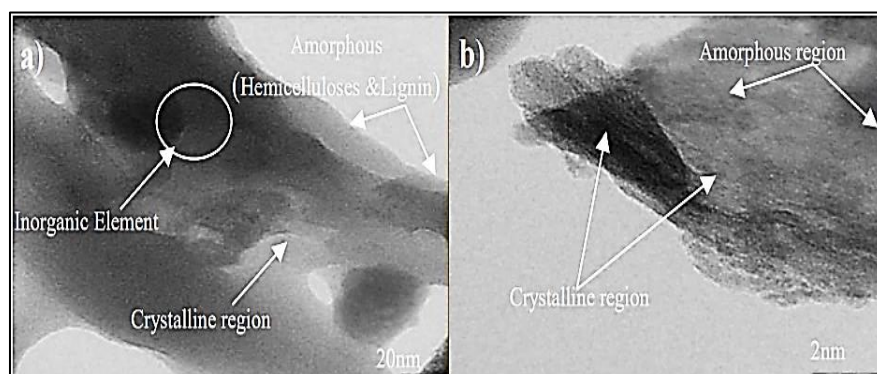
Figure 2.12: SEM Micrograph of Raw OPEFB (Rosli, et al., 2017).
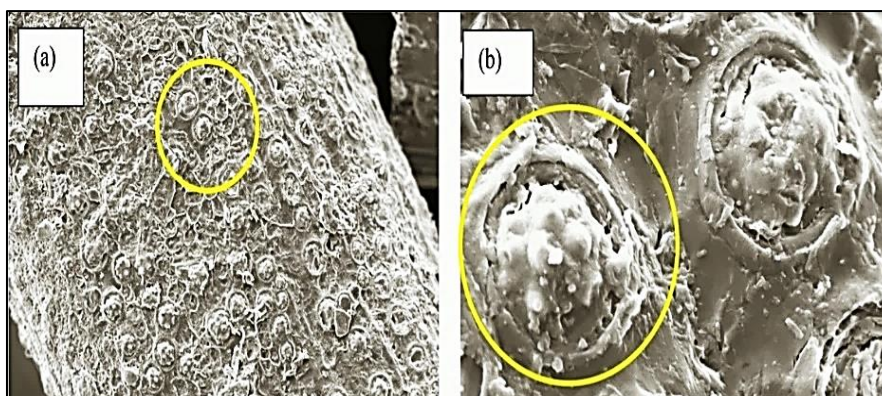
Figure 2.13: SEM Images (a) and (b) for The Surface Structure of Native OPEFB Fibre at Different Magnifications (200x; 2000 x) (Rosli, et al., 2017).

The surface morphology of OPEFB fibre will change greatly with the increase of pretreatment temperature. As shown in Figure 2.14 (a), there is a smooth, strong, and orderly structure in the untreated OPEFB fibres. Figure 2.14 (b) to (d) shows small cracks and pores on the fibre surface. Looking into Figure 2.14 (e), fibre breakage is more pronounced at pretreatment temperatures as high as 190°C. Figure 2.14 (f) illustrates that OPEFB fibres pretreated below 200°C will suffer extensive damage and destruction. To be sure, the increase in pretreatment temperature will significantly disrupt the fibre surface of OPEFB, resulting in higher structural accessibility and yielding more reducing sugars. (Solihat, et al., 2017).
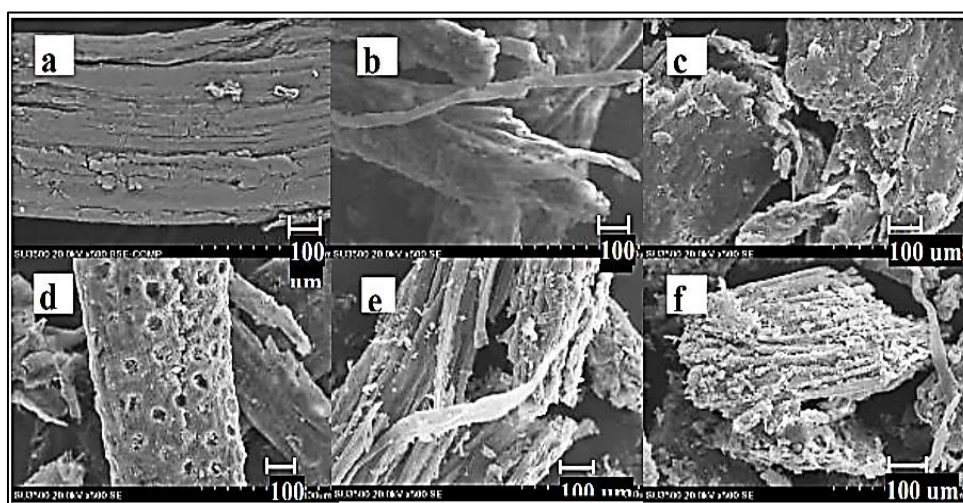
Figure 2.14: Morphology Changes in OPEFB Fibre Surface Under Different Pretreatment Temperature (a) Untreated (b) 160 °C (c) 170 °C (d) 180 °C (e) 190 °C (f) 200 °C (Solihat, et al., 2017).

Other than that, it is unlikely to recognize the circular-shaped silica bodies in the untreated OPEFB [Figure 2.15 (a)] and the treated OPEFB [Figure 2.15 (b)] at 160 °C. Figure 2.15 (c) and (d) show few voids with part of the silica bodies attached to the pretreated fibre at 170 °C and 180 °C. As presented in Figure 2.15 (e) and (f), higher temperatures of 190 and 200 °C will enhance the formation of huge cracks, leading to extensive removal of silica bodies from the fibre strand. In short, more porosity can be observed in the surface morphology of pretreated OPEFB compared to raw OPEFB (Solihat, et al., 2017).
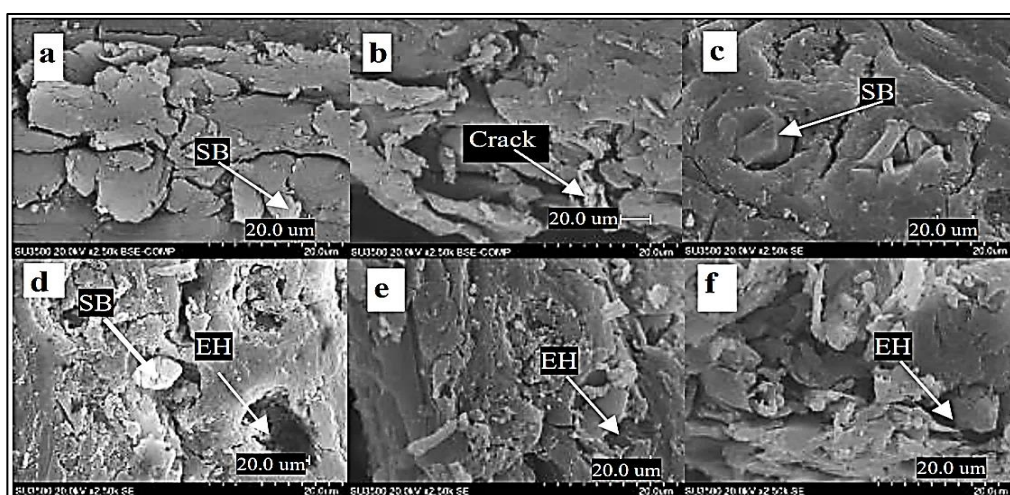
Figure 2.15: Morphology Changes of Silica Bodies Properties in OPEFB under Different Temperatures (a) Untreated (b) 160 °C (c) 170 °C (d) 180 °C (e) 190 °C (f) 200 °C (*SB: Silica Bodies *EH: Empty Holes) (Solihat, et al., 2017).

2.7.2   Changes in Crystallinity

Figure 2.16 illustrates the XRD analysis of native OPEFB fibres and powders (< 250 µm). Two primary peaks can be observed at $2\theta = 16$ and $2\theta = 22.5$, representing the peak I_{011} and I_{002}, respectively. Besides, peak I_{011} is related to hemicellulose and lignin base in the amorphous region, while the crystalline region of cellulose is represented by peak I_{002} (Nazir, et al., 2013). Rosli, et al. (2017) studied that the crystallinity of native OPEFB fibre and its powder samples was 40% and 37%, respectively. This result showed that smaller particle size has positively contributed to the reduction of the crystallinity index.
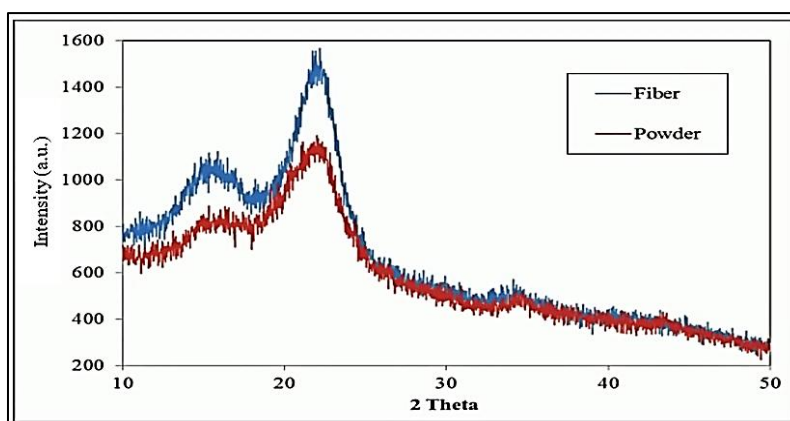
Figure 2.16: XRD of Native OPEFB Fibre and Powder (Rosli, et al., 2017).

Furthermore, the total crystallinity index (TCI) value can be calculated to determine the effect of organosolv pretreatment on the degree of crystallinity in OPEFB. Figure 2.17 shows the glucan-rich spectrum with a higher absorption band and a lower absorption band at 897 cm^{-1} and 1428 cm^{-1} respectively. After pretreatment, amorphous cellulose will increase and crystalline cellulose will decrease, resulting in a higher digestibility of cellulose. Mondylaksita, et al. (2020) found that the crystallinity of pretreated OPEFB was reduced by 24.48% compared with the initial TCI value of 1.25 for untreated OPEFB.
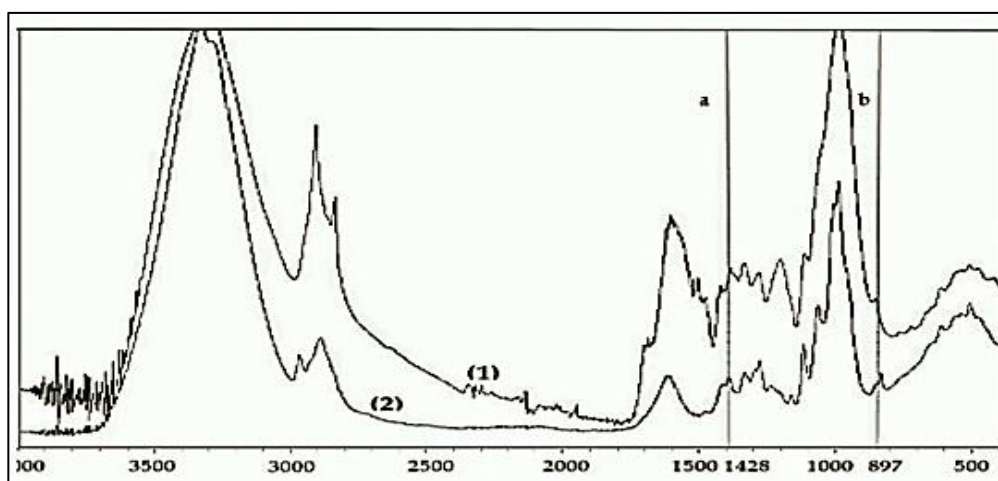
Figure 2.17: FTIR Spectra of (a) Untreated OPEFB (b) Glucan-rich Fraction under Optimum Organosolv Pretreatment (Mondylaksita, et al., 2020).

2.7.3 Functional Group Changes

The functional groups in raw OPEFB can be identified with the FTIR spectrum obtained from FTIR spectroscopy, as shown in Figure 2.18. Strong and broad

absorption is observed at the wavenumber of 3355 cm^{-1}, which indicates the hydrogen-bonded (O-H) stretching within the hydroxyl group of cellulose (Khalil, et al., 2001). Besides, the significant wavenumber of 2900 cm^{-1} indicates the C-H stretch of methylene (CH$_2$) from the hydroxymethyl (CH$_2$-OH) group in cellulose (Xiao, et al., 2014). Moreover, various functional groups also lead to the formation of many sharp and well-defined absorption bands, which are located within the fingerprint spectra region (1800 – 600 cm^{-1}). Table 2.2 summarizes the wavenumber and characterisation in the spectra of raw OPEFB.

According to FTIR analysis, pretreatment does not lead to the generation of new functional groups. Instead, there are only changes in the position of bands and their intensity. Compared with the untreated fibre, the pretreated OPEFB fibre showed a slight band rise at 3300 cm^{-1} (O-H stretching) and 2921cm^{-1} (CH$_2$ stretching). Other than that, the O-H stretch zone of cellulose is said to have a wavenumber of 3000 to 3600 cm^{-1}. The decrease of absorption band peak in the region of 2854 cm^{-1} indicates a rupture portion in methyl and methylene of cellulose, leading to a higher cellulose loss in pretreated fibre. Moreover, there is a reduction of intensity at wavenumber 1732 cm^{-1} (C=O ester bond between xylan and lignin), due to a decrease in hemicellulose content and subsequent hydrolysis of xylan. The destruction of the ester bond between cellulose and lignin causes the pretreated fibre to have a stronger band at 1317 cm^{-1}, thus allowing more exposition of cellulose (Solihat, et al., 2017).
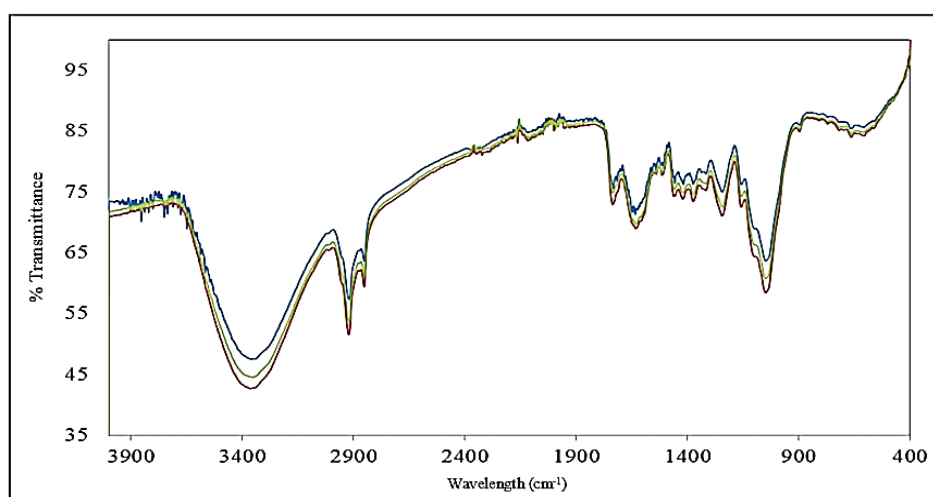
Figure 2.18: FTIR spectra of OPEFB (Rosli, et al., 2017).

Table 2.2: Characterisation of FTIR Wavenumber in Native OPEFB (Rosli, et al., 2017).

Wavenumber (cm^{-1})	Compound
3355	O-H stretching in cellulose
2850 – 2920	C-H and CH$_2$ stretching in cellulose and hemicellulose
1733	C=O stretching in unconjugated ketone, ester, and carbonyl groups
1635	O-H bending in cellulose
1541	C=C stretching from lignin aromatic ring
1375	C-H bending in cellulose and hemicellulose
1244	C-O-C bonding of aryl-alkyl ether
1049	Aromatic C-H in-plane deformation (O-deformation in primary alcohol)
667	C-O out of plane bending mode

2.7.4 Thermal Stability Changes

Thermogravimetric analysis (TGA) is used to explore the thermal stability of OPEFB. The TGA of raw OPEFB shows a water loss of about 10% at the temperature of 110 °C. Besides, the degradation of hemicelluloses, pectin, and wax occurs at a low temperature of 150 to 230 °C. There will be significant changes after 230 °C, owing to the degradation of cellulose. Cellulose degradation will stabilize at 350 °C, followed by the slow decomposition of the lignin phase. Generally, OPEFB-cellulose has thermal stability of 325 °C and two thermal degradation phases are identified as follows: water losses below 200 °C and cellulose chain depolymerization in the temperature range of 200 °C to 390 °C. Moreover, there are no decomposition phases of hemicelluloses and lignin above the following temperature: 180 °C and 390 °C respectively. For native OPEFB, the formation of ash and the accumulation of char has contributed to more or less 25% of residual mass at 700 °C (Johar, Ahmad and Dufresne, 2012; Fahma, et al., 2010; Jahan, et al., 2010).

2.8 Optimisation Modelling

Mardawati, et al. (2018) optimised the pretreatment of OPEFB with the aid of Response Surface Methodology (RSM) along with Box-Behnken Design

(BBD). In this context, the optimal degradation rate of lignin was achieved at 27.68% with 65% ethanol pretreatment for 65 minutes. The model's validity with the experimental result was up to 86.55%. According to Figure 2.19, as the ethanol concentration and response time increased, the degradation rate of lignin was higher. A higher concentration can provide a greater potential for delignification. Besides, sufficient reaction time is essential for processing OPEFB fibre structures that are resistant to organic solvents and thermal erosion. However, large particle size will not cause significant lignin degradation, owing to its small porosity that restricts the access of ethanol to degrade lignin.
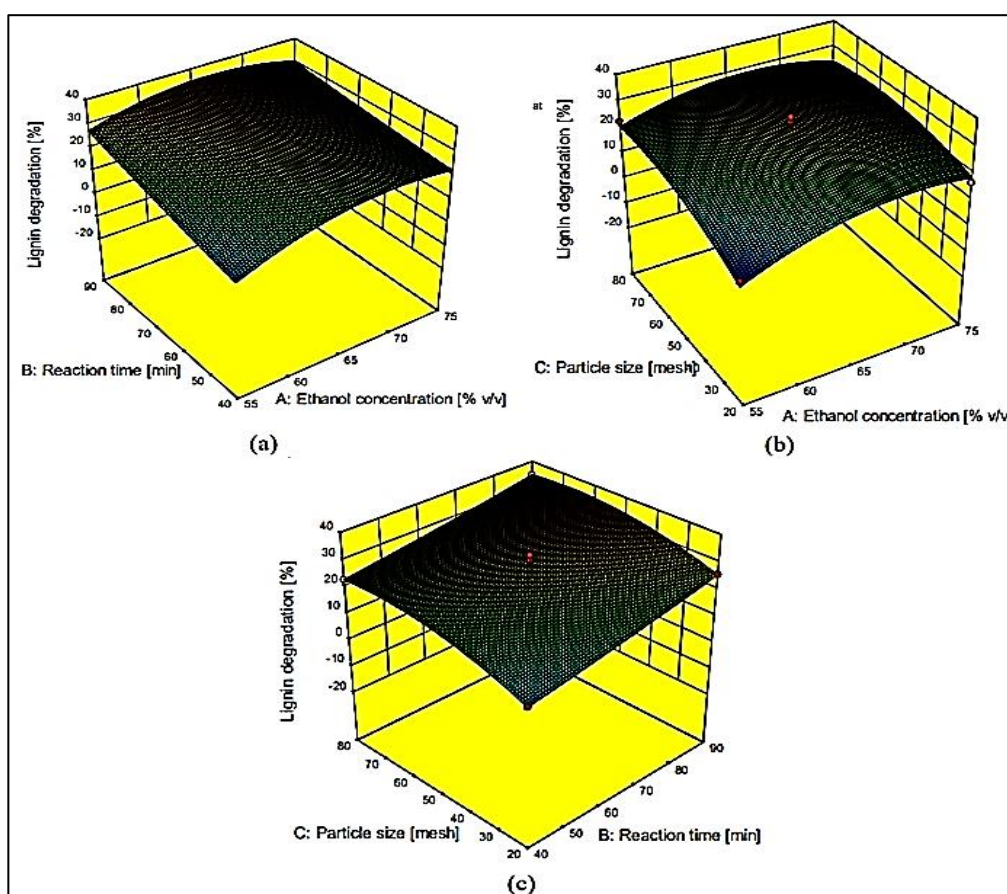
Figure 2.19: Response Surface Plots of Parameters' effects on Lignin Degradation (Mardawati, et al.,2018).

Goh, et al. (2011) in their study revealed the interaction effect of sulphuric acid (SA) concentration, temperature, and residence time through 3D response surface plots shown in Figure 2.20. At low temperatures (160°C), an increase in SA concentration was very significant, highlighting an increase in

sugar yield from 0% to 100%. However, SA was rapidly decomposed at a high temperature above 180 °C, thus adversely impact the sugar yield. Besides, a relatively short reaction time and dilute acid medium did not effectively dissolve lignin and hemicellulose. As a result, the accessibility of cellulose was limited and led to a lower glucose recovery.

With a longer reaction time under concentrated acid pretreatment, the biomass surface and glucose components may be destroyed and decomposed. Lignin is also recondensed thus leading to the reduction of pulp's digestibility. Moreover, a special finding where a higher glucose yield was attained under low reaction time and temperature, or high reaction time and temperature. For the pretreatment time shorter than 90 minutes, there was a complete dissolution of hemicellulose and a higher digestibility extent towards complete digestion. The change in SA concentration has a steeper slope compared with the change in temperature and time, indicating its dominant effect on glucose recovery.
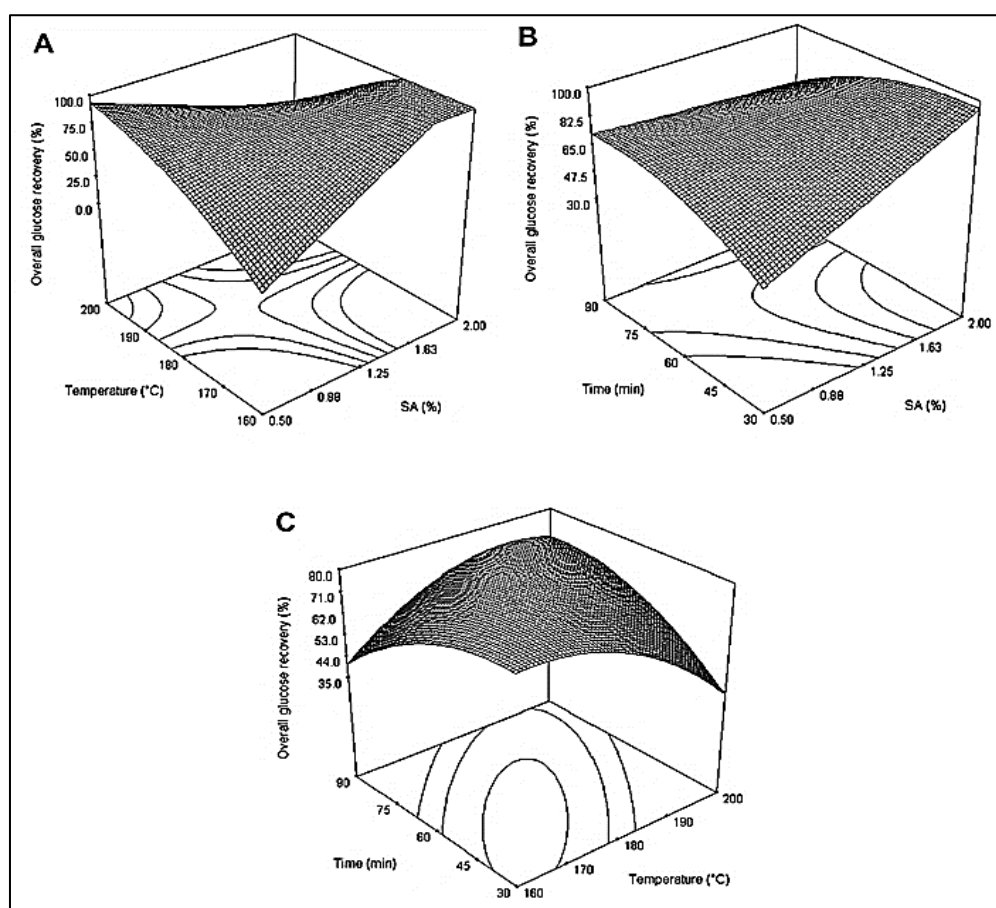
Figure 2.20: Response Surface Plots of Parameters' Effects on Glucose Recovery (Goh, et al., 2011).

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Overview of Research Methodology

Figure 3.1 shows a flow chart that presents the overall procedures of the research.
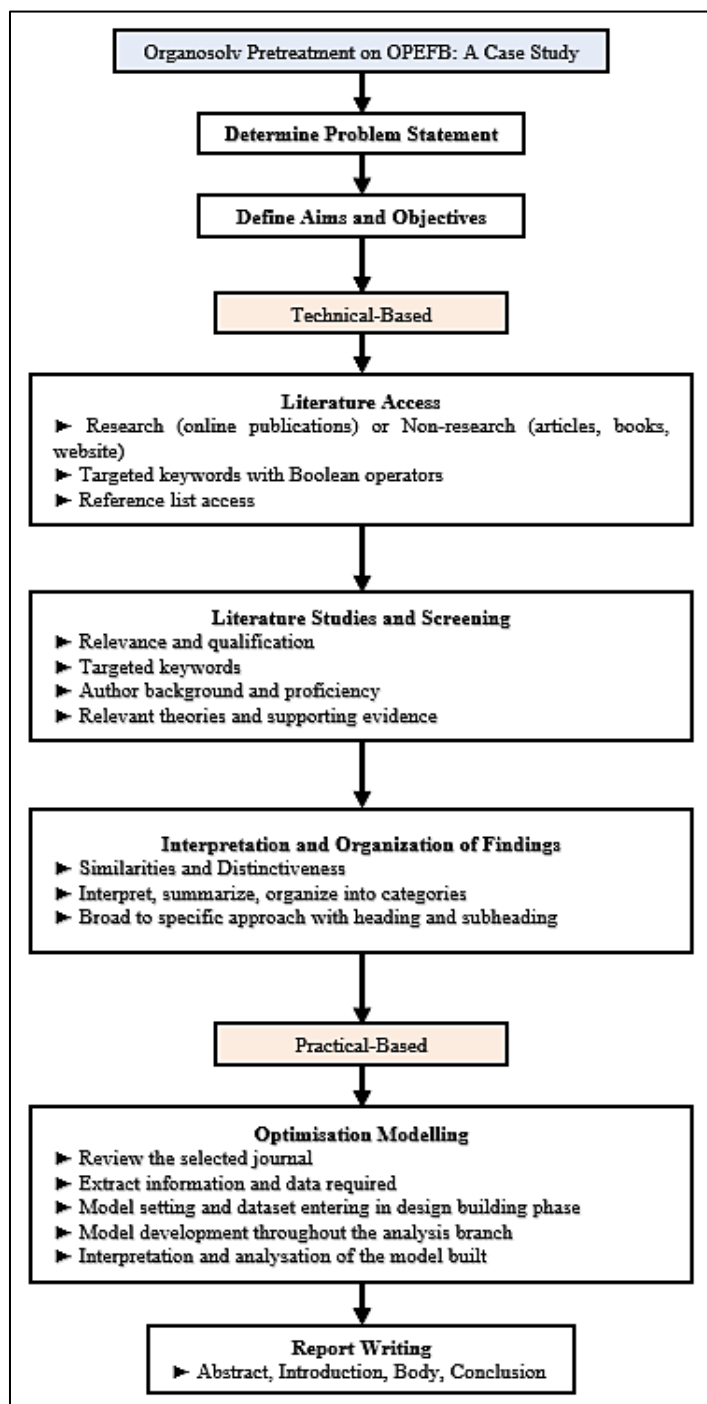
Figure 3.1: Flow Chart of Case Study.

3.2 Determine Problem Statement, Aims, and Objectives of the Study

There are several unsolved and existing problems in the field studied. Besides, there are many proposed solutions from various studies, but no consensus has been reached on the best solution (Dr. Irfan, 2017). These problems may also be recent issues that are lacking or not fully researched in the field of interest. It is worth noting that the extensive discovery of these problems reveals the aims and objectives of the research. In this context, the importance of research has also been addressed. The identified problem statements associate with the respective objectives will assist the author to have bigger and clearer pictures for the entire research's flow and direction, especially the scope of literature involved. Besides, a discussion was carried out with the project supervisor at the beginning of the research. The background of the research title was explained, along with supported journals that emphasize two terms: Organosolv pretreatment and OPEFB. Also, it then discussed several defined issues and listed the potential objectives of the study. Moreover, the scope was limited to a specific topic to ensure a comprehensive study through the problem statement identified in Chapter 1.3 and the goals and objectives stated in Chapter 1.4.

3.3 Literatures Access

Two main types of literature were accessed, either research or nonresearch. The former will be academic publications, while the latter can refer to news articles, books, reports, websites, etc. Various online publication resources, journals, and articles related to the organosolv pretreatment on OPEFB were openly accessible for further comparative research. It is vital to assure all the information obtained from reliable sources and thus provide high quality and high validation of study. The keywords including 'Organosolv pretreatment', 'OPEFB', 'cellulose recovery', 'delignification', 'modelling', and more were applied for targeted database searching. In fact, synonyms or related terms, spelling changes, and common names were also being accessed thoroughly to obtain potential information. Boolean operators including 'and', 'or', 'not' were used to further refine the results and improve the relevance of information obtained. Therefore, the search time can be reduced, and it is also possible to significantly avoid searching for irrelevant journals (Reynolds and Dippenaar,

2018). Other than that, the reference list provided in various journals and articles was discovered for more accession to papers in the field of interest.

3.4 Literatures Studies and Screening

There are more than 80 journals and articles that have been studied thoroughly. According to research needs, certain parts were very important for in-depth reading (Dr. Irfan, 2017). Besides, it is essential to screen research papers based on the degree of relevance and qualifications of the research, so a comprehensive analysis can be provided. This was attained by initially focus on the significant keywords mentioned in Section 3.3, followed by reading the research abstract. Moreover, the author's background and proficiency in their studies also help in the selection of high-quality papers. It is noteworthy to ensure accurate problem statements, aims and objectives, applicable materials and methods, results and discussion with relevant theories, and last but not least, assumptions and arguments based on supporting evidence. Furthermore, the author must also be wary of being underpredicted or overlooked the goals and objectives of the research. According to the above screening guidelines, less relevant papers were excluded. Then, the findings of the selected journals and articles were evaluated in-depth and all applicable information was collected.

3.5 Interpretation and Organization of Findings

Generally, this step has covered the findings and information extracted from the research papers studied. These findings can cause controversy and are associated with influential theories and judgments. In addition to the analysis of researchers' work related to others or so-called similarities, it is prominent to seek the distinctiveness between researchers' approaches and ideas (Dr. Irfan, 2017). This information was interpreted, summarized, and further organized into their respective categories for comparative studies. For instance, multiple theories from various research papers were grouped according to the theoretical framework. This grouping can provide a great overview of the significant approaches towards the concept delivered. Moreover, a broad-to-specific approach was applied along with the establishment of new headings and subheadings. A general issue was delivered in the heading and then narrowed down to increasingly specific issues for the defined problem and thesis

statement in the subheadings (Doheny, 2021). Thereby, the background and facets of the topic were developed and thus outlined the research's framework.

3.6   Optimisation Modelling of Organosolv Pretreatment on OPEFB

A Central Composite Design (CCD) generally deals with a higher number of experiments and more levels, as well as considering the points outside the minimum and maximum range. Thereby, CCD was being highlighted as the suitable model to study for the organosolv pretreatment on OPEFB (Zare, 2021). Besides, Central Composite Design (CCD) and Response Surface Methodology (RSM) using combined mathematical and statistical techniques to design experiments, build models and evaluate the effects of factors, hence further searching the optimum conditions of factors for desired responses. The following paragraphs present the detailed procedures and specifications for optimisation modelling.

A study by Goh, et al. (2011) was selected to be reviewed due to its good compatibility of the research field with this project, particularly the process parameters studied. The experimental matrix to optimise organosolv pretreatment on OPEFB was statistically designed by RSM coupled with CCD using Design-Expert Software Version 10.0.3 (Stat Ease, USA). Based on the preliminary one factor-at-a-time (OFAT) experiments, process factors such as concentration, temperature, and time were identified to have significant effects on responses, thereby being selected for building the model. Three factors CCD was applied with 6 replications of the center point, generating a total number of 20 experimental runs and developing a quadratic model with a five-level design.

Moreover, the studied range for the three chosen factors was set as follows: Sulphuric Acid Concentration (A) at 0.5 – 2.0 %, Reaction Temperature (B) at 160 – 200 °C, and Residence Time (C) at 30 - 90 min. Correspondingly, three numeric process factors' names with their units and prescribed High (+1) Low (-1) coded levels were initially keyed in, as shown in Figure 3.2. The two responses (EOL recovery and GLU recovery) were then set with their units, as presented in Figure 3.3.

Figure 3.2: Process Factors Setting with Unit and Level.

Figure 3.3: Responses Setting with Unit.

Finished the design-building phase, it was then viewing the design layout, where the values of actual response 1 and response 2 were then entered accordingly to the dataset provided in the reviewed journal. Moreover, the standard deviations of the EOL and GLU recovery after organosolv

pretreatment were obtained from six independent experiments (run 1, 3, 12, 15, 16, 17) performed under the same conditions. Figure 3.4 presents the CCD matrix for the experiment of 20 trials.

		Std	Run	Factor 1 A:SA Conce... %	Factor 2 B:Reaction T... °C	Factor 3 C:Residence... min	Response 1 EOL Recovery %	Response 2 GLU Recovery %
		17	1	1.25	180	60	26.3	77
		5	2	0.88	170	75	2.1	55.6
		15	3	1.25	180	60	26.3	77
		8	4	1.63	190	75	52	61.2
		7	5	0.88	190	75	18.7	87.2
		12	6	1.25	200	60	47.2	61.1
		6	7	1.63	170	75	47.8	81.1
		2	8	1.63	170	45	18.6	98.4
		3	9	0.88	190	45	24.5	66.3
		1	10	0.88	170	45	0	57.1
		14	11	1.25	180	90	37.8	65.4
		20	12	1.25	180	60	26.3	77
		9	13	0.5	180	60	0	57.9
		10	14	2	180	60	43.4	88.3
		19	15	1.25	180	60	26.3	77
		18	16	1.25	180	60	26.3	77
		16	17	1.25	180	60	26.3	77
		4	18	1.63	190	45	48.7	61.8
		13	19	1.25	180	30	9.7	71.4
		11	20	1.25	160	60	19.4	70.2

Figure 3.4: CCD Matrix of 20 Experimental Runs.

Under the Analysis branch, the default transformation selection of none has remained. Moving forward, there was a suggested model shown in the Fit Summary table and the program will default to the "Suggested" model for in-depth statistical study. The linear model for ethanol organosolv lignin (EOL) recovery can be ruled out from predicting response, due to its Prob > F falls below 0.05. Whereas, the linear model for glucose (GLU) recovery has a very low R^2 coefficient value, signifying a bad estimate of the response. Besides, the cubic model is aliased which would not be useful for modelling purposes, thus it should not be chosen.

On the other hand, the quadratic model usually comes out best with low "Std. Dev.", high "R-Squared", and low "PRESS" values compared to the two-factorial interaction (2FI) model. It is worth study greater synergistic effects

wherein a modified option was being chosen from the Process Order pull-down list. A manual reduction of the model via removing insignificant terms provided an improved model. Figure 3.5 shows the selected models and significant terms in the Model tab.
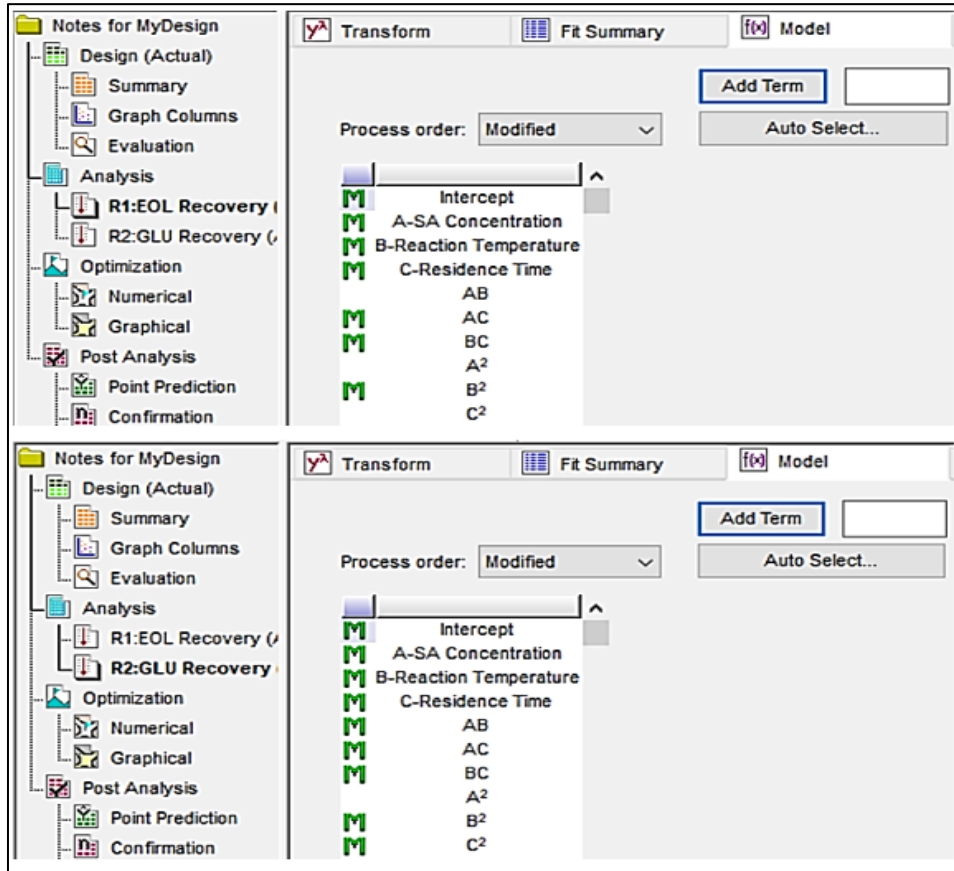
Figure 3.5: Selection of Model and Significant Terms.

A second-order polynomial regression model expressed by Equation 3.1 was fitted to correlate the relationship between the process variables and the experimental responses obtained, thus predicting the optimal point. The equation for three factors stated as Equation 3.2 was applied in this project.

$$Y = \beta_o + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum \sum_{i<j=1}^{n} \beta_{ij} x_i x_j \tag{3.1}$$

$$Y = \beta_o + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 \\ + \beta_{22} x_2^2 + \beta_{33} x_3^2 \tag{3.2}$$

Y is the predicted response, x_i and x_j are coded independent variables, whereas $\beta_o, \beta_i, \beta_{ii}, \beta_{ij}$ are the intercept, linear, quadratic, and interaction constant coefficients respectively. Apart from that, the statistical significance of the experimental model, coefficients, and residue were analysed using the analysis of variance (ANOVA). Response surfaces and contour plots were developed using the fitted quadratic polynomial equation obtained from regression analysis (Goh, et al., 2011). Through the response surfaces, contour plots, and any relevant information, the three organosolv pretreatment factors (A: SA Concentration, B: Reaction Temperature, C: Residence Time) were analysed for their correlation or interactive effects on the EOL and GLU recovery.

3.7   Report Writing

The outlined framework in the previous step will be utilized with the four elements to write the research report accordingly (Winsor, 2016):

(i)   Executive Summary/Abstract: A summarization section that provides the reader with the key facts and information of the entire research.

(ii) Introduction: A context of the research with the identified problem statement and objectives. It also provides an overview of the research scope, research methods, as well as structure outline.

(iii) Body: Headings and subheadings developed towards different approaches will involve respective analysis, discussion, and any relatable recommendations, associated with supported graphics or data.

(iv) Conclusion: The main findings met against the defined objectives in (i) were being summarised clearly and concisely. Any future actions and perspectives in the field of interest were discussed as well.

CHAPTER 4

RESULTS AND DISCUSSION

4.1   Effect of Different Solvents on Delignification, Cellulose Recovery/ Yield, Sugar Yield

Organosolv pretreatment is carried out using organic or aqueous solvents to dissolve and extract lignin, thereby providing more accessible cellulose. According to Figure 4.1, different types of solvents are usually used in organosolv pretreatment such as high or low boiling point alcohols, organic acids, and ketones. It is of interest, to figure out the inherent physical and chemical properties of different types of solvents that may affect the practicality and efficiency of organosolv pretreatment. Combining various studies and works of literature, parameters affecting delignification, cellulose recovery/yield, and sugar yield for different types of organosolv pretreatments were analysed.
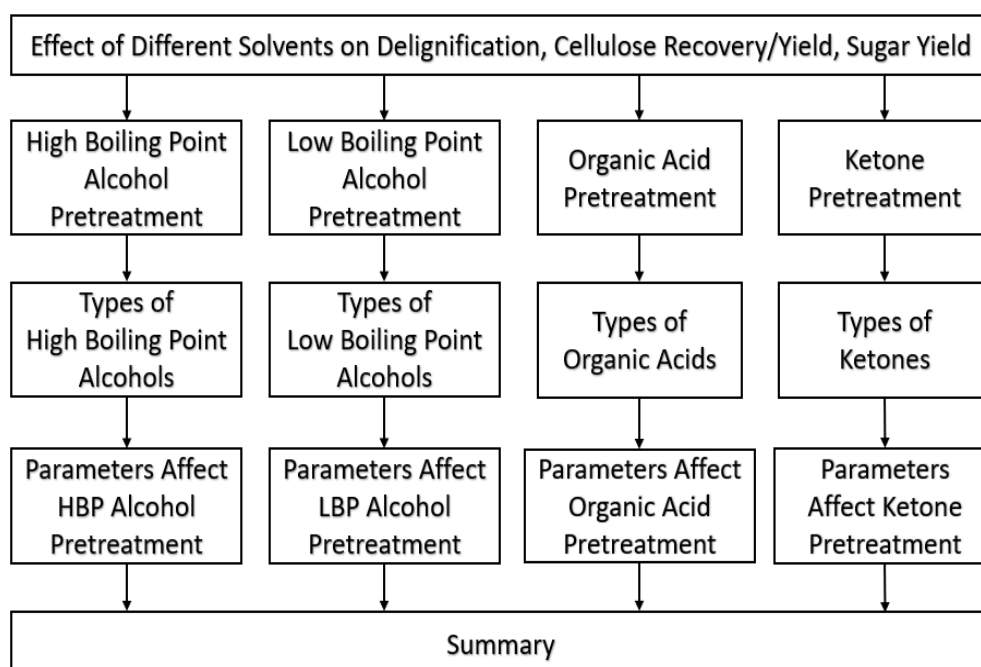
Figure 4.1: The Flowchart Outlines for Section 4.1.

Table 4.1 compares different types of organosolv pretreatments, whereas Table 4.2 compares different properties of common organic solvents used in pretreatment. Moreover, the effects of influential parameters such as concentration, temperature, and time on organosolv pretreatment and characterisation of pretreated OPEFB were discussed as well.

Table 4.1: Comparison Between Different Types of Organosolv Pretreatments.

Parameter	HBP Alcohol Pretreatment	LBP Alcohol Pretreatment	Organic Acid Pretreatment	Ketone Pretreatment
Reaction Yield	Moderate to High	Moderate to High	Low to Moderate	Moderate
Pretreatment Condition	High	Mild	Mild	Mild
Operational Cost	High	Moderate	High	Moderate
Energy Efficiency	Moderate	Low to Moderate	Low to Moderate	Moderate
Solvent Recovery	Easy	Moderate	Moderate	Moderate
Process Risk	Mild	Significant	Mild	Significant
Environmental Impact	Low	Low	Low	Low

Table 4.2: Properties, Green Solvent Rating, and Organosolv Pretreatment Efficiency of Different Types of Solvents.

Organic Solvent	Boiling Point [a] (°C)	Flash Point [a] (°C)	Hansen Parameter [a] (M Pa$^{1/2}$)				Green Solvent Rating [b]				Lignin Removal (LR)	Cellulose Recovery (CR)
			Total	δ_D	δ_P	δ_H	Environment	Health	Safety	Waste		
Ethylene glycol	197	111.1	32.9	17.0	11.0	26.0	8	7	10	5	Moderate	High
Glycerol	290	176	36.1	17.4	12.1	29.3	7	8	10	6	Moderate	High
Ethanol	78	13	26.5	15.8	8.8	19.4	8	8	6	3	Moderate	High
Methanol	65	11 - 12	29.6	15.1	12.3	22.3	9	5	5	4	Moderate	High
Acetic Acid	118	39	21.4	14.5	8.0	13.5	8	6	8	4	Moderate	Low
Formic Acid	101	69	24.9	14.3	11.9	16.6	8	4	7	4	High	Low
Acetone	56	-17.2	19.9	15.5	10.4	7.0	9	8	4	3	Moderate	Moderate

Score 1 (red: least green) to 10 (green: greenest)

Environment: Impacts of solvent on environment

Health: Potential exposure risk; Acute or chronic effects on human health

Safety: Explosion and flammability; Storage and handling of solvent

Waste: Recoverability and recyclability; Incineration; Wastewater treatment; Volatile Organic Compound (VOC)

[a] (Wei Kit Chin, et al., 2020)   [b] (Henderson, et al., 2011)

4.1.1 High Boiling Point Alcohol Pretreatment

HBP alcohol pretreatment poses an advantage of lower process risk compared to LBP alcohol pretreatment and ketone pretreatment. LBP alcohol and ketone have high volatility, which can lead to the possibility of combustion with ignition sources and cause high flammability hazards. Unlike other pretreatments that prefer high operating pressure conditions, HBP alcohol pretreatment can be efficiently performed under atmospheric pressure, thereby achieving high reaction yields with lower energy consumption. However, the energy efficiency may be limited by the solvent recovery system which may require higher energy to recover HBP alcohol.

4.1.1.1 Types of High Boiling Point Alcohols

Compared with other solvents, ethylene glycol and glycerol with high flash points are less volatile, so they have less flammability and explosive hazards, and therefore score the greenest in terms of safety. Theoretically, the Hildebrand solubility parameter (δ) is a numerical estimation indicator for the solubility interaction between materials. The δ value of isolated lignin (Klason lignin) is in the range between 22.5 to 24.5 $MPa^{1/2}$. Solvents close to this δ value range are easily miscible with lignin and cause the lignin to dissolve. Compared with glycerol, the δ value of ethylene glycol is closer to that of lignin, which indicates that ethylene glycol has more promising lignin solubility and extractability. This can be proven by Chin, et al. (2019) where higher lignin extraction (45.9 %) was obtained with 30 v/v% ethylene glycol pretreatment at 80 °C for 30 mins, compared to a low lignin removal of 28.65 % achieved with 30 v/v% glycerol pretreatment as reported by Ibrahim, Hassan and Badri (2012). However, using more stringent pretreatment conditions (85 °C, 7 hr) without adding catalyst for further research, the optimum delignification was achieved at 55.1 % with a lower glycerol concentration of 20 v/v%. This can be partly attributed to the higher hydrogen bonding parameter (δ_H) of glycerol which promotes higher lignin solubility.

On the other hand, HBP alcohols exhibit greater potential for higher cellulose yields than delignification. This finding is consistent with the views of Chin, et al. (2019), using ethylene glycol pretreatment, in which the maximum cellulose recovery of 93.1 % was attained compared to the highest lignin

removal of 48.2 %. Ibrahim, Hassan and Badri (2012) observed a similar trend, where up to 60 % cellulose recovery and 55.1 % delignification were achieved with glycerol pretreatment. It is undeniable that organosolv pretreatment with glycerol or ethylene glycol keeps the cellulose almost intact, while allowing most of the lignin and hemicellulose content to degrade, thus achieving good selectivity.

4.1.1.2 Parameters Impact on HBP Alcohol Pretreatment

Generally, the three potential parameters that affect organosolv pretreatment are considered to be concentration, reaction temperature and residence time. Chin, et al. (2019) showed that a lower glycerol concentration of 10 v/v% promoted the extraction of Klason lignin, but limited the removal of soluble lignin. Correspondingly, the low lignin removal rate may due to the low binding capacity of lignin (Fatriasari, Anita and Risanto, 2016). Besides, another study by Fatriasari, Anita and Risanto (2016) reported that a higher glycerol load would increase the removal rate of lignin. Glycerol has a highly polar structure, which allows the solvent to easily penetrate the fiber, thereby achieving more effective delignification. Moreover, Ibrahim, Hassan and Badri (2012) reported that when the glycerol concentration was increased from 10 v/v% to 30 v/v%, the recovery rate of α-cellulose increased as well. A higher glycerol concentration prevents the dissolution of xylan and restricts further degradation reaction, thereby ensuring higher cellulose recovery and sugar yield (Fatriasari, Anita and Risanto, 2016).

Other than that, Chin, et al. (2019) observed that as the ethylene glycol concentration increased above 50 v/v%, the delignification efficiency was decreased. Ibrahim, Hassan, and Badri (2012) reported a similar trend, where an excessive glycerol concentration of 30 v/v% did not support further lignin removal. High solvent concentration promotes the counterproductive process known as lignin condensation, in which lignin fragments establish intermolecular bonds with lignin residues on biomass, thereby restricting the depolymerization of lignin. The lipophilic compounds in glycerol may inhibit the removal of lignin as well (Sun and Chen, 2008). Furthermore, Chin, et al. (2019) obtained a maximum recovery of α-cellulose (95.8 %) and β-cellulose (61.7 %) with 50 v/v% and 90 v/v% ethylene glycol, respectively. At higher

concentrations of ethylene glycol, the recovery rate of α-cellulose was lower than that of β-cellulose. This is because ethylene glycol has a higher capability in swelling α-cellulose up to 180 %.

On the other hand, Chin, et al. (2020) observed a rising in delignification (56.1 % to 71.5 %) and hemicellulose removal (52 % to 78 %), but a reduction in cellulose recovery (92 % to 78.5 %) as the temperature increased from 60 to 140 °C. Generally, an increase in temperature will enhance the cleavage of glycosidic bonds between cellulose and hemicellulose, while also make the lignin degradation process more intense. Hence, there will be a greater formation of the open and deepened microfiber surface structure, signifying the removal of hemicellulose and lignin, thereby improving the ingress and penetration of the solvent into the trapped cellulose (Ibrahim, Hassan and Badri, 2012). However, high temperature may cause further sugar degradation and result in lower cellulose recovery. According to Figure 4.2, the effect of elevated temperature on lignin extraction and cellulose recovery is still small compared to hemicellulose removal. This finding explains that hemicellulose is naturally amorphous and more susceptible to heat compared to cellulose, thus hemicellulose can be decomposed and hydrolysed more quickly by solvents at higher temperatures.
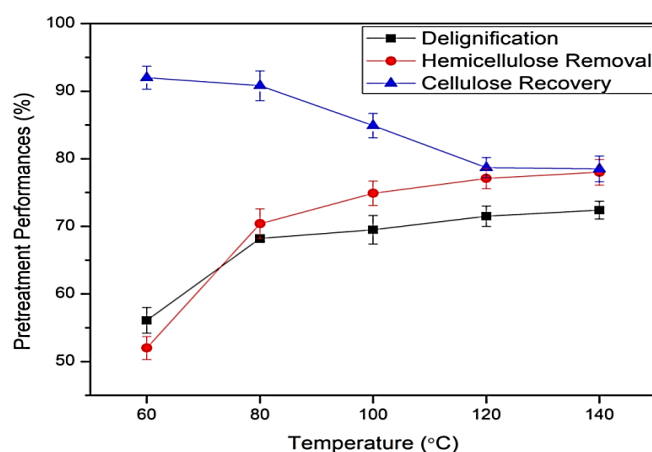
Figure 4.2: Pretreatment Performance from 60 °C to 140 °C (Chin, et al., 2020).

Moreover, Fatriasari, Anita, and Risanto (2016) also showed in their research that as the pretreatment time was increased, the lignin removal rate was higher. A longer pretreatment duration provides sufficient activation energy for

the interaction between the solvent and lignin, thereby causing more frequent collisions between molecules and leading to hydrogen bond breakage. In the study of Chin, et al. (2020), the result obtained a significant dropped in hemicellulose content (53 % to 85.2 %) with an increased reaction time from 15 mins to 45 mins, whereas less impact on cellulose recovery (91.8 % to 88 %) and delignification (63.1 % to 72.8 %). This may be due to the rapid decomposition of hemicellulose which is more susceptible to heat under the prolonged pretreatment duration. Other than that, Choopakar, et al. (2018) reported that the holocellulose content in the fibre pretreated at a shorter reaction time of 15 min (Condition C: Figure 4.3) was higher compared to the holocellulose content attained at 60 min (Condition D: Figure 4.4). At a pretreatment duration of 15 min and above, there will be reassociation of hydrogen bonds and generation of secondary by-products from carbohydrates which may lead to further cellulose and hemicellulose degradation, thus resulting in a lower holocellulose content (Fatriasari, Anita and Risanto, 2016).
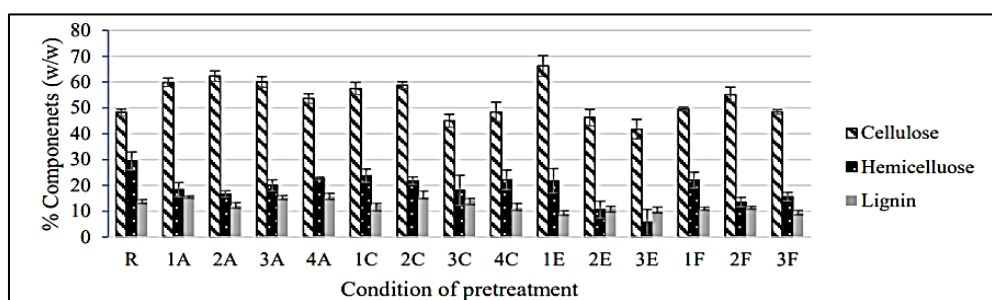
Figure 4.3: Components of Pretreated EFB at 15 min: Raw Material (R); DW (A); WG (C); Alkaline WG (E); Acidic WG (F) with Substrate Loading: 5 % (1). 10 % (2); 15 % (3), 20 % (4) (Choopakar, et al., 2018).
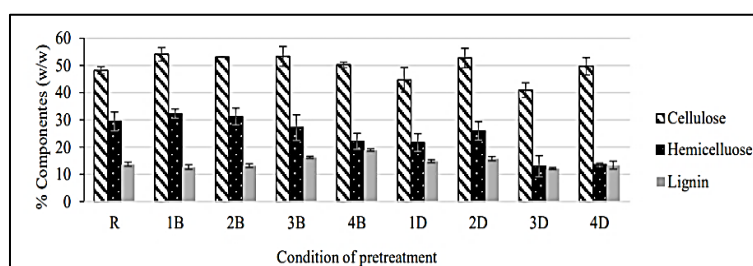
Figure 4.4: Components of Pretreated EFB at 60 min: Raw Material (R); DW (B); WG (D) with Substrate Loading: 5 % (1). 10 % (2); 15 % (3), 20 % (4) (Choopakar, et al., 2018).

4.1.2   Low Boiling Point Alcohol Pretreatment

LBP alcohol pretreatment is much cheaper as compared to HBP alcohol pretreatment which requires higher material costs and high pretreatment conditions (higher solvent consumption and elevated operating temperature). On the contrary, the mild pretreatment conditions employed in pretreatment with LBP alcohol and ketone can obtain acceptable delignification and cellulose yield at moderate operating costs. Besides, LBP alcohols tend to evaporate readily from the biomass solid, providing an easy solvent recovery process. However, the solvent recovery rate may be limited by the miscibility of the aqueous-organic solvent system, and this difficulty also applies to the pretreatment with organic acids and ketones. Generally, both LBP and HBP alcohols have low toxicity and are easily biodegradable, so they have less impact on the environment.

4.1.2.1   Types of Low Boiling Points Alcohols

Ethanol and methanol with relatively low boiling points (< 100 °C) will require higher operating pressures and potentially form volatile mixtures of low flashpoints. Compared with HBP alcohols and organic acids, pretreatment with LBP alcohols may cause a higher risk of ignition and difficult operation on a commercial scale, thereby given a lower safety rating. Besides, LBP alcohols are referred to as potentially water-miscible solvents, similar to organic acids and ketones. Therefore, they are quite difficult to recover from the aqueous organic solvent system, thus given a lower waste rating.

Based on the total Hansen solubility parameter, it is worth mentioning that ethanol should have a greater lignin solubility compared with HBP alcohol, owing to its δ value is closer to the Hildebrand solubility parameter of lignin. Nurfahmi, et al. (2016) found that a higher ethanol concentration (20 v/v%) with a more severe operating temperature (120 °C) was required for initiating lignin removal. Whereas, Ibrahim, Hassan and Badri (2012) reported that a delignification occurred with a lower glycerol concentration of 10 v/v% at lower pretreatment temperatures (65 - 85 °C). This finding explains that a lower δ_H value of ethanol compared to that of ethylene glycol and glycerol has signified its lower capability in solubilizing the lignin, even at elevated concentrations and temperatures.

4.1.2.2   Parameters Impact on LBP Alcohol Pretreatment

According to Nurfahmi, et al. (2016), it was observed that when the ethanol concentration increased from 35 v/v% to 60 v/v%, lignin degradation and total sugar production were increased. As shown in Figure 4.5, the Kappa value was significantly reduced when the ethanol concentration exceeded 35 v/v%, which signified a greater degree of lignin degradation. Organosolv pretreatment with higher ethanol concentration can hydrolyse and cleave the ether bond between lignin and hemicellulose. Hence, the lignin and hemicellulose are decomposed from the lignocellulose structure, thus providing higher lignin removal and more holocellulose conversion into sugar. However, Nurfahmi, et al. (2016) reported a low sugar production at a high ethanol concentration of more than 60 %. This finding was in agreement with the latter studies by Lee, et al. (2020). A heavy concentration will promote sugar degradation reaction thus lead to sugar loss. Also, Nurfahmi, et al. (2016) observed an increase in the Kappa value when the ethanol concentration exceeded 60 v/v%. Mohamad (2015) found a similar trend in which ethanol concentration higher than 70 v/v% led to a reduced delignification yield. This is because lignin may recondense under high solvent concentration during pretreatment, thus result in lower lignin removal.
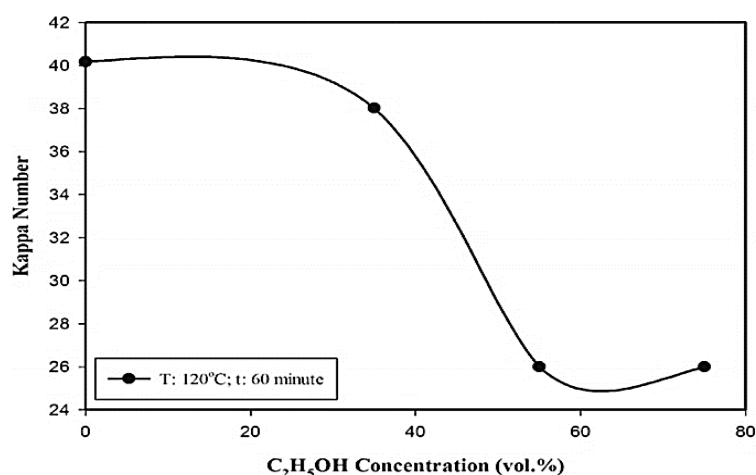
Figure 4.5: Effect of Ethanol Concentration on Kappa Number at the Optimum Pretreatment Condition (Nurfahmi, et al., 2016).

Other than that, Goh, et al. (2011) found out that the energy provided by low temperature was not sufficient to overcome the activation energy of lignin dissolution, thus achieved lower delignification and lower cellulose recovery.

Using ethanol pretreatment, Nurfahmi, et al. (2016) reported that as the heating temperature was increased from 80°C to 120°C, sugar content and delignification in the pulp were increased. Lee, et al. (2020) observed an increment in reducing sugar yield when the temperature was increased from 40 to 50 °C, but a reduced yield at 60 °C as shown in Figure 4.6. A higher temperature promotes a higher reaction rate for lignin extraction, resulting in more accessible cellulose. However, under severe pretreatment temperature, sugar may degrade into inhibitory compounds. The higher vapor pressure in the solvent caused by the higher operating temperature may reduce the cavitation intensity, making effective pretreatment unlikely.
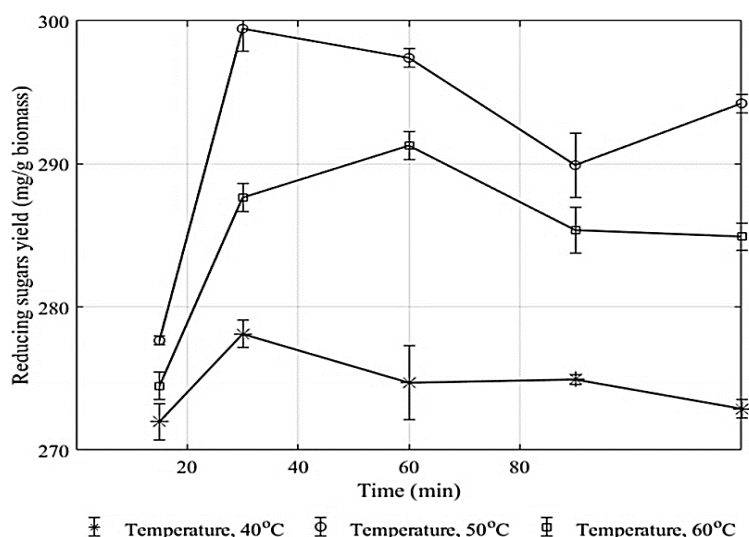
Figure 4.6: Effect of Different Temperature and Time on Reducing Sugar Yield (Lee, et al., 2020).

On the other hand, a shorter pretreatment time is difficult to dissolve lignin and hemicellulose, while a higher pretreatment time decomposes glucose and recondenses lignin (Goh, et al., 2011). Mardawati, et al. (2018) observed higher delignification efficiency at a longer reaction time. A prolonged time allows sufficient thermal attack on the OPEFB fibre structure which is more resistant to organic solvent. Besides, Lee, et al. (2020) observed that a further extended pretreatment duration above 30 min has reduced the sugar yield. A similar finding was reported by Nurfahmi, et al. (2016), where a longer heating time to 90 minutes promoted greater lignin solubilization but reduced sugar yield. They claimed that the thermal dissolution of carbohydrates, especially

hemicellulose fractions has occurred during prolonged pretreatment duration, which may probably result in a lower sugar yield.

4.1.3   Organic Acid Pretreatment

Organic acid pretreatment requires only mild pretreatment conditions, usually lower temperature and shorter reaction time under pressurized conditions. However, this pretreatment will lead to acetylation and formylation reactions between the solvent and cellulose, resulting in lower enzymatic sugar conversion rates compared to other pretreatments. Nevertheless, effective delignification yield can still be achieved. Organic acid pretreatment requires a higher energy consumption for solvent recovery and will produce a certain degree of corrosiveness during the pretreatment process. Therefore, higher operational cost and equipment cost require for this pretreatment compared to the pretreatment with LBP alcohols and ketones.

4.1.3.1   Types of Organic Acids

Acid is usually corrosive and harmful to human health, thus contributing to a lower health rating. In addition to the difficulty of solvent recovery, the lower waste rate is also attributed to the further wastewater treatment of the processed acid before disposal. The δ values of acetic acid and formic acid are very close to that of lignin, thus providing high efficiency for delignification compared to other types of solvents. Compared with acetic acid, formic acid is correlated with a higher δ_H value, indicating a higher hydrogen bonding capability to dissolve lignin. This finding is in agreement with Hidayati, Zuidar and Satyajaya (2017) where an increase in the ratio of formic acid to acetic acid concentration has maximized the lignin extraction. The results of this study also reported the tendency of organic acids to acetylate and formylate with cellulose, thereby provided lower cellulose recovery compared with lignin removal.

4.1.3.2   Parameters Impact on Organic Acid Pretreatment

There were only several works of literature on the organosolv pretreatment of OPEFB with formic acid and acetic acid, which may be due to the corrosiveness of these acids. Harahap, et al. (2020) in their study showed that sugar yield increased with an increase in acetic acid concentration up to 15 % at 125 °C.

According to the research by Hidayati, Zuidar and Satyajaya (2017), there was a reduction of cellulose and hemicellulose in the pretreated OPEFB as the formic acid concentration increased above 10 v/v% at 130 °C. This proves that the synergy between concentration and temperature greatly impacts cellulose recovery and sugar yield. A high acid concentration destroys the glycosidic bonds of cellulose and hemicellulose, then degrades and dissolves long-chain polysaccharides into lower content. During the pretreatment process, the possibility of acetylation reaction leads to the substitution of acetyl groups for the hydroxyl groups of cellulose, thereby inhibiting the effective binding of cellulase and cellulose thus resulting in lower cellulose recovery (Zhao, Cheng and Liu, 2009). In the study performed by Nazir, et al. (2013), 20 v/v% of formic acid pretreatment with 10 v/v% hydrogen peroxide provided effective extraction of lignin and hemicellulose fractions. A higher concentration of formic acid will cleave and hydrolyse α-aryl and β-aryl ether linkages in lignin macromolecules, causing the lignin to dissolve (Hidayati, Zuidar and Satyajaya, 2017). Conversely, acid concentrations higher than 25 v/v% led to re-lignin polymerization, thereby a lower delignification was achieved.

Using oxalic acid pretreatment, Solihat, Hermiati and Adi (2020) reported that the yield of glucose and sugar both increased gradually with increasing temperature. Harahap, et al. (2020) observed a similar trend for acetic acid pretreatment. A higher thermal attack easily degrades OPEFB macromolecules such as polysaccharides and lignin into small fragments, thereby disintegrating the lignocellulose structure so that more cellulose is converted into glucose and sugar. A latter study by Solihat, Hermiati and Adi (2020) reported a reduction in reducing sugar yield at temperatures above 160 °C with reaction times longer than 10 min, as shown in Figure 4.7. On the contrary, the result also figured out that long pretreatment time (15 min) at high temperature (200 °C) allowed efficacious reduction of biomass recalcitrant and thus achieved the highest reducing sugar yield of 69.84 %. This proves that the synergy between temperature and time greatly affects the sugar yield.
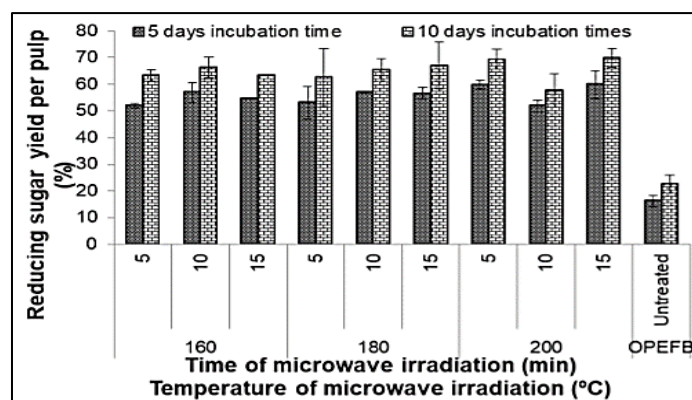
Figure 4.7: Time and Temperature Effect on Reducing Sugar Yield per Pulp with Oxalic Acid Pretreatment (Solihat, Hermiati and Adi, 2020).

The previously cited research by Harahap, et al. (2018) showed an increased sugar yield with the pretreatment duration increased from 15 min to 60 min. This trend was in good agreement with the study by Solihat, Hermiati, and Adi (2020). A longer pretreatment duration provides sufficient activation energy for the cleavage of the hydrogen bonds between cellulose, thereby providing a higher sugar yield. Referring to Figure 4.8, in the research of Harahap, et al. (2020), the acetic acid pretreatment was extended from 60 min to 90 min and obtained a relatively lower recovery of sugar. This is due to the further decomposition of cellulose and hemicellulose at high reaction time, thus formed inhibitory products such as furfural and HMF.
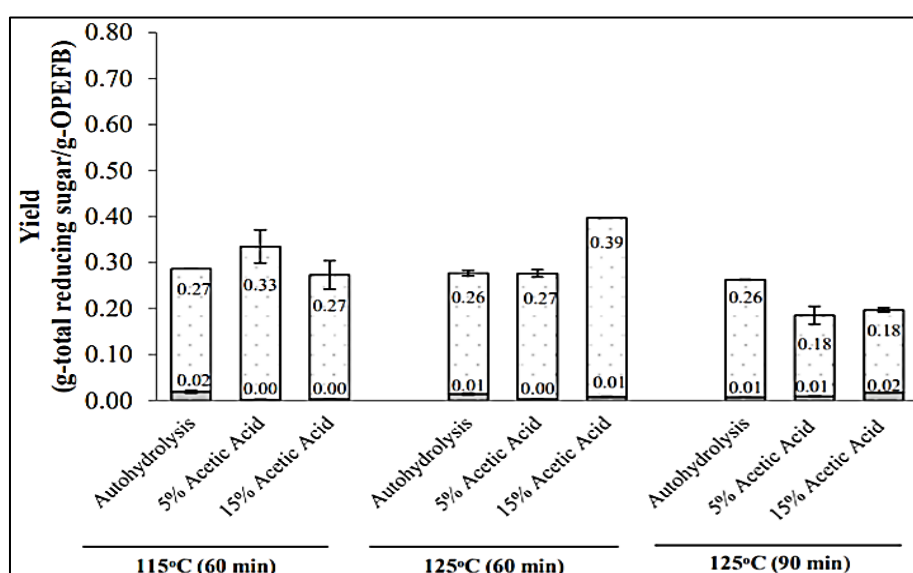
Figure 4.8: Effects of Different Acetic Acid Concentration on the Reducing Sugar Yield (Harahap, et al., 2020).

4.1.4 Ketone Pretreatment

Although the material cost of ketones is higher than that of LBP alcohols, it can achieve a moderate delignification rate and cellulose digestibility under mild pretreatment conditions. Similar to LBP alcohol pretreatment, ketone has low boiling point characteristics, so higher operating pressure is required in the pretreatment which signifies more energy consumption. Additionally, significant process risks will increase the investment cost of process safety. Since the solvent consumption is lower in the ketone pretreatment compared to other pretreatments, the investment cost can be partially compensated.

4.1.4.1 Types of Ketones

Generally, acetone and other common organic solvents studied for organosolv pretreatment are less toxic to the environment and are easily biodegradable. Hence, they can be used as green solvents and meet environmental protection requirements. Acetone has a low boiling point and flash point compared with other solvents, resulting in a higher potential towards flammability and explosion hazards, thus greatly reducing the safety level. Moreover, acute exposure to acetone has no gross toxic effect, thus providing a greener score for the health level. According to the Hansen solubility parameter, the determined δ_H value for acetone is the lowest among other solvents, indicating that acetone has a low lignin solubility and extractability. However, adding an acid catalyst during the pretreatment process can provide high selectivity to lignin, resulting in higher delignification. Using acid-catalysed acetone pretreatment, a previous study by Palamae, et al. (2014) reported a delignification of nearly 47.0 % and moderate retention of cellulose (48.1 % - 53 %).

4.1.4.2 Parameters Impact on Ketone Pretreatment

Research on the acetone pretreatment of OPEFB is very limited. Palamae, et al. (2014) found that higher temperatures and reagent concentrations promoted the removal of hemicellulose. Sarwono, Pusfitasari and Ghozali (2016) used acetone for pretreatment on OPEFB and found that the rise in reaction temperature increased the conversion rate to a maximum of 26.5 % at 400°C. A higher reaction temperature has enhanced the defragmentation of the polymer, where the solvolysis of hemicellulose and lignin may occur at temperatures

higher than 190°C. Besides, a higher reaction pressure resulted from a higher reaction temperature will increase the solvent's density, allowing more effective medium penetration into the biomass components and thus attaining a greater decomposition. A previous study by Fan, et al. (2011) showed that when acetone pretreatment was performed at 275°C, the highest conversion yield was 65.3 %. Acetone is a polar aprotic solvent with a high dipole moment of 2.88, which indicates that the ability to provide hydrogen ions during the solvolysis process is low. Hence, acetone pretreatment provides the lowest conversion yield compared with other organosolv pretreatments (Fan, et al., 2011).

4.1.5   Summary

The specific selection of solvents and pretreatment conditions are relatively important in impacting delignification, cellulose recovery or yield, and sugar yield. It should be noted that the selections are closely related to the principal product required in the organosolv process, either cellulose or lignin. Looking into the operating conditions, a higher concentration can hydrolyse and cleave the α-aryl and β-aryl ether linkages in macromolecules (polysaccharides and lignin). A higher temperature provides sufficient thermal attack to degrade the polysaccharides and lignin into small fragments. Besides, a longer pretreatment duration provides sufficient activation energy for the interaction between the solvent and lignin, thereby causing more frequent collisions between molecules and leading to hydrogen bond breakage. All these sufficient pretreatment conditions can disintegrate the lignocellulosic structure, thus given high delignification and more holocellulose conversion into sugar. However, heavy concentration, excessive temperature, and prolonged duration promote the counterproductive process such as further decomposition of cellulose and hemicellulose into inhibitory compounds, while also lignin recondensation which restricts the depolymerization of lignin. This will subject to low lignin removal as well as low cellulose recovery or sugar yield. Moving forwards, it is hard to decide the optimum conditions of each pretreatment parameter in which the interactive effects between different parameters' conditions would give distinctive outcomes. Thereby, their interactive concepts were analysed and discussed in-depth in Sections 4.3.2 and 4.3.3 through an optimised model.

4.2   Effect of Different Catalysts on Delignification, Cellulose Recovery/ Yield, Sugar Yield

The addition of catalysts in organosolv pretreatment mainly increases the rate and extent of hemicellulose dissolution and the cleavage of ether bonds between lignin (Mondylaksita, et al., 2020). Figure 4.9 depicts different types of catalysts used in organosolv pretreatment, which can be classified into acid catalyst and base catalyst. The discussion compared acid-catalysed and base-catalysed organosolv pretreatment, as shown in Table 4.3. With reference to various studies and literature, the concentration impacts of different catalysts on delignification, cellulose recovery/yield, and sugar yield were analysed and compared. Also, the physical and chemical characterisations of organosolv pretreated OPEFB were discussed. A summary of different researches using different types of solvents and catalysts was tabulated in Table 4.4.
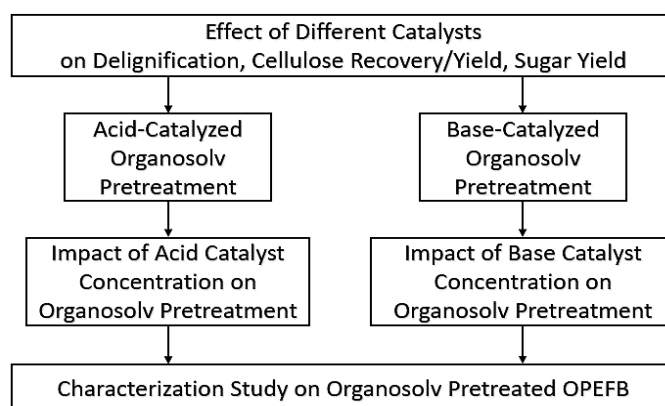
Figure 4.9: The Flowchart Outlines for Section 4.2.

Table 4.3: Comparison between Acid-Catalysed and Base-Catalysed Organosolv Pretreatment.

Parameter	Organosolv Pretreatment	
	Acid-Catalysed	Base-Catalysed
Solubilization of hemicellulose	#	*
Solubilization of lignin	*	#
Alteration of lignin structure	*	#
Increase accessible surface area	#	#
Acetylation of cellulose	*	-

\# positive and major effect, * positive but minor effect, – negative effect

4.2.1   Acid-Catalysed Organosolv Pretreatment

Markom (2016) studied that H_2SO_4 catalysed pretreatment has reduced the hemicellulose content and increased the Klason lignin content in the pretreated fibre. Using NaOH catalysed pretreatment, the results of this study showed that the hemicellulose content in the pretreated fiber was increased compared to the decreased Klason lignin content. Acids tend to degrade hemicellulose polymers than lignin, whereas alkalis are more selective in lignin removal by cleaving the ester linkage between lignin and xylan (Fatriasari, Anita, and Risanto, 2016).

Palamae, et al. (2014) studied peracetic acid pretreatment and reported a lignin removal of nearly 45.9 % to 47.0 %, moderate retention of cellulose (48.1 % - 53 %), and high retention of hemicellulose (almost 100 %). Peracetic acid reacts with the uronic and hexenuronic acid groups that mainly bonded to xylan, thereby cleaving the glycosidic bond. For hydrogen peroxide catalysed pretreatment, there was less significant delignification (< 2 %), 38.5 % of cellulose retention, and 26 % of hemicellulose removal. They claimed that OPEFB pretreated with peracetic acid can retain more cellulose content and obtain a higher degree of delignification. Other than that, Ibrahim, Hassan and Badri (2012) reported that acetic acid catalysed glycerol pretreatment with an S/L ratio of 1:20 for 7 hr provided a higher holocellulose yield of 85.17 %, compared to NaOH catalysed glycerol pretreatment and crude glycerol pretreatment. In short, it is recommended that acid catalysts provide higher pretreatment efficiency than alkaline catalysts.

4.2.1.1 Impact of Acid Catalyst Concentration on Organosolv Pretreatment

Sulphuric acid is the most commonly used acid catalyst for organosolv pretreatment. A previous study by Goh, et al., 2011 involved H_2SO_4 catalysed pretreatment and reported that when the concentration of H_2SO_4 was increased from 0.5 v/v% to 2.0 v/v% at 160 °C, the yield of glucose was increased as well. The H^+ ions in the acid dissolve the content of hemicellulose and acid-soluble lignin, thereby destroying the chemical bonds in the fiber. This destruction depolymerizes cellulose, hemicellulose, and lignin, leading to higher glucose yield (Kim and Kim, 2013; Palamae, et al., 2014). Besides, Nurfahmi, et al. (2016) claimed that the diluted acid concentration can prevent the possibility of

the formation of inhibitory compounds, thereby providing better sugar yield. Duangwang and Sangwichien (2013) supported this finding where the optimum sugar yield of 80 – 90 % was obtained at H_2SO_4 concentration above 1 w/v%.

On the other hand, Chin, et al. (2019) observed a reduction of α-cellulose recovery in ethylene glycol pretreated fiber with an increase of H_2SO_4 concentration above 2 v/v%. This reduction may be due to the ability of H_2SO_4 to degrade the α-cellulose into β-cellulose, which supports the finding shown in Figure 4.10, where more than 100 % β-cellulose recovery was obtained at 5 v/v% H_2SO_4. Correspondingly, Fatriasari, Anita and Risanto (2016) pointed out that a higher acid load than glycerol caused a significant reduction in sugar yield, as shown in Figure 4.11. A high acid concentration suggests a more intensive decomposition reaction, which potentially degrades the carbohydrates into inhibitory and toxic compounds (furfural, HMF, phenolic acid). These inhibitory compounds lead to a reduction of cellulose recovery and sugar yield (Palamae, et al., 2014; Harahap, et al., 2020).
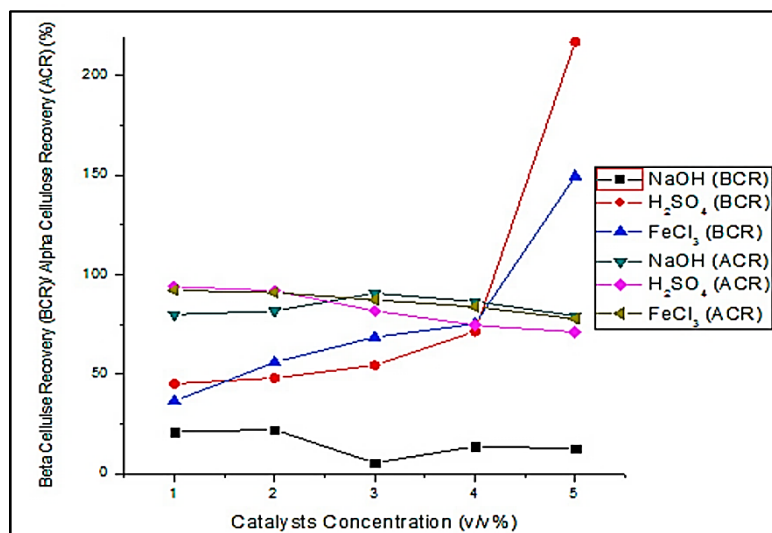
Figure 4.10: α and β Cellulose Recovery of Selected Catalyst (Chin, et al., 2019).
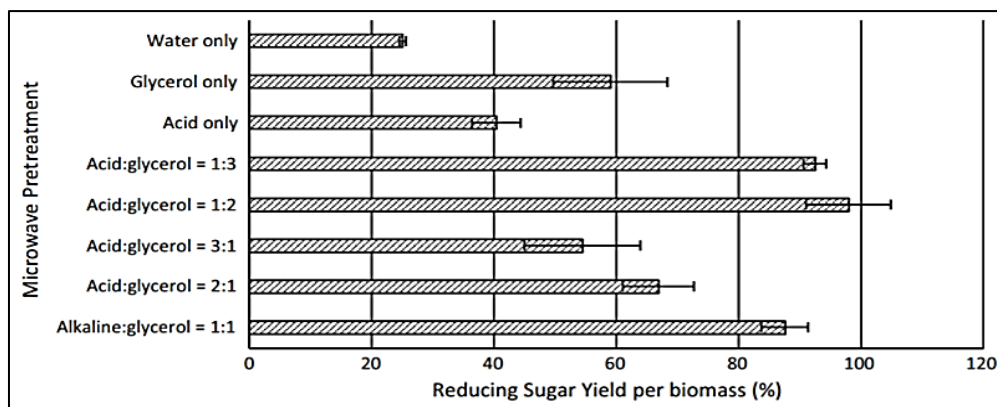
Figure 4.11: Microwave-assisted Organosolv Pretreatment on Sugar Yield at Different Solvent Ratio (Fatriasari, Anita and Risanto, 2016).

A previous study by Goh et al. (2011) showed a lower delignification (48 %) with 0.88 v/v% H_2SO_4-ethanol pretreatment at 190 °C for 75 min. However, a higher H_2SO_4 concentration of 1.63 v/v% at 190 °C with a shorter pretreatment time provided an increase of delignification yield to 81 %. A higher H_2SO_4 concentration above 1 v/v% gradually increased the lignin removal, as shown in Figure 4.12. The high delignification was attributed to the likelihood of α-aryl and β-aryl ether linkages in the lignin macromolecule for being disrupted and cleaved in a higher acidic condition (Kim and Kim, 2013; Hidayati, Zuidar and Satyajaya, 2017). Using 0.07 % H_2SO_4 ethanol pretreatment at 210 °C for 90 min, Mondylaksita et al. (2020) reported a delignification of 90 %. More severe pretreatment conditions with diluted acid can provide a greater delignification efficiency.
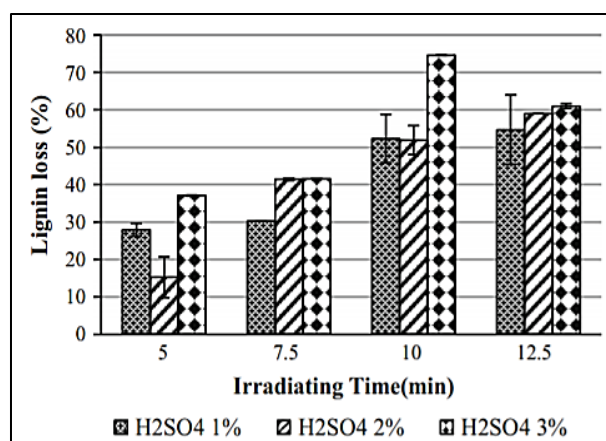
Figure 4.12: Lignin Removal of H_2SO_4 catalysed glycerol pretreated OPEFB (Fatriasari, Anita and Risanto, 2016).

4.2.2   Base-Catalysed Organosolv Pretreatment

In the study of Fatriasari, Anita and Risanto (2016), compared with 1:1 H_2SO_4-glycerol pretreatment and glycerol pretreatment, 1:1 NaOH-glycerol pretreatment obtained the highest sugar yield. This finding was consistent with the view of Choopakar, et al. (2018), where the concentration of reducing sugars obtained by NaOH-glycerol pretreatment is higher than that of H_2SO_4-glycerol pretreatment and glycerol pretreatment, as shown in Figure 4.13. Lee, et al. (2020) also observed a similar trend for ethanol pretreatment catalysed by NaOH or H_2SO_4.
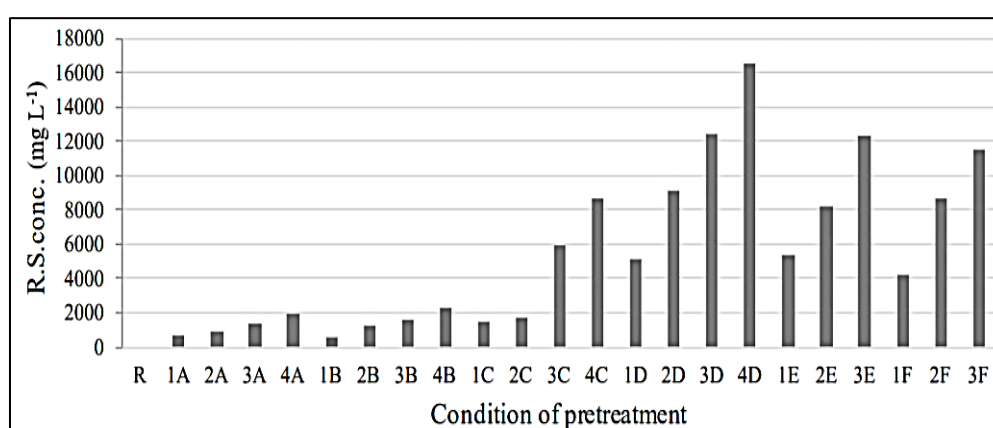
Figure 4.13: Reducing Sugar Concentration (R.S.conc.); Raw Material (R); DW 15 min (A); DW 60 min (B); WG 15 min (C); WG 60 min (D); Alkaline WG 15 min (E); Acidic WG 15 min (F) with Substrate Loading: 5 % (1). 10 % (2); 15 % (3), 20 % (4) (Choopakar, et al., 2018).

It was worth noting that the delignification achieved by NaOH catalyst was higher than that of H_2SO_4 catalyst, as shown in Figure 4.14. Besides, Lee, et al. (2020) reported the lowest lignin content of 10.8 % (high lignin removal) in OPEFB pretreated with NaOH, compared with that of 11.3 % for H_2SO_4-pretreated OPEFB and 13.0 % for pretreated OPEFB without catalyst. This finding was comparable with the work reported earlier by Ibrahim, Hassan and Badri, 2012, where a higher delignification of 70.3 % achieved by [glyN-pretreatment], followed by [gly-pretreatment] and [glyA-pretreatment].
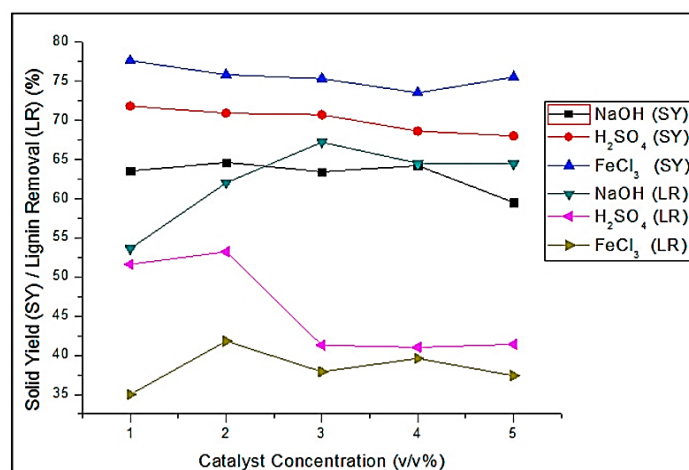
Figure 4.14: Solid Yield or Lignin Removal of Catalysts (Chin, et al., 2019).

4.2.2.1 Impact of Base Catalyst Concentration on Organosolv Pretreatment

Choopakar, et al. (2018) proved that NaOH-catalysed glycerol pretreatment was more effective in reaching the highest holocellulose content (87.98 %) with a minimum load of 5 %, as shown by Condition 1E in Figure 4.3. Besides, Ibrahim, Hassan, and Badri (2012) reported a similar holocellulose yield of 82.03 %. Unlike acid catalysts, NaOH catalysts swell the fiber structure along with less formation of inhibitory products, and can usually remove acetyl and uronic acid in hemicellulose. This reduces the polymerization and crystallinity degree of cellulose, while increasing the surface area and porosity thus allowing more solvent access to the holocellulose content (Zulkiple, Maskat and Hassan, 2016; Lee, et al., 2020). In a previous study by Chin, et al. (2019) involving ethylene glycol pretreatment using 3 v/v% NaOH, the highest recovery rate of α-cellulose was reported to be 90.6 %. NaOH catalyst claims to make cellulose denser and thermodynamically more stable than native cellulose, thereby increasing the recovery of cellulose (Palamae, et al., 2014).

Moreover, Hanim Saleh and Akhmar Mohd Nasir (2016) found that the yield of hemicellulose increased as the KOH concentration increased from 1M to 5M. The hydroxide anion from the alkaline catalyst causes the swelling of cellulose, and at the same time effectively cleaves and breaks the benzyl ester and glycosidic bonds between lignin and hemicellulose, resulting in more hemicellulose dissolution. Palamae, et al. (2014) found that an increase in H_2O_2 concentration at 55 °C resulted in greater isolation of the hemicellulose fraction.

This was because of a lesser decomposition of H_2O_2 at 55 °C against 75 °C, thereby more available reagent can potentially solubilize the fibre compounds. The study also described that as temperature and reagent concentration increased, alkaline substances rapidly decomposed and led to a low generation of perhydroxyl and hydroxyl radicals which responsible for polysaccharides decomposition.

Other than that, Ibrahim, Hassan and Badri (2012) reported lower Klason Lignin in the glycerol pretreated OPEFB catalysed with NaOH. Using ethanol pretreatment catalysed with KOH, Hanim Saleh and Akhmar Mohd Nasir (2016) observed a similar reduction trend in lignin content. Alkaline catalysts are capable to extract nearly all lignin and a portion of hemicellulose at mild pretreatment conditions. In other words, alkaline catalyst promotes the removal of lignin but also encourages degradation of carbohydrates or sugar loss to a minimum extent.

4.2.3   Characterisation Study on Organosolv Pretreated OPEFB

This section will be discussed the changes in the chemical composition (cellulose, hemicellulose, lignin), physical property (surface area, size, roughness, components distribution), and supramolecular structure (bonds, functional groups, crystallinity index) of organosolv pretreated OPEFB. Characterisation instruments used for organosolv pretreatment study are usually SEM, XRD, FTIR, and TGA.

4.2.3.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is commonly used to analyse the pretreatment effect on the structure and mechanical properties, including surface, morphology, and microstructure changes in biomass. SEM micrograph of raw OPEFB showed a stiff, hard, and uneven adjacent surface with embedded white granule silica bodies (phytoliths), along with a matrix layer of lignin, hemicellulose, waxes, and inorganic compounds (Nazir, et al., 2013; Markom, 2016). According to Solihat, Hermiati and Adi (2020), exposure to higher heating temperature and longer pretreatment time will disrupt the fiber surface and produce more cracks on the circular crater, thereby significantly remove silica bodies and influentially destructed the morphology structures of OPEFB,

as shown in Figure 4.15. This finding was agreeable with the views of Chin, et al. (2020), where higher temperatures influentially destructed the morphology structures of OPEFB, thus formed more open and deepened surface structures. This will lead to a large amount of lignin extraction and easily hydrolysed amorphous hemicellulose.
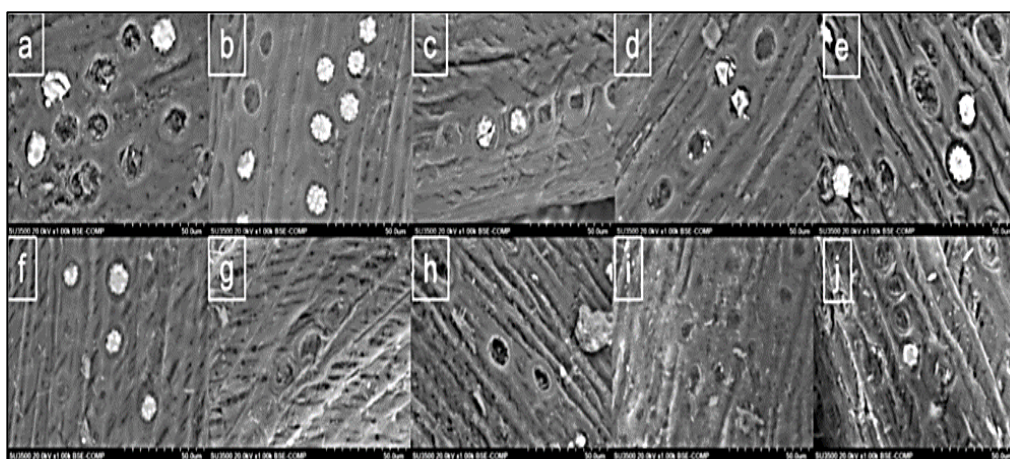
Figure 4.15: SEM Micrograph of OPEFB before pretreatment (a) and after treatment at 160ºC for 5 min (b) 10 min (c) 15 min (d); 180ºC for 5 min (e) 10 min (f) 15 min (g); 200ºC for 5 min (h) 10 min (i) 15 min (j) (Solihat, Hermiati and Adi, 2020).

These morphological changes are complied with the previous research, which observed a rougher, porous, and opened structure on the irregular fibril surfaces of organosolv pretreated OPEFB. The study of Fatriasari, Anita and Risanto (2016) showed that the surface of glycerol pretreated OPEFB catalysed with acid was cracked, loose and irregular. The irregular pores may be attributed to the fact that glycerol having a highly polar polyalcohol structure easily penetrates the fiber, thereby cleaving the structural chain between lignin and carbohydrate. The addition of acid catalyst swells up cellulose while increasing the reactive surface area and porosity for more cellulose exposure (Sun, et al., 2015; Fatriasari, Anita and Risanto, 2016). This finding was in line with the morphological observation by Markom (2016) after acid or alkaline catalysed pretreatment.

Other than that, Hidayati, Zuidar and Satyajaya (2017) reported that the pretreatment splitted apart the fibre bundles into dispersed fibres, along with a

significant reduction in fibres' diameter. The pretreated fibre is deformed and chemically split into short fibres, which leads to the reduction of the fibres' length and volume, thereby enhancing the surface area and making cellulose easier to access (Kim and Kim, 2013; Sun, et al., 2015).

4.2.3.2 X-Ray Diffraction (XRD)

The crystallinity index (CI) is a parameter that determines the relative amount of crystalline and amorphous regions in biomass. Solihat, Hermiati and Adi (2020) observed two main peaks at 2θ of 14 - 18° and 20 - 25°, corresponded to the amorphous and crystalline region, respectively. The finding of this work was comparable to the previously reported work by Nazir, et al. (2013), in which the extracted cellulose fibre showed a single sharp crystalline peak at $2\theta = 22.5$ ℃ (I_{002}) and an amorphous peak at $2\theta = 16$ ℃ (I_{am}).

The high-intensity crystalline peak indicates more cellulose or an increase in crystalline nature and structure (higher crystallinity index), owing to the depolymerization and dissolution of main amorphous components (hemicellulose and lignin). Besides, the amorphous peak with smaller intensity indicates the entrapped cellulose fibre in the amorphous region of cellulose, hemicellulose, and lignin. According to Figure 4.16, Solihat, Hermiati and Adi (2020) observed a similar trend of peaks, and it is reported that as the temperature increased, the amorphous and crystalline peaks moved slightly to the bottom. This study also reported a similar trend with increasing pretreatment duration. The shifted amorphous peak is due to more amorphous components removal, while the crystalline shifted peak allows more cellulose digestibility.
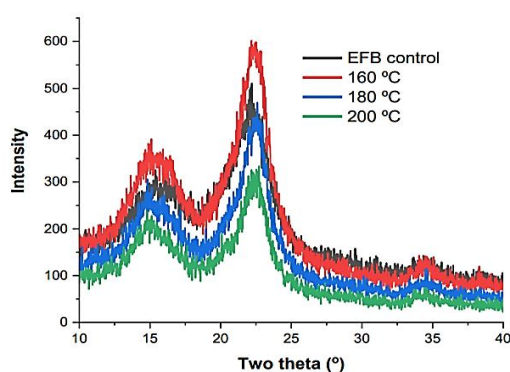
Figure 4.16: X-ray Diffractogram of Untreated and Treated OPEFB at Different Temperatures (Solihat, Hermiati and Adi, 2020).

Several works of literature have proven that organosolv pretreatment can destroy crystalline cellulose, thereby reducing the crystallinity of pretreated OPEFB. Using 50 v/v% ethanol pretreatment catalysed by 0.07 % H_2SO_4, Mondylaksita, et al. (2020) reported that the crystallinity index (CI) for pretreated OPEFB was 0.95, which was 24.48 % lower than the initial index value. Using ethylene glycol pretreatment, Chin, et al. (2019) reported that as the solvent concentration increased from 10 v/v% to 90 v/v%, the CI value decreased moderately from 0.805 % to 0.786 %. With the further addition of 2 % H_2SO_4 or 3 % NaOH, the crystallinity indexes obtained for pretreated fibre were 0.799 % and 0.773 %, respectively. It is undeniable that higher solvent and catalyst concentrations can further reduce the CI value, indicating more cellulose swelling and dissolution. Moreover, it is also worth mentioning that alkaline catalysts can reduce the crystallinity of pretreated fibers better than acidic catalysts.

On the other hand, there was an argument by Markom (2016) that showed an increment of CI value in the acid or alkaline catalysed pretreated fibre. Solihat, Hermiati and Adi (2020) reported a similar finding where the CI value in the pretreated fibre was increased from an initial 0.1396 to 0.2133, at a higher heating temperature (200 °C) and longer pretreatment duration (10 min). The increase in crystallinity may be attributed to the destruction of larger molecules in the fiber, as well as the dissolution and removal of hemicellulose and lignin under higher pretreatment conditions, thus exposing more crystalline cellulose structure (Solihat, Hermiati and Adi, 2020; Zulkiple, Maskat and Hassan, 2016). In short, the contradictory results among researchers are mainly based on the following two viewpoints: Swelling and dissolution of cellulose fraction; Extraction of amorphous hemicellulose and lignin (Sun, et al., 2015).

4.2.3.3   Fourier Transform Infrared Spectroscopy (FTIR)

Several characteristic bands were analysed to determine the chemical changes in lignin and carbohydrates components of OPEFB. In this section, the contradictory results among researchers are mainly based on the following two viewpoints: Swelling and dissolution of cellulose fraction; Extraction of amorphous hemicellulose and lignin (Sun, et al., 2015). According to Abdul, et al. (2016), the bonds between polysaccharides (cellulose and hemicellulose)

were mainly referred to as the absorption bands between 3600 cm^{-1} to 2600 cm^{-1}, as well as 900 cm^{-1} to 500 cm^{-1}. Besides, the adsorption bands between 1800 cm^{-1} to 900 cm^{-1} were largely attributed to the bonds within the structure of lignin and hemicellulose.

  For the FTIR spectra of the raw OPEFB shown in Figure 4.17, Pasma, Daik and Maskat (2013) observed two peaks at 1501 and 1512 cm^{-1}, indicating the C=C stretching and C=C aromatic vibration of lignin, respectively. However, these two peaks were not observed in the spectra of the delignified OPEFB and OPEFB cellulose, which signified the partial removals of lignin. Owing to C=O stretching, hemicellulose peaks at 1735 and 1732 cm^{-1} were observed in the spectra of raw OPEFB and delignified OPEFB, instead of OPEFB cellulose that shows successful hemicellulose extraction. In the FTIR spectra for the glucan-rich fraction, Mondylaksita, et al. (2020) found that the higher absorption band was at 897 cm^{-1} and a lower absorption band was at 1428 cm^{-1}, thus corresponded well with the cellulose spectra analysed by Pasma, Daik and Maskat (2013). These shifted bands showed an increase in amorphous cellulose and a decrease in crystalline cellulose, indicating a higher digestibility of cellulose in the pretreated fibre.
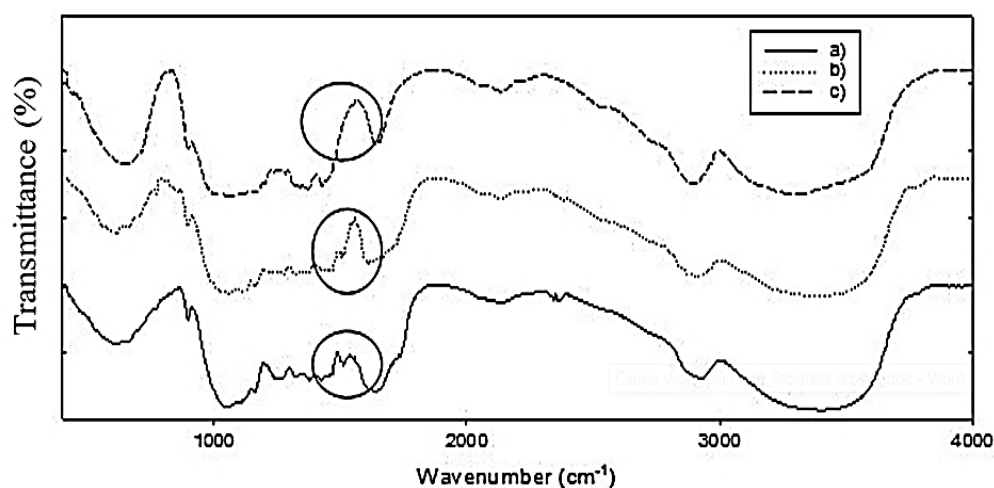
Figure 4.17: FTIR Spectra for (a) Raw OPEFB (b) Delignified OPEFB (c) OPEFB Cellulose (Pasma, Daik and Maskat, 2013).

  Moreover, Solihat, Hermiati and Adi (2020) observed a slight decrease in peak intensity at 1714 cm^{-1} (no.3) and 1370 cm^{-1} (no.9) after pretreatment. These peaks correspond to the cleavage of the C=O ester bond between lignin-

xylan and deformation vibration of the C-H bond in hemicellulose, respectively. The result of this study also showed some sharper lignin-associated peaks at 1600 cm^{-1} (no.5), 1507 cm^{-1} (no.6), 1456 cm^{-1} (no.7), 1270 cm^{-1} (no.11) after pretreatment, suggesting the release of lignin and their coprecipitation on the pulp. The finding also stated that hemicellulose was more easily degraded than lignin. Furthermore, more significant peaks were noticed at 1425 cm^{-1} (no.8), 1323 cm^{-1} (no.10), 1105 cm^{-1} (no.14), 1054 cm^{-1} (no.15), and 897 cm^{-1} (no.17), referring to the stretching vibration of –CH$_2$ shear, C-H, C-O, C-C, and β-glycosidic linkage in cellulose. Corresponding to the XRD pattern discussed in Section 4.2.3.2, the significant shift of the peak shown in Figure 4.18 further confirms that a higher pretreatment temperature will reduce the amorphous compound in OPEFB, thereby allow more cellulose digestibility.
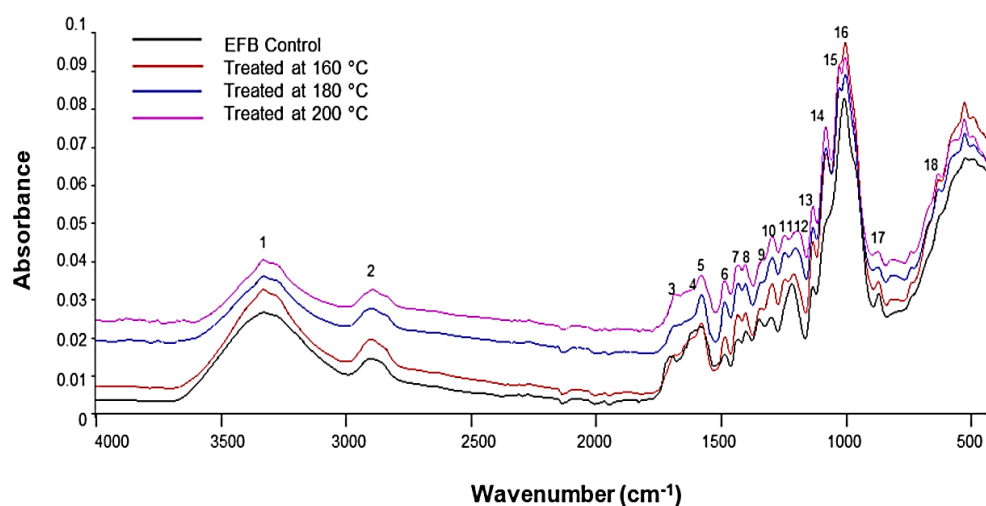
Figure 4.18: FTIR Spectra of Untreated and Treated OPEFB at Different Temperatures (Solihat, Hermiati and Adi, 2020).

4.2.3.4 Thermogravimetric analysis (TGA)

According to the study of Nazir, et al. (2013), OPEFB degraded at the temperature below 400 ℃ as follows: hemicellulose, cellulose, and lignin degraded at 180 ℃, 300 ℃, and 400 ℃, respectively. The thermal degradation of cellulose occurs with water loss at a temperature below 200 ℃, while the cellulose chain depolymerizes in a temperature range between 200 to 390 ℃.

Correspondingly, Sun, et al. (2015) reported a substantial degradation between 200 °C to 400 °C and a small weight loss at 100 °C owing to the

evaporation of moisture content. This finding corresponded well with the thermogram obtained by Pasma, Daik and Maskat (2013), as shown in Figure 4.19. For delignified OPEFB, there was a peak (shoulder) at nearly 300 °C which indicates the thermal decomposition of hemicellulose, whereas no peak (tail) in the range of 400 °C to 600 °C, indicating a successful lignin extraction. Besides, no shoulder and tail were found in the thermogram of OPEFB Cellulose, which indicates that both hemicellulose and lignin have been successfully removed. Moreover, the results of this study also showed a thermal decomposition at nearly 310 °C, which represents a successful cellulose recovery. It is thus, of interest, to figure out that the pretreated fibre has a high degradation temperature and high thermal stability due to the partial dissolution and removal of hemicellulose and lignin from the substrate.
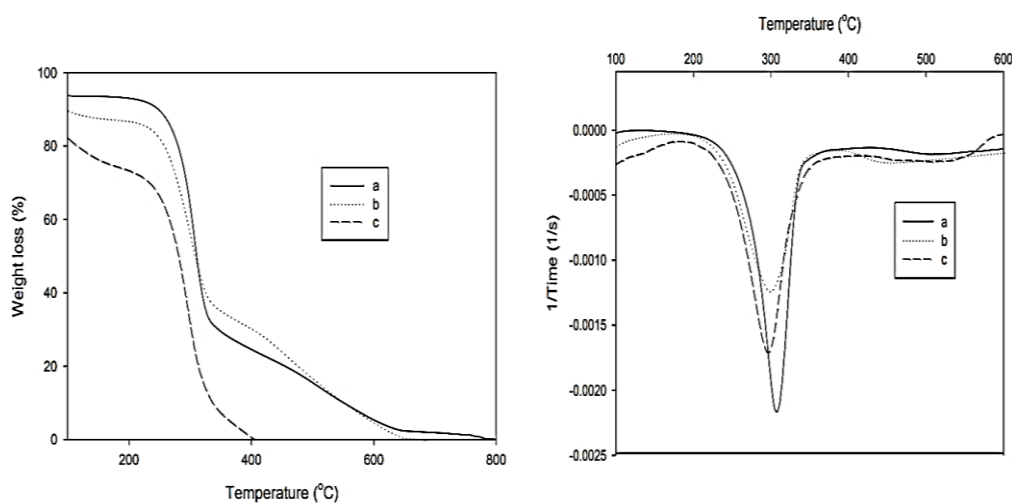
Figure 4.19: TGA Thermogram of (a) OPEFB Cellulose (b) Delignified OPEFB (c) Raw OPEFB (Pasma, Daik and Maskat, 2013).

Table 4.4: Summary of Organosolv Pretreatment with Different Solvents and Different Catalysts at Different Operating Conditions.

Solvent	Catalyst	Pretreatment Conditions				Optimum Conditions	DLP/ LC	CR/ CY	SY	Reference
		SC (%)	CC (%)	PT (°C)	RT (min)					
Ethanol	-	55-75	-	160	40-90	S/L: 1:10; SC: 65% PT: 160 °C; RT: 65 min	27.68 (P)	-	-	Mardawati, et al. (2018)
Ethanol	-	20-80	-	40-60	30-60	SC: 60%; PT: 48.20 °C RT: 30 min	13.00 (C)	-	35.70	Lee, et al. (2020)
Ethanol	NaOH	10-90	1-5	80	30	SC: 50%; CC: 3% PT: 80 °C; RT: 30 min	67.20 (P)	90.60 (R)	-	Chin, et al. (2019)
Ethanol	NaOH	20-80	2	40-60	30-60	SC: 60%; CC: 2% PT: 120 °C; RT: 60 min	10.80 (C)	-	40.20	Lee, et al. (2020)
Ethanol	H_2SO_4	10-90	1-5	80	30	SC: 50%; CC: 1-2% PT: 80 °C; RT: 30 min	53.20 (P)	95.80 (R)	-	Chin, et al. (2019)
Ethanol	H_2SO_4	20-80	2	40-60	30-60	SC: 60%; CC: 2% PT: 120 °C; RT: 60 min	11.30 (C)	-	38.60	Lee, et al. (2020)
Ethanol	H_2SO_4	65	0.5-2.0	160-200	45-90	S/L: 1:8; SC: 65% CC: 2%; PT: 160 °C RT: 78 min	70-80 (P)	96.03 (P)	-	Goh, et al. (2011)

*SC: Solvent Concentration, CC: Catalyst Concentration, PT: Pretreatment Temperature, RT: Retention Time, S/L: Solid to Liquid Ratio, DLP: Delignification Percentage, LC: Lignin Content, CR: Cellulose Recovery, CY: Cellulose Yield, SY: Sugar Yield

Table 4.4 (Continued)

Solvent	Catalyst	Pretreatment Conditions				Optimum Conditions	DLP/ LC	CR/ CY	SY	Reference
		SC (%)	CC (%)	PT (°C)	RT (min)					
Ethanol	H_2SO_4	0.5-2.0	35-75	80-120	30-90	S/L: 1:10; SC: 55% CC: 0.5%; PT: 120 °C RT: 60 min	-	-	98.89	Nurfahmi, et al. (2016)
Ethanol	H_2SO_4	50	0.13	180-220	30-120	S/L: 1:10; SC: 50% CC: 0.07%; PT: 210 °C RT: 90 min	90.00 (P)	80.00 (P)	-	Mondylaksita, et al. (2020)
Glycerol	-	70	-	65-85	3-7 hr	S/L: 1:20; SC: 70% PT: 85 °C; RT: 7 hr	55.10 (P)	70.79 (R)	-	Ibrahim, et al. (2012)
Glycerol	NaOH	70	5	65-85	3-7 hr	S/L: 1:20; SC: 70% CC: 5%; PT: 85 °C RT: 7 hr	70.30 (P)	82.03 (Y)	-	Ibrahim, et al. (2012)
Glycerol	NaOH	NA	5-20	121	15, 60	CC: 5%; PT: 121 °C RT: 15 min	9.17 (C)	87.98 (C)	-	Choopakar, et al. (2018)
Glycerol	H_2SO_4	NA	1-3	NA	5-12.5	S/C: 1:2; CC: 1% RT: 12.5 min	59.16 (P)	98.00 (Y)	55.85	Fatriasari, et al. (2016)

Table 4.4 (Continued)

Solvent	Catalyst	Pretreatment Conditions				Optimum Conditions	DLP/ LC	CR/ CY	SY	Reference
		SC (%)	CC (%)	PT (°C)	RT (min)					
Glycerol	CH$_3$COOH	70	5	65-85	3-7 hr	S/L: 1:20; SC: 70% CC: 5%; PT: 85 °C RT: 7 hr	51.00 (P)	85.17 (R)	-	Ibrahim, et al. (2012)
Ethylene Glycol	NaOH	50	3	60-140	15-75	SC: 50%; CC: 3% PT: 80 °C RT: 45 min	75.10 (P)	90.40 (R)	-	Chin, et al. (2019)
AA: FA	HCL	AA: 70-100 FA: 0-30	0.5	130	60	AA: FA=85:15 CC: 0.5% PT: 130 °C RT: 60 min	7.78 (C)	75.00 (C)	-	Hidayati, et al. (2017)
AA	-	5-15	-	115-125	60-90	SC: 15%; PT: 125 °C RT: 60 min	-	-	40.00	Harahap, et al. (2020)
FA	H$_2$O$_2$	20	10	85	2 hr	SC: 20%; CC: 10% PT: 85 °C; RT: 2 hr	-	64.00 (Y)	-	Nazir, et al. (2013)

Table 4.4 (Continued)

Solvent	Catalyst	Pretreatment Conditions				Optimum Conditions	DLP/ LC	CR/ CY	SY	Reference
		SC (%)	CC (%)	PT (°C)	RT (min)					
Oxalic Acid	-	1	-	160-200	2.5	S/L: 1:10; SC: 1% PT: 180 °C RT: 2.5 min	25.26	-	-	Solihat, et al. (2017)
Oxalic Acid	-	1	-	160-200	5-15	S/L: 1:10; SC: 1% PT: 160 °C; RT: 10 min	-	-	46.13	Solihat, et al. (2020)
Acetone	-	50	-	300-400	5 hr	SC: 50%; PT: 400 °C RT: 5 hr	-	26.50 (Y)	-	Sarwono, et al. (2016)
Acetone	-	20	-	275	60	SC: 20%; PT: 275 °C RT: 60 min	-	65.30 (Y)	-	Fan, et al. (2011)
Acetone	$C_2H_4O_3$	80	10-30	35-75	6-12	SC: 2%; CC: 20% PT: 35 °C; RT: 9 hr	47.00 (P)	53.00 (C)	-	Palamae, et al. (2014)
Acetone	H_2O_2	80	10-30	35-75	6-12	SC: 2%; CC: 10% PT: 75 °C; RT: 9 hr	<2.00 (P)	38.50 (C)	-	Palamae, et al. (2014)

Table 4.4 (Continued)

Solvent	Catalyst	Pretreatment Conditions				Optimum Conditions	DLP/ LC	CR/ CY	SY	Reference
		SC (%)	CC (%)	PT (°C)	RT (min)					
-	NaOH	-	4	121	60	S/L: 1:10; CC: 4% PT: 121 °C RT: 60 min	20.40 (C)	48.50 (C)	84.40	Markom (2016)
-	H_2SO_4	-	4	121	60	S/L: 1:10; CC: 4% PT: 121 °C RT: 60 min	31.20 (C)	47.70 (C)	34.00	Markom (2016)
-	H_2SO_4	-	4	121	60	S/L: 1:10; CC: 4% PT: 121 °C RT: 60 min	30.00 (P)	36.10 (C)	84.00	Kim and Kim (2013)
-	KOH	-	1M-5M	30-50	2-6 hr	CC: 3M; PT: 40 °C RT: 4 hr	-	29.37 (Y)	-	Hanim Saleh, et al. (2016)

4.3   Model Building in Response Surface Methodology

Corresponding to the study by Goh, et al. (2011), the evaluation of organosolv pretreatment was based on 20-runs of the CCD model generated by Design-Expert software, as shown in Table 4.5. The table shows considerable variation in the actual, predicted, and residual value of EOL and GLU recovered from the pretreated OPEFB under different parameters' conditions. Besides, the result reveals a good agreement between the predicted value and the actual experimental data, owing to the small residual value between them.

Table 4.5: Experimental and Predicted Value of EOL and GLU Recovery.

Run	Actual Value		Predicted Value		Residual	
	EOL.R	GLU.R	EOL.R	GLU.R	EOL.R	GLU.R
1	26.30	77.00	24.66	75.88	1.64	1.12
2	2.10	55.60	10.75	54.43	8.65	1.17
3	26.30	77.00	24.66	75.88	1.64	1.12
4	52.00	61.20	53.75	62.64	1.75	1.44
5	18.70	87.20	18.67	84.13	0.028	3.07
6	47.20	61.10	49.32	61.28	2.12	0.18
7	47.80	81.10	45.82	81.58	1.98	0.48
8	18.60	98.40	17.68	102.04	0.92	3.64
9	24.50	66.30	25.44	66.43	0.94	0.13
10	0.000	57.10	0.62	56.28	0.62	0.82
11	37.80	65.40	35.22	66.85	2.58	1.45
12	26.30	77.00	24.66	75.88	1.64	1.12
13	0.000	57.90	-1.41	63.74	1.41	5.84
14	43.40	88.30	50.73	88.01	7.33	0.29
15	26.30	77.00	24.66	75.88	1.64	1.12
16	26.30	77.00	24.66	75.88	1.64	1.12
17	26.30	77.00	24.66	75.88	1.64	1.12
18	48.70	61.80	42.51	63.54	6.19	1.74
19	9.70	71.40	14.09	69.35	4.39	2.05
20	19.40	70.20	16.57	69.43	2.83	0.77

*EOL.R: Ethanol Organosolv Lignin Recovery, GLU.R: Glucose Recovery

4.3.1 Statistical Analysis

The significance of the model, individual terms, and their interaction on the responses (EOL and GLU recovery), were examined through the analysis of variance (ANOVA) thus testing and verifying the adequacy and ability of the fitted second-order model (Goh, et al., 2011). Figure 4.20 and Figure 4.21 show ANOVA of the regression model for EOL recovery and GLU recovery, respectively.

```
Response    1              EOL Recovery
      ANOVA for Response Surface Reduced Quadratic model
Analysis of variance table [Partial sum of squares - Type III]
              Sum of                 Mean        F      p-value
Source        Squares     df    Square    Value   Prob > F
Model         4665.80      6    777.63    43.48   < 0.0001    significant
  A-SA Concen 2718.78      1    2718.78  152.01   < 0.0001
  B-Reaction 1 1072.56     1    1072.56   59.97   < 0.0001
  C-Residence  456.64      1    456.64    25.53    0.0002
  AC           162.14      1    162.14     9.07    0.0100
  BC           142.80      1    142.80     7.98    0.0143
  B²           116.79      1    116.79     6.53    0.0239
Residual       232.51     13     17.89
  Lack of Fit  232.51      8     29.06
  Pure Error     0.000     5      0.000
Cor Total     4898.31     19

Std. Dev.        4.23          R-Squared        0.9525
Mean            26.39          Adj R-Squared    0.9306
C.V. %          16.03          Pred R-Square    0.8401
PRESS          783.03          Adeq Precision  22.046
-2 Log Likeliho 105.82         BIC             126.79
                               AICc            129.15
```

Figure 4.20: ANOVA for EOL Recovery.

```
Response    2              GLU Recovery
      ANOVA for Response Surface Reduced Quadratic model
Analysis of variance table [Partial sum of squares - Type III]
              Sum of                 Mean        F      p-value
Source        Squares     df    Square    Value   Prob > F
Model         2455.40      8    306.93    42.86   < 0.0001    significant
  A-SA Concen  588.92      1    588.92    82.25   < 0.0001
  B-Reaction 1  77.42      1     77.42    10.81    0.0072
  C-Residence    7.56      1      7.56     1.06    0.3264
  AB          1182.90      1   1182.90   165.20   < 0.0001
  AC           173.06      1    173.06    24.17    0.0005
  BC           191.10      1    191.10    26.69    0.0003
  B²           182.39      1    182.39    25.47    0.0004
  C²            99.52      1     99.52    13.90    0.0033
Residual        78.77     11      7.16
  Lack of Fit   78.77      6     13.13
  Pure Error     0.000     5      0.000
Cor Total     2534.17     19

Std. Dev.        2.68          R-Squared        0.9689
Mean            72.25          Adj R-Squared    0.9463
C.V. %           3.70          Pred R-Square    0.8561
PRESS          364.55          Adeq Precision  26.518
-2 Log Likeliho  84.17         BIC             111.13
                               AICc            120.17
```

Figure 4.21: ANOVA for GLU Recovery.

A higher Fischer F test value and a lower p-value of less than 0.05 can be used to verify the significance of each regression coefficient. The regression models for EOL recovery and GLU recovery were significant with a very low probability value ($p < 0.0001$), along with the higher F test value of 43.48 and 42.86 respectively. Besides, the value of "Prob > F" less than 0.05 indicates the model terms are significant. A, B, C, AC, BC, and B^2 were significant ($p < 0.05$) to affect the EOL recovery. Apart from that, A, B, AB, AC, BC, B^2, and C^2 were significant ($p < 0.05$) in influencing the GLU recovery. However, residence time (C) was insignificant for this response owing to its "Prob > F" value larger than 0.10. Consequently, the significant model terms have contributed to the fitted quadratic equations (expressed as coded values) as shown in Equation 4.1 and Equation 4.2, which were analysed by multiple regression using the Design-Expert software. In the equation, a positive sign represents a synergistic effect, and a negative sign represents an antagonistic effect.

$$\text{EOL recovery,} \ y_1(\%) = 24.83 + 13.04A + 8.19B + 5.34C + 4.50AC$$
$$-4.22BC + 2.07B^2 \qquad (4.1)$$

$$\text{GLU recovery,} \ y_2 \ (\%) = 75.96 + 6.07A - 2.20B - 0.69C - 12.16AB$$
$$-4.65AC + 4.89BC - 2.63B^2 - 1.94C^2 \qquad (4.2)$$

Where,

A = SA Concentration (%)

B = Reaction Temperature (°C)

C = Residence Time (min)

Other than that, R-squared determines the goodness of fit of the selected regression model. The computed R^2 coefficient for EOL recovery and GLU recovery were 0.9525 and 0.9689 respectively, implying that 95.25 % and 96.89 % of the variability in the respective response could be explained by the process variables and their interactions. In other words, the R^2 coefficient was closely resembled unity, indicating that the graph plots of the model lie close enough to the straight line, given a convincing good estimate of the system responses within the research range. Therefore, the correlation between the experimental

value and the predicted value can be accepted (Mardawati, et al., 2018). The adjusted R^2 for EOL recovery and GLU recovery was 0.9306 and 0.9463 respectively, which signifies that only 6.94 % and 0.05 % of the total variations were not predicted by the respective model. Equivalently, the predicted R^2 for EOL recovery and GLU recovery was 0.8401 and 0.8561 respectively. It is also worth mentioning that the adjusted and predicted R^2 values were within 0.2 among each other.

Furthermore, the statistical parameter "Adeq Precision" measures the signal-to-noise. In the analysis, adequate precision was provided as 22.046 for EOL recovery and 26.518 for GLU recovery, much higher than the desirable ratio of 4. This shows that there are many appropriate signals, and the modified regression model can be used to navigate the design space. Other than that, the residual can be divided into two parts: lack of fitting error (LOF) and pure error. However, the sum of squares (SS) and mean squares (MS) of pure error were zero, which signifies that no P-value and F-value for lack of fit test (Thoai, 2016). In this situation, more unique design points than model coefficients may be the potential factor leading to no lack of fit statistics.

4.3.2 Interactive Effects of Process Variables on Glucose Recovery

The synergistic effects of SA concentration (A), reaction temperature (B), and residence time (C) on the recovery of GLU and EOL were examined through the 3D response surface contour graph and the diagnostic graph. These graphs illustrate the responses at each interactive effect between two varying process variables while keeping the other variable constant at the midpoint value.

Figure 4.22 characterises a positive interactive effect of temperature and SA concentration on GLU recovery for a pretreatment duration of 60 min. Looking into each variable, SA concentration showed a higher linear effect on GLU recovery ($p < 0.0001$), while temperature had a smaller effect on GLU recovery ($p = 0.0072$). However, the quadratic effect of these two variables was highly significant, with a p-value less than 0.0001. Based on the graph, under diluted acid conditions, the recovery rate of glucose gradually increases as the temperature rises. Besides, it was observed that at a low temperature of 160 °C, the recovery rate of glucose increased sharply with the increased SA

concentration, and the maximum recovery rate was achieved under the concentrated condition above 1.63 % SA. The amount of energy supplied at low temperatures was insufficient to overcome the activation energy for the solubilization of biomass. In this case, the amount of hydrolysing agent (H_3O^+) used as the catalyst will significantly affect the pretreatment reaction, which in turn affects the recovery rate of glucose.

Apart from that, it can be noted that a critical concentration of hydronium ion greater than 1 % was required to effectively hydrolyse and dissolve the lignin fragments into the solvent, thus given a higher GLU recovery. However, as the temperature was increased, the positive impact of the concentrated acid medium was decreased. There was a significant decline in GLU recovery with the addition of SA concentration >1 % at temperatures higher than 180 °C. This finding explains the rapid decomposition of sugar under severe pretreatment conditions. In addition to excessively higher temperatures, undesirable toxic substances may be formed, including organic acids (e.g. acetic acid, acetaldehyde) which cause a severe reduction in hydrolysis activity. In this situation, the applied enzyme may also be disrupted in terms of its membrane structure and functionality, leading to a decrease in enzymatic activity (Loh, Kassim and Bukhari, 2018).
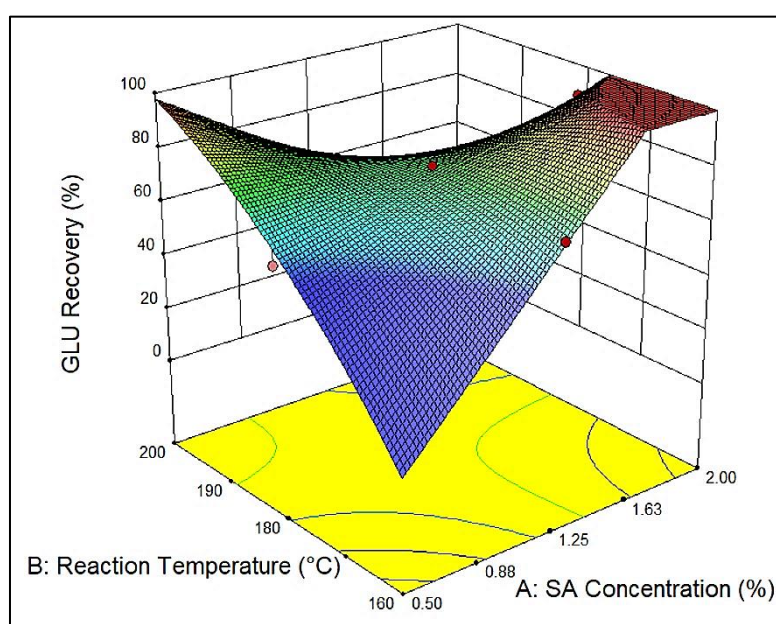

Figure 4.22: 3D Response Surface of the Interaction between SA Concentration (A) and Reaction Temperature (B) on GLU Recovery.

Figure 4.23 provides a 3D representation of the significant interactive effects (p = 0.0005) between SA concentration and residence time on GLU recovery at 180 °C. As shown in the figure, the obtained slope for changes in SA concentration was steeper than the changes in residence time, showing a more significant influence of concentration on GLU recovery. This similar trend can justify with the higher F value (82.25) and low p-value (< 0.0001) of SA concentration compared to residence time with a low F value (1.06) and higher p-value (0.3264). Besides, it is worth noting that the use of a concentrated SA medium can achieve high GLU recovery in a short residence time. Under diluted acid conditions, a moderate recovery of glucose was obtained at a long residence time. Thereafter, the recovery was declined insignificantly as the concentration of SA was increased. Apart from that, low glucose recovery was attained at two approaches: short residence time with diluted SA concentration; long residence time with a concentrated acidic medium. The finding explains that a relatively short time and diluted acidic medium are insufficient to solubilize the lignin and hemicellulose. Moreover, the biomass that has been pretreated for a long time under highly acidic conditions may undergo glucose decomposition. Also, lignin may condense at this stage and limit the digestibility of pulp by absorbing the cellulolytic enzymes from the solvent.
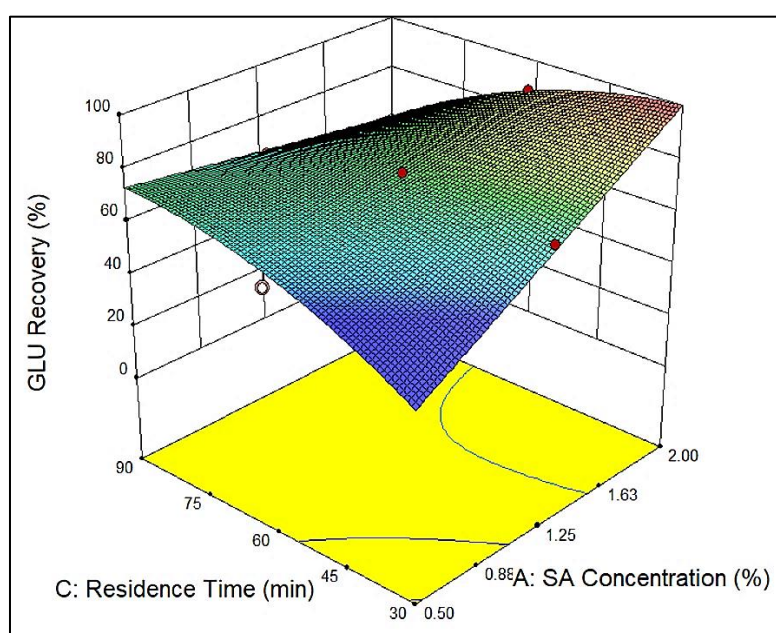

Figure 4.23: 3D Response Surface of the Interaction between SA Concentration (A) and Residence Time (C) on GLU Recovery.

Figure 4.24 shows the 3D response surface plot, which depicts the effect of the interaction between temperature and time on the GLU recovery at a SA concentration of 1.25 %. According to the graph, it is worth noting that temperature was seemed to have a slightly greater effect on GLU recovery than time, although both of the process variables were implied relatively low F values corresponding with a less significant effect. Besides, the quadratic influence of these two variables was significant with a p-value of 0.0003. A high glucose recovery rate of 77 % was observed at the midpoints of both factors B (60 mins) and C (180 °C). Another relatively higher recovery of glucose was observed at high reaction temperature and long residence time. Under severe pretreatment conditions, hemicellulose is almost completely dissolved in the solvent and resulting in a higher digestibility of the pulp, which can explain this finding. Moreover, the low GLU recovery rate was obtained at two approaches as follows: long residence time at a low temperature; short residence time at a high temperature. This finding can be explained that severe temperature and prolonged duration could lead to potential glucose decomposition due to the formation of inhibitory products.
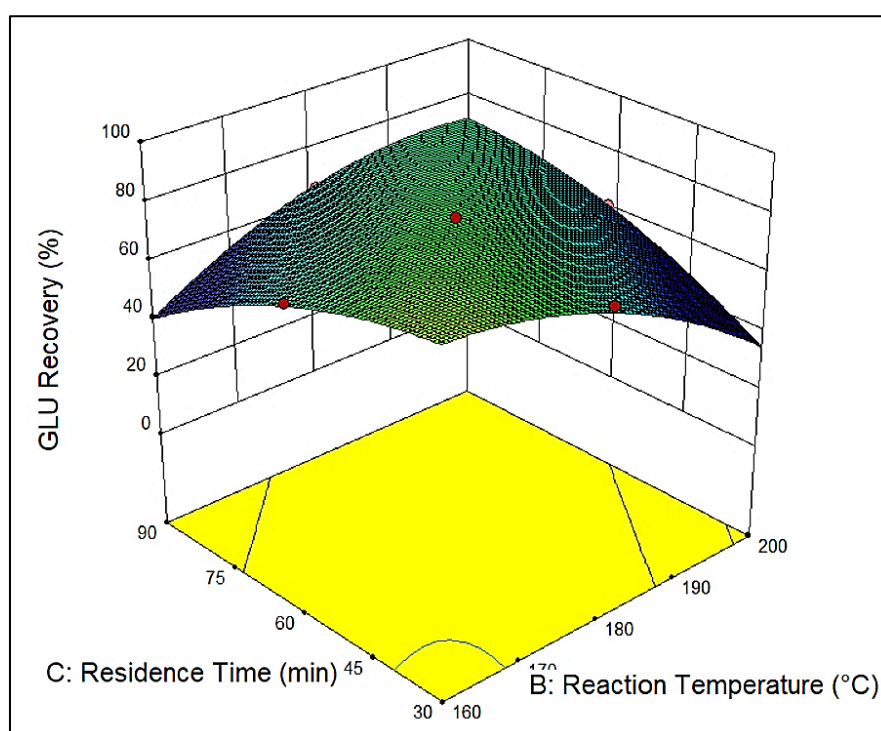

Figure 4.24: 3D Response Surface of the Interaction between Reaction Temperature (B) and Residence Time (C) on GLU Recovery.

4.3.3 Interactive Effects of Process Variables on EOL Recovery

SA concentration and residence time showed a strong and directly proportional interaction (p = 0.0100) with EOL recovery at 180 °C. In this case, concentration and time have a significant effect on the recovery of EOL, which is due to their small p values < 0.0001 and 0.0002 respectively. According to the reported p-value, concentration has a higher effect compared to time. According to Figure 4.25, it is worth observing that by extending the pretreatment time using diluted acidic media, there is no significant effect on the recovery rate of EOL, indicating low delignification efficiency. In the case of insufficient residence time, the concentration of SA cannot effectively increase the recovery rate of EOL. As the concentration of SA increases, a more pronounced effect of residence time can be observed, where the maximum EOL recovery rate (maximum delignification) was achieved in a concentrated acidic medium for a prolonged duration. The fibrous structure of OPEFB is generally resistant to thermal attack and acidic media without giving sufficient reaction duration. Therefore, harsh conditions may be preferred to break down the structure. This finding has previously been demonstrated in the study of Mardawati, et al. (2018), where the degradation of lignin increases with a greater pretreatment severity (higher concentration and longer reaction time) at smaller particle sizes.
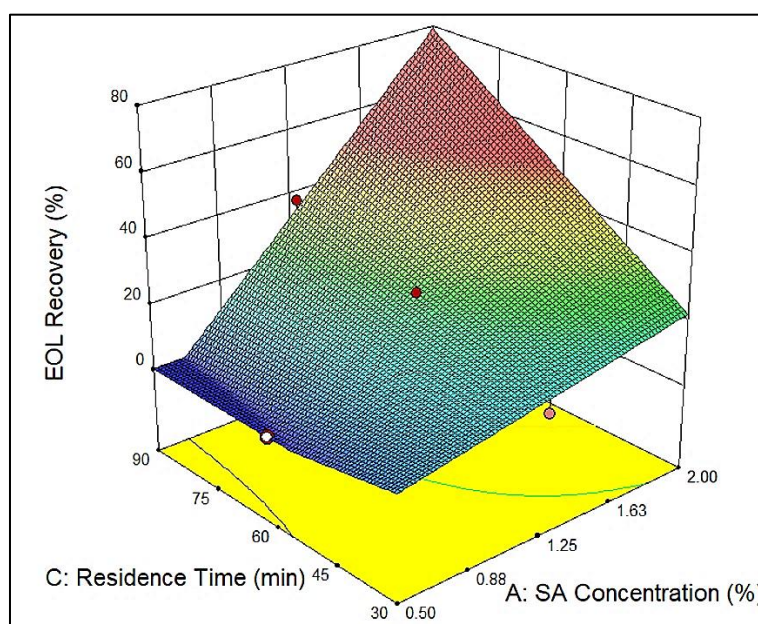
Figure 4.25: 3D Response Surface of the Interaction between SA Concentration (A) and Residence Time (C) on EOL Recovery.

Based on Figure 4.26, different interactions between reaction temperature and residence time at SA concentration of 1.25 % were studied. Compared with the residence time, it is worth observing that the influence of temperature was highly significant on the recovery rate of EOL, in conjunction with its low p-value of less than 0.0001. The quadratic effect of these two variables was significant with a p-value of 0.0143. At low temperatures, a longer pretreatment time was required to obtain a higher EOL recovery rate. The model has predicted that a less significant reduction of EOL recovery rate under the condition of continuously increasing pretreatment duration at high temperature. This situation explains that excessively high temperatures under prolonged duration may initiate lignin recondensation, resulting in a decrease in EOL recovery or in other words, a decrease in delignification.
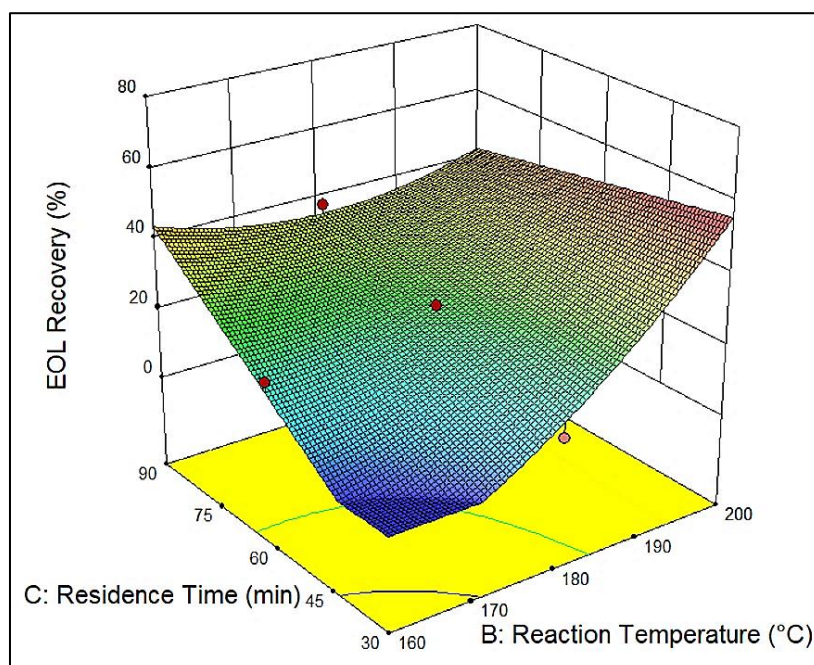
Figure 4.26: 3D Response Surface of the Interaction between Reaction Temperature (B) and Residence Time (C) on EOL Recovery.

4.3.4   Validation of Statistical Model

Corresponding to the discussion in Section 4.3.2 and Section 4.3.3, there is an interaction between process variables until a certain point where the graph lines begin to intersect each other. However, the parallel lines signify that there is no interaction, which does not cover throughout the interaction analysis. Figure

4.27 (a) and (b) present the interaction plots of a positive correlation between SA concentration and GLU recovery at low temperature and short residence time, respectively. Whereas, a negative interaction between SA concentration and GLU recovery was observed at high temperature for case (a) and at long residence time for case (b). Moreover, Figure 4.27 (c) shows a positive relationship between reaction temperature and GLU recovery at long residence time compared to negative interaction happened at short residence time.

Figure 4.27: Interaction Plot of (a) Concentration and Temperature; (b) Concentration and Time; (c) Temperature and Time.

Other than that, Figure 4.28 (a) shows the interaction between SA concentration and EOL recovery changes direction based on the residence time. Regardless of the pretreatment duration, positive interaction between

concentration and EOL recovery can be observed. However, the interaction effect of the long residence time is greater than that of the short residence time. Furthermore, Figure 4.28 (b) depicts the strong interaction between reaction temperature and EOL recovery at short residence time, whereas less interaction at long residence time.
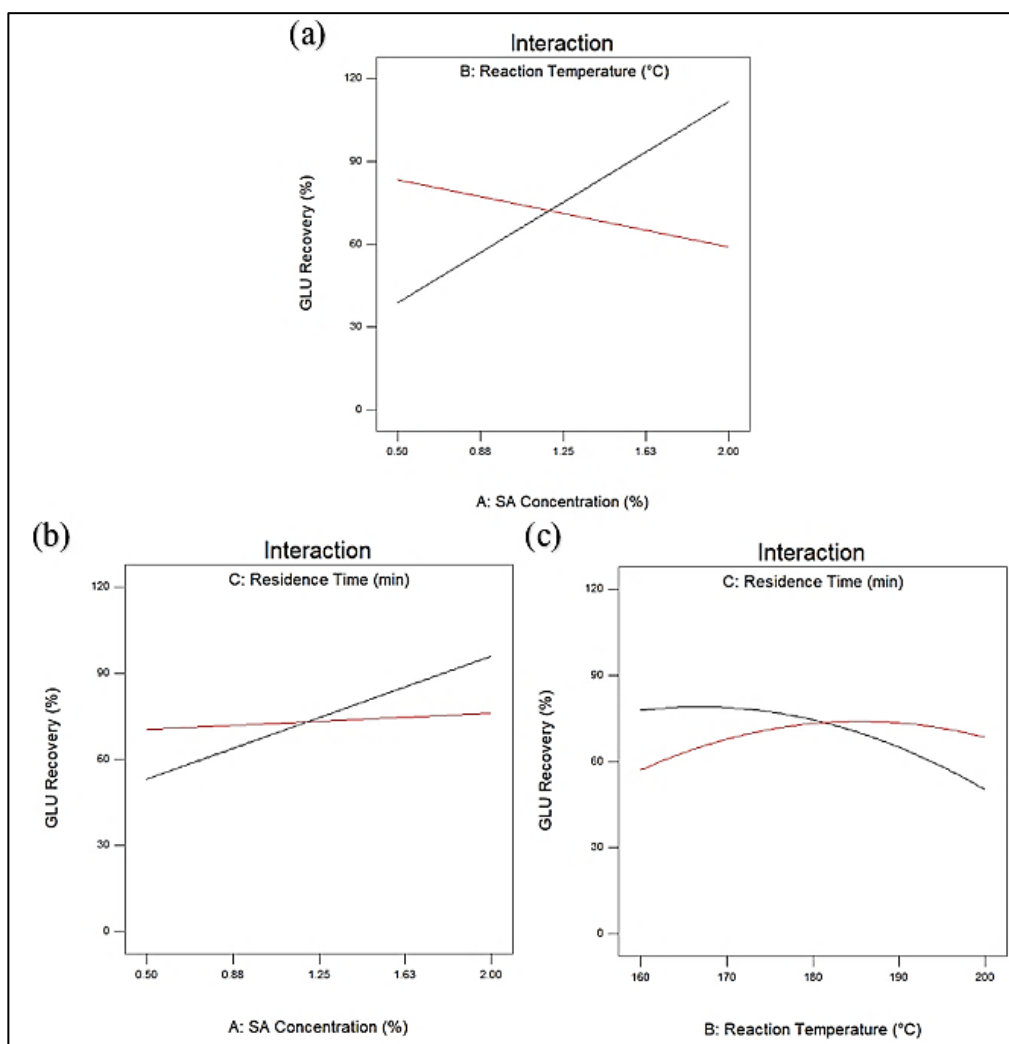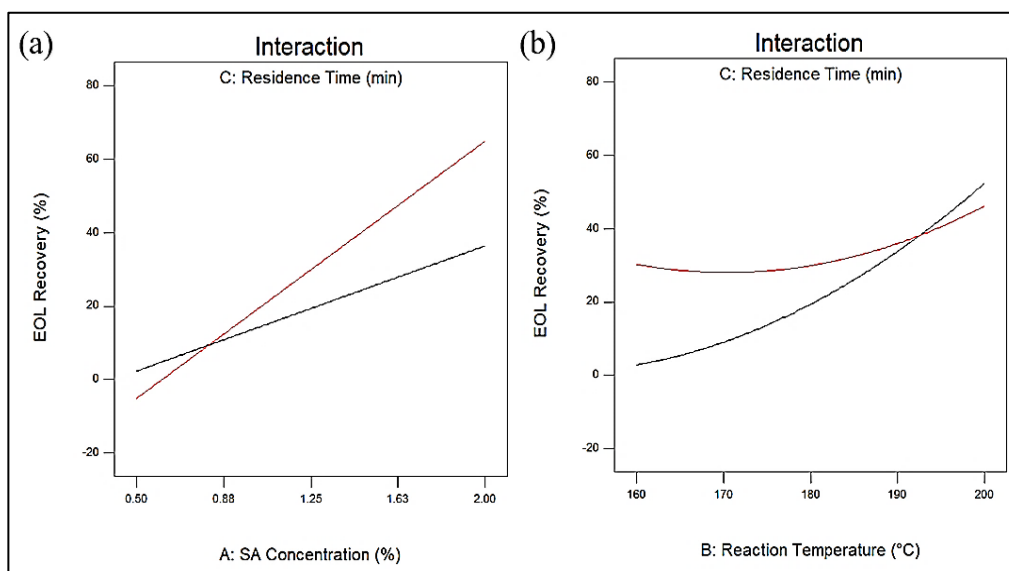

Figure 4.28: Interaction Plot of (a) Concentration and Time; (b) Temperature and Time.

The diagnostic plots were being examined to ensure that the statistical assumptions are consistent with the ANOVA data analysis. Figure 4.29 and Figure 4.30 show the normal probability plot in terms of the percentage of studentized residuals for GLU recovery and EOL recovery, respectively. It can be seen that the standard deviation between the actual response and the predicted response follows a normal distribution, where the residuals are distributed near the straight line, indicating that the experimental results have no abnormalities.

Although some runs differed more from their predicted value than others, the graph plots of residuals versus predicted response show that most runs still lied within the red control limits, which are ± 4.00453 for GLU recovery and ± 3.80652 for EOL recovery. However, only one outlier is observed on this plot which may be assumed to result from physical causes such as a mechanical breakdown, thus subjecting to ignorance of this discrepant value in the analysis.

Hence, this finding confirms the assumption of constant variance and shows that the model used is adequate.

Looking into the graph plots of predicted versus actual values for both GLU and EOL recovery, it was obvious to note that the points lied close to the straight line, indicating the predicted and actual responses were in satisfying agreement with each other. However, there are some noticeable points above and below the diagonal line, which represent overestimated and underestimated responses that may be caused by the failure of experimental analysis equipment.
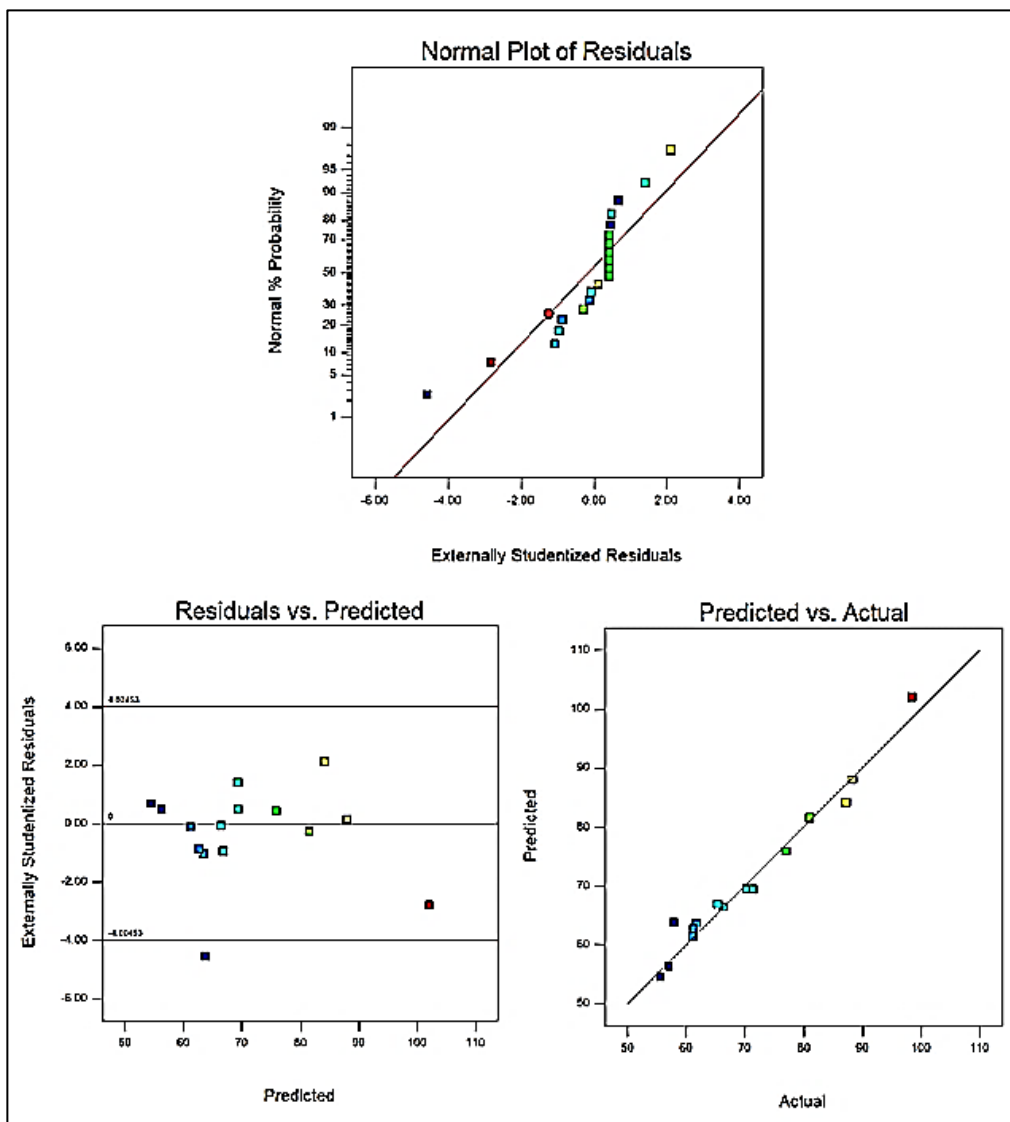
Figure 4.29: Diagnostic Plots for GLU recovery.
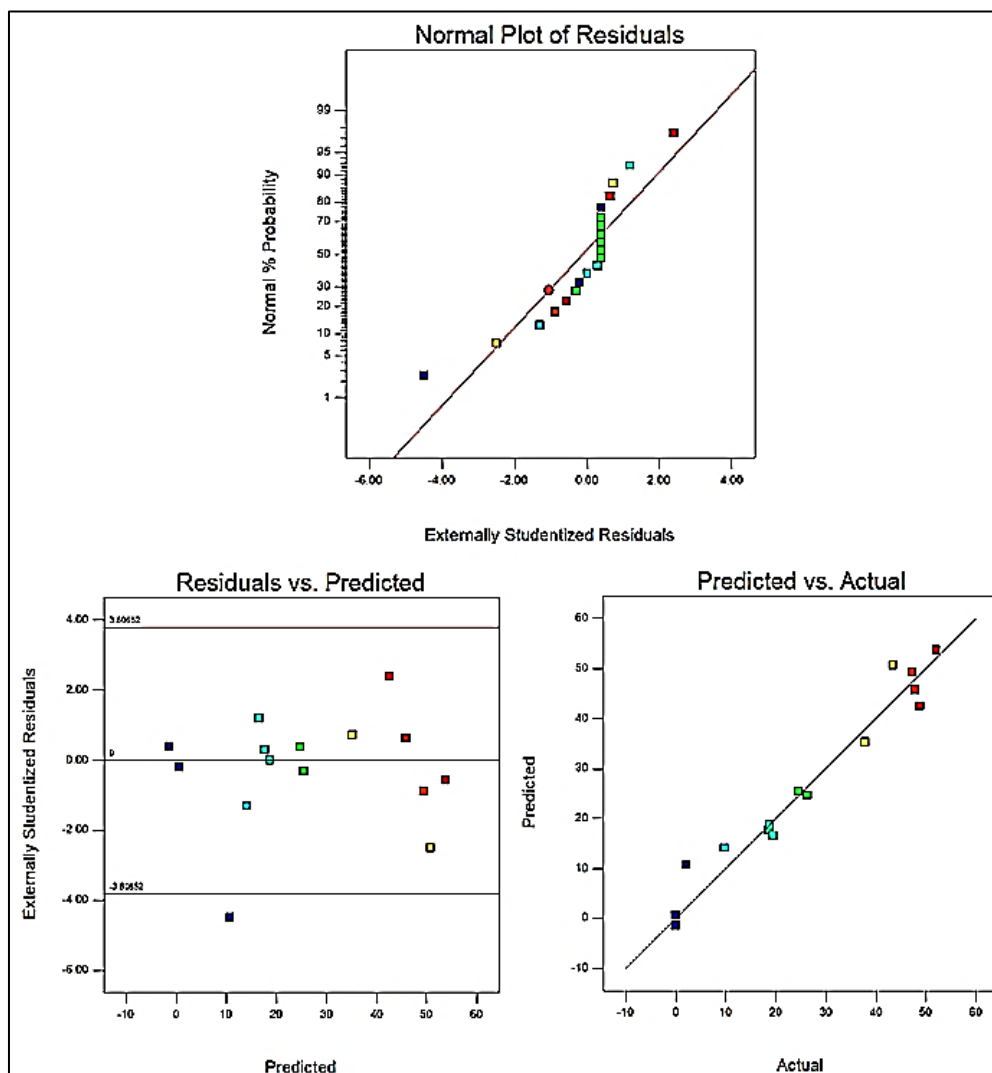
Figure 4.30: Diagnostic Plots for EOL Recovery.

4.3.5 Summary

The significant synergistic effects among sulphuric acid (SA) concentration, reaction temperature, and residence time have greatly varied GLU recovery and EOL recovery of organosolv pretreated OPEFB. Based on the RSM modelling, the optimum conditions of process variables were listed as follows: 1.97 % SA; 172 °C; 68 min, which given a predicted GLU recovery and EOL recovery of 99.07 % and 53.37 % respectively. This determined optimum conditions and responses were in good agreement with the outcomes obtained by Goh, et al. (2011) as follows: 2 % SA; 160 °C; 78 min, which given GLU recovery of 100 %. Conjuntively, good model desirability of 1 has revealed that the adopted surface response model was valid for optimising the organosolv pretreatment on OPEFB.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1   Conclusions

In this research project, the comparative study between different types of organosolv pretreatments on OPEFB was first carried out. HBP or LBP alcohol pretreatment have outstanding performances compared with organic acid pretreatment and ketone pretreatment, particularly in the aspect of higher reaction yield. Besides, pretreatment with LBP alcohol or ketone could lead to high process risk due to highly volatile solvents used. Despite the high energy consumption of operating processes, all the studied organosolv pretreatments allow solvent recovery which would compensate for the high operational cost. Their pretreatment processes are considered environmentally friendly as well.

The effect of different solvents and catalysts used in organosolv pretreatment were studied and compared. HBP or LBP alcohols were tended to provide high cellulose recovery and moderate delignification compared with organic acids and ketones. Organic acids may potentially lead to acetylation and formylation reactions with cellulose, resulting in low cellulose recovery compared to other solvent types. Other than that, acid-catalysed pretreatment tended to degrade hemicellulose polymers than lignin, while base-catalysed pretreatment was more selective in delignification. Also, acid catalysts provided higher pretreatment efficiency than alkaline catalysts.

The potential process factors that affect the efficiency of organosolv pretreatment had been explored in this research. The higher the concentration of solvent and catalyst, the higher the delignification, cellulose recovery/yield, and sugar yield. A similar concept was applied for reaction temperature and residence time. However, any severe condition of a process factor or a combination between them may lead to the generation of undesirable inhibitory compounds thus limiting the cellulose recovery and sugar yield. In this situation, lignin recondensation may occur and cause a decrease in delignification. Moving forwards, for organosolv pretreated OPEFB, more cracks and a porous

surface with lower crystallinity index were investigated, along with typical spectra signified the removal of hemicellulose and lignin.

Based on the organosolv pretreatment model built via Design-Expert Software, the synergistic effects between SA concentration, temperature, and time were analysed to be significant in impacting both recoveries of EOL and GLU. Compared to temperature and time, SA concentration possessed the most dominant influence on the responses. At low temperatures or short durations, GLU recovery increased sharply with an increase in SA concentration. For the case of temperatures higher than 180 °C or prolonged pretreatment time, GLU recovery significantly declined with the addition of SA concentration >1 %. A more pronounced effect of pretreatment time on EOL recovery was observed with an increasing SA concentration. Excessively high temperatures under prolonged durations slightly reduced EOL recovery (less delignification). Other than that, the optimum process conditions (1.97 % SA; 172 °C; 68 min) predicted a GLU recovery of 99.07 %, which was in good agreement with 100 % GLU recovery obtained by Goh, et al. (2011). To conclude, all the objectives were achieved at the end of this research project.

5.2   Recommendations for Future Work

Several improvements are recommended for future related projects to ensure the significance and comprehensiveness of the information delivered:

1) Different samples of lignocellulosic biomass involving hardwood, softwood, and grass should be studied for organosolv pretreatment.

2) Additional pretreatment parameters including solvent to liquid ratio, particle size, and biomass loading should be considered, hence leading to a more complex study that may greatly contribute to new findings.

3) The model developed in Design Expert should involve broader perspectives' analysis for different factors on the responses.

4) Different responses including sugar yield and biofuel yield should be included to discover any potential energy optimisation for the development of renewable energy.

5) Laboratory experiments are suggested to be performed, thus verifying the outcome of the model built.

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