



Faculty of Engineering

Subcritical Water-supercritical CO₂ (SCW-SCCO₂) Hydrothermal Liquefaction (HTL) of Oil Palm Derived Lignin via Low-Transition-Temperature Mixtures (LTTMs) into Bio-oil

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**Master of Engineering
2025**

Subcritical Water-supercritical CO₂ (SCW-SCCO₂) Hydrothermal
Liquefaction (HTL) of Oil Palm Derived Lignin via Low-Transition-
Temperature Mixtures (LTTMs) into Bio-oil

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A thesis submitted

In fulfillment of the requirements for the degree of Master of Engineering

(Chemical Engineering)

Faculty of Engineering
UNIVERSITI MALAYSIA SARAWAK
2025

DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.


.....

Signature

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ACKNOWLEDGEMENT

First and foremost, I would like to sincerely thank Dr. Yiin Chung Loong, my supervisor at Universiti Malaysia Sarawak (UNIMAS), whose understanding of the field and insight guided me throughout my project. Being a mechanical engineering student, learning about renewable energy was a worthwhile experience that, with the support of my supervisor, enabled me to finish this research project.

I would like to thank the management, assistant engineers, laboratory technicians, science officers and other staffs from the department and faculty of the Universiti Malaysia Sarawak for their assistance. I would like to acknowledge the funding supports from Ministry of Higher Education, Malaysia, Fundamental Research Grant Scheme, FRGS/1/2020/TK0/UNIMAS/03/2 which helped me financially as a Graduate Research Assistant. Thank you to Jennie Siew Zhen Ngu and Prof. Dr. Armando T. Quitain from Kumamoto University (KU) for collaborating with this research by conducting experiments and providing significant data for research work. I am also appreciative of Masranti Plantation Sdn Bhd for supplying a large amount of EFB, which made the project's launch possible.

Finally, but just as importantly, I want to thank my friends and family for their ongoing encouragement to finish my research endeavour and for their unending support in every way.

ABSTRACT

Our current environmental challenges demand long-term prospective efforts for sustainable development to be solved. The pursuit of green energy has designed more environmentally friendly designer solvents are produced known as Deep Eutectic Solvents (DES) and later dubbed Low Transition Temperature Mixtures (LTTMs). Empty Fruit Bunch (EFB) from the oil palm industry was delignified using LTTMs to extract lignin and later undergo subcritical water-supercritical CO₂ (SCW-SCCO₂) hydrothermal liquefaction (HTL) to produce bio-oil. The hydrogen bonding in choline chloride (ChCl)-malic acid LTTMs have been determined through FT-IR analysis. This system's delignification of EFB removed a considerable 31.98% of lignin in just 4 hours and the LTTMs showed a recoverability $\geq 90\%$ (1st recovery = 93.8% & 2nd recovery = 91.1%). SCW-SCCO₂ HTL was investigated in this research, and ideal conditions were found at 275°C, 25 MPa, with a 1:3 lignin-to-water ratio. Phenolic compounds were identified using GC-MS analysis as the primary target compounds in bio-oil analysis, suggesting a route from EFB to lignin, derivatives, and eventually phenolics. Based on the kinetic studies, the rate constant increased from 9.59×10^{-4} to $1.06 \times 10^{-3} \text{ s}^{-1}$ with temperatures between 250-300°C. A temperature-dependant kinetic model was demonstrated using the Arrhenius equation, which estimated the activation energy (E) to be 4.2 kJ/mol and the pre-exponential factor (A) to be $2.13 \times 10^{-3} \text{ s}^{-1}$. An empirical kinetic model (modified Reverchon-Sesti Osseo) was used in predicting the bio-oil yield with an outcome of R² for 250°C (0.87), 275°C (0.104) and 300°C (0.843).

Keywords: Lignin, bio-oil, low transition temperature mixtures

Liquefikasi Hidrotermal (HTL) Air Subkritis-superkritis Karbon Dioksida (SCW-SCCO₂) dari Lignin Kelapa Sawit melalui Campuran Suhu-Transisi-Rendah (LTTMs) menjadi Bio-minyak

ABSTRAK

Cabaran alam sekitar memerlukan usaha jangka panjang untuk pembangunan mampan. Usaha mencari tenaga hijau telah mencipta pelarut-pelarut reka bentuk yang lebih mesra alam yang dikenali sebagai Pelarut Eutektik Mendalam (DES) dan kemudiannya dinamakan Campuran Suhu Transisi Rendah (LTTMs). Buah Tandans Kosong (EFB) dari industri kelapa sawit telah dideglignifikasi menggunakan LTTMs untuk mengekstrak lignin dan mengalami likuifikasi hidrotermal (HTL) air subkritis-superkritis karbon dioksida (SCW-SCCO₂) untuk menghasilkan bio-minyak. Pemadanan hidrogen dalam LTTMs choline chloride (ChCl)-asid malik telah ditentukan melalui analisis FT-IR. Pengelupasan EFB oleh sistem ini telah mengeluarkan sejumlah 31.98% lignin dalam masa 4 jam sahaja, dan LTTMs menunjukkan kebolehsembuhan $\geq 90\%$ ($1^{st} = 93.8\%$ & $2^{nd} = 91.1\%$). SCW-SCCO₂ HTL telah disiasat dan keadaan ideal ditemui pada suhu 275°C, tekanan 25 MPa, dengan nisbah 1:3 lignin-ke-air. Sebatian fenolik dikenal pasti melalui GC-MS analisis sebagai sebatian utama, mencadangkan laluan dari EFB kepada lignin, derivatif, dan sebatian fenolik. Berdasarkan kajian kinetik, pemalar laju meningkat dari 9.59×10^{-4} hingga $1.06 \times 10^{-3} \text{ s}^{-1}$ dengan suhu antara 250-300°C. Model kinetik yang bergantung pada suhu telah ditunjukkan menggunakan persamaan Arrhenius, yang menganggarkan tenaga pengaktifan (E) sebanyak 4.2 kJ/mol dan faktor pra-eksponen (A) sebanyak $2.13 \times 10^{-3} \text{ s}^{-1}$. Model kinetik empirik (Reverchon-Sesti Osseo yang diubahsuai) telah digunakan untuk meramalkan hasil bio-minyak dengan keputusan R^2 untuk 250°C (0.87), 275°C (0.104), dan 300°C (0.843).

Kata kunci: *Lignin, bio-bahan api, campuran suhu transisi rendah.*

TABLE OF CONTENTS

	Page
DECLARATION	i
ACKNOWLEDGEMENT	ii
ABSTRACT	iii
<i>ABSTRAK</i>	iv
TABLE OF CONTENTS	v
LIST OF TABLES	ix
LIST OF FIGURES	xi
LIST OF ABBREVIATIONS	xiv
CHAPTER 1 INTRODUCTION	1
1.1 Background	1
1.2 Problem Statement	4
1.3 Hypothesis	5
1.4 Research Questions	6
1.5 Research Objectives	6
1.6 Scope of Work	7
CHAPTER 2 LITERATURE REVIEW	8
2.1 Potential and Challenges of Biomass	8
2.2 EFB Application in Green Chemistry	10
2.2.1 EFB Availability in Malaysia	10
2.2.2 Characteristics of EFB	13

2.2.3	Characteristics of Lignin	19
2.3	Conventional Pretreatment Approaches in Extraction of Lignin from Biomass	21
2.4	General Definition of DESs/LTTMs	25
2.5	Characterisation of LTTMs	26
2.5.1	Chemistry	27
2.5.2	Density	31
2.5.3	Viscosity	33
2.5.4	Conductivity	33
2.5.5	Biopolymer Solubility	34
2.6	Application of Green Solvents (LTTMs) in Extraction of Lignin from Biomass	36
2.7	HTL of Lignin	45
2.7.1	Temperature	50
2.7.2	Pressure	51
2.7.3	Lignin-to-water Ratio	52
2.7.4	Catalysts	53
2.7.5	Reaction time	54
2.7.6	Enzymatic pre-treatment	55
2.7.7	Reaction mechanisms of HTL in converting lignin.	56
2.8	Bio-Based Fuels Produced from Hydrothermal Liquefaction	63

2.8.1	Characteristics of Bio-Oil	63
2.8.2	Other Types of Biofuels	67
	CHAPTER 3 METHODOLOGY	70
3.1	Introduction	70
3.2	Materials	71
3.3	Experimental Procedures	71
3.3.1	EFB Pretreatment and Lignin Content Analysis	71
3.3.2	LTTMs Synthesis	73
3.3.3	Characterisation of LTTMs	73
3.3.4	Recoverability of LTTMs	73
3.3.5	Delignification of Biomass using LTTMs	74
3.3.6	Characterisation of Extracted Lignin	75
3.3.7	Reaction Mechanism of SCW-SCCO ₂ HTL of Extracted Lignin	81
3.3.8	Investigation on Kinetics of SCW-SCCO ₂ HTL	83
	CHAPTER 4 RESULTS AND DISCUSSION	86
4.1	Introduction	86
4.2	Characterisation of LTTMs	86
4.2.1	Structural Analysis of LTTMs	88
4.2.2	Recoverability of LTTMs	90
4.3	Delignification of Biomass using LTTMs	91

4.4	Characteristics of EFB Derived Lignin	94
4.4.1	Structural Analysis	94
4.4.2	Thermal Analysis	95
4.4.3	Crystallinity	97
4.4.4	Glass Transition Behavior	99
4.4.5	MALDI-TOF-MS Analysis	100
4.4.6	SEM Analysis	104
4.5	The Effect of Process Parameters of SCW-SCCO ₂ HTL of Lignin	106
4.5.1	Temperature	107
4.5.2	Pressure	109
4.5.3	Lignin-to-water ratio	111
4.6	Kinetic study of HTL of Lignin	113
4.6.1	HTL of Lignin with Respect to Time	114
4.6.2	Equation Fitting	116
	CHAPTER 5 CONCLUSION AND RECOMMENDATION	123
5.1	Conclusions	123
5.2	Recommendations	124
	REFERENCES	126
	APPENDICES	162

LIST OF TABLES

	Page
Table 2.1 Major Centres of Global Oil Palm Cultivation in 2020 (Goggin et al., 2020)	11
Table 2.2 Physical Properties of EFB (Law et al., 2007)	13
Table 2.3 Mechanical Properties of Oil Palm Residue	14
Table 2.4 Chemical Properties of EFB (Chang, 2014)	17
Table 2.5 Advantages and Disadvantages of Conventional Pretreatment Approaches and Green Solvents in Extraction and HTL of Lignin	24
Table 2.6 Classification of Eutectics Based on the Nature of the Complexing Agent and Their Respective General Formulas (Kalhor & Ghandi, 2019; Smith et al., 2014)	28
Table 2.7 Summary of Biomass Delignification using Green Solvents	39
Table 2.8 Summary on HTL Studies of Lignin Conversion to Bio-oil and Value-added Chemicals.	46
Table 2.9 Possible Reaction Mechanisms of HTL in Breaking Down Lignin Under Specified Operating Conditions with their Generated Products	57
Table 2.10 Comparison of Different Kinetic Studies of Lignin Degradation using HTL	62
Table 2.11 Comparison of Selected Properties of Bio-oils Produced by HTL of Swine Manure and Pyrolysis of Wood and Heavy Fuel Oil.	67
Table 4.1 Summary of Process Parameters of HTL of Lignin	106
Table 4.2 Major Compounds Identified in Bio-oils (Temperature)	109
Table 4.3 Major Compounds Identified in Bio-oils (Pressure)	111
Table 4.4 Major Compounds Identified in Bio-oils (Lignin-to-water Ratio)	113
Table 4.5 Summary of SCW-SCCO ₂ HTL of Lignin with Respect to Time	114
Table 4.6 Kinetic Parameters Determined from Model Fitting	117
Table 4.7 Summary of Activation Energy of Lignin	118

Table 4.8 Normalized Yield Y and Z Constant of Bio-oils at Various Reaction Times.

121

LIST OF FIGURES

	Page
Figure 2.1 Summary of Supply and Demand (IEA, 2021)	8
Figure 2.2 Overview of Bioenergy Resource Availability in Malaysia (SEDA Malaysia, 2021)	9
Figure 2.3 Malaysian Oil Palm Producers by Category (MPOB, 2022)	12
Figure 2.4 Cross-section View of a Fibrous Strand (left, top, 170X), Longitudinal View (right, top), Interior View Showing Starch Granules (left, bottom), and Fibrous Elements (right, bottom, 110X) (Law et al., 2007).	14
Figure 2.5 Three main phenylpropanoid monomers of lignin (Hatfield & Vermerris, 2001)	19
Figure 2.6 Molecular structures of HBA and HBD for the synthesis of DESs or LTTMs (Francisco et al., 2013)	26
Figure 2.7 Phase Diagram for Eutectic Formation in a Binary System (Smith et al., 2014)	27
Figure 2.8 Schematic Representation of the Hydrogen Bonding Interaction Between Urea and ChCl to Form LTTM (Tomé et al., 2018)	30
Figure 2.9 Composition of Biopolymers and Corresponding Monomers in Typical Lignocellulosic Biomass (Hernández-Beltrán et al., 2019)	35
Figure 2.10 Application of Bio-oil	64
Figure 3.1 Research Methodology Flow Chart	70
Figure 3.2 Workflow of Biomass Pretreatment	72
Figure 3.3 Rotavapor R-300	74
Figure 3.4 Dried Lignin in Powder Form	75
Figure 3.5 FT-IR Frontier Perkin Elmer	76
Figure 3.6 TG/DTA 6200 system	77
Figure 3.7 Rigaku MiniFlex 600 Diffractometer	78
Figure 3.8 Hitachi DSC-7020 System	79

Figure 3.9	Shimadzu Biotech AXIMA Performance System	80
Figure 3.10	JEOL JIB-4601 F Multibeam System	81
Figure 3.11	Depiction of the Batch Reactor (left) Inside the Reactor Furnace (right)	83
Figure 4.1	Hydrogen Bonding Mechanism of ChCl and Malic Acid to Form LTTM	87
Figure 4.2	From left; Fresh solvent, 1 st Recovery and 2 nd Recovery Solvent	87
Figure 4.3	FT-IR Analysis of Malic Acid, Choline Chloride and LTTMs/Fresh Solvent	89
Figure 4.4	FT-IR analysis of Fresh, 1 st Recovery and 2 nd Recovery Solvent	91
Figure 4.5	Delignification of EFB	92
Figure 4.6	FT-IR Spectra Analysis of EFB Derived Lignin	95
Figure 4.7	TGA, DTG and DTA Analysis of EFB Derived Lignin	97
Figure 4.8	XRD Analysis of EFB derived lignin	98
Figure 4.9	DSC and DDSC Analysis of EFB Derived Lignin	100
Figure 4.10	MALDI TOF (1-500Da) Analysis	102
Figure 4.11	MALDI TOF (2000Da) Analysis	103
Figure 4.12	SEM Images (2500x) of EFB Derived Lignin	105
Figure 4.13	SEM Images (7000x) of EFB Derived Lignin	105
Figure 4.14	SEM Images (30000x) of EFB Derived Lignin	105
Figure 4.15	FTIR Analysis on Effect of Liquefaction Temperature	108
Figure 4.16	FTIR Analysis on Effect of Liquefaction Pressure	110
Figure 4.17	FTIR Analysis on Effect of Liquefaction Lignin-to-water Ratio	112
Figure 4.18	Bio-oil Yield with Respect to Reaction Time	115
Figure 4.19	Conversion with Respect to Reaction Time	116
Figure 4.20	Relation Between Liquefaction Reaction Rates and Solid Residue Contents	117
Figure 4.21	Arrhenius Plot of HTL of Lignin	119

Figure 4.22	Plot of Z Constant Versus Reaction Time	122
Figure 4.23	Comparison of Experimental Data with Modified Reverchon-Sesti Osseo model	122

LIST OF ABBREVIATIONS

AIL	Acid Insoluble Lignin
ASL	Acid Soluble Lignin
DESs	Deep Eutectic Solvents
DSC	Differential Scanning Calorimetry
EFB	Empty Fruit Bunch
FELCRA	Federal Land Consolidation and Rehabilitation Authority
FELDA	Federal Land Development Authority
FRIM	Forest Research Institute Malaysia
FT-IR	Fourier-Transform infrared spectroscopy
GW	Gigawatts
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
HPLC	High performance liquid Chromatography
HTL	Hydrothermal Liquefaction
ILs	Ionic Liquids
LTTMs	Low-Transition-Temperature Mixtures
MPOB	Malaysian Palm Oil Board
MPOC	Malaysian Palm Oil Council
MALD	Matrix-Assisted Laser Diffraction
NECPs	National Energy and Climate Plans
OPF	Oil Palm Fronds
OPT	Oil Palm Trunks
PORIM	Palm Oil Research Institute of Malaysia

PV	Photovoltaic
RISDA	Rubber Industry Smallholders Development Authority
SCW-SCCO ₂	Subcritical Water- Supercritical CO ₂
TGA	Thermogravimetric Analyser
UNIMAS	Universiti Malaysia Sarawak
XRD	X-ray Diffractometry

CHAPTER 1

INTRODUCTION

1.1 Background

The growing world populace has led to a global society which is presently over reliant on fossil fuels as a primary source of energy. However, the rapid consumption of this non-renewable energy increases the environmental impacts such as global warming and pollution as well as brings substantially more harm to human health. Therefore, to mitigate this problem, researchers have been progressively exploring cheap, economical, and renewable energies as an excellent approach to provide a continuous supply of energy for the future generations without the use of fossil fuels (Breyer et al., 2022). In this context, lignocellulosic biomass is regarded as the most abundant renewable source worldwide (Kucharska et al., 2018) while it is a great alternative for replacing fossil feedstocks to obtain biofuels and bio-based materials to achieve environmental sustainability (Clauser et al., 2021).

The bioconversion of lignocellulosic biomass is complex and incompetent due to biomass recalcitrance, complication in the lignocellulosic matrix, cellulose crystallinity, and lignin inhibition (Vélez-Mercado et al., 2021). Almost 70% of the total biomass is obtained from cellulose and hemicellulose that are strongly connected to the lignin component via hydrogen and covalent bonds which strengthens the rigidity of the plant cell wall and make it robust (Ufodike et al., 2020). It makes up 15–35 wt% of lignocellulosic biomass and is a profuse sustainable resource for the manufacture of fuels chemicals and fuels. In contrast with cellulose and hemicellulose, lignin is a non-saccharide macromolecular material with a complex structure. Various conventional methods for dissociating biomass into their major

components, such as lignin, cellulose and hemicellulose have been investigated by several research works. Methods like steam pre-treatment, steam explosion, acidic and alkaline pre-treatment, and supercritical fluids which disintegrate the complex materials in biomass into monomeric units have been introduced and investigated over the recent years (Ashokkumar et al., 2022). Nonetheless, these methods appear to be less effective, expensive and non-environmentally friendly (Tan et al., 2021) which calls for alternative pre-treatment methods that are rapid and cost-and-energy effective.

Vast advancements in the field of solvent development focus on formulating environmentally friendly and safer solvents of any kind that satisfies the green chemistry metrics and sustainable development goals. Green solvents encompass those which are non-toxic, non-volatile, recyclable, biodegradable, which the synthesis should not incur high cost and preferably made from materials that are readily available (Das et al., 2017). Solvents of current interest that are recognized as green solvents include water, supercritical fluids, organic carbonates, ionic liquids (ILs), deep eutectic solvents (DESs), and bio-based solvents (Welton, 2015). Recently, DESs have been extensively acknowledged as analogues of ILs and developed as the new representative for green solvents (Hussin et al., 2020). DESs can easily be synthesized from readily available natural sources, simply by mixing two solid starting materials, hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) at moderate temperature without the need for further purification steps to form liquid eutectics by hydrogen bond interactions. DES constitutes of a group of easily tuneable eutectic mixtures that are adjustable to suit for specific applications, ascribed to their high number of HBDs present in the mixture (Bernasconi et al., 2017). Lignin is one of the main products from biomass pretreatment using DESs. Nevertheless, valorization of lignin still require

further research and development since the recalcitrant nature of lignin limits its ability in generation of valuable products (Banu et al., 2019).

In recent years, thermochemical conversion of biomass for bio-oil production has attracted extensive research attention as a significant source of renewable energy. In this regard, hydrothermal liquefaction (HTL) of biomass for bio-oil production offers several advantages compared to other thermochemical conversion technologies, such as pyrolysis and gasification. For instance, HTL's ability to achieve 30% liquefaction is favorable, with energy and cost benefit ratios of 0.956 and 1.02, respectively (Banu et al., 2018). These performance metrics suggest that HTL may be a more energy-efficient and cost-effective process for converting biomass into liquid fuels when compared to pyrolysis (Vardon et al., 2012). HTL is a thermochemical liquefaction process using water as the main reaction medium at sub- or supercritical states for depolymerization of biomass to form bio-oil (Arturi et al., 2019). The liquid (bio-oil) yield and the product distribution are dependent on various process conditions such as reaction temperature, pressure, residence time, heating rate, solvent and catalyst used (Gollakota et al., 2018). During HTL, various decomposition reactions are involved, such as depolymerization, repolymerization, cleavage of ether bond, demethoxylation and hydrolysis (Ciuffi et al., 2021).

Biomass delignification using green solvents is still an underdefined process as many researchers mainly studied the efficiency of lignin extraction from biomass and their thermal stability without considering the potential of value-added products that can be produced from the green solvents-extracted lignin through HTL technology since lignin is an important source of phenolic and aromatic compounds (Dénier et al., 2016). As such, this research aims to close this gap by providing a comprehensive picture of the SCW-SCCO₂ HTL behaviour,

such as the high bio-oil yields, favourable energy and cost ratios achieved in the conversion of biomass-derived lignin. This research highlights its results with characteristics of LTTMs, delignification of biomass using LTTMs, characteristics of EFB derived lignin, the effect of process parameters of SCW-SCCO₂ HTL of lignin and finally the kinetic of HTL of lignin.

1.2 Problem Statement

In most recent years, the pretreatment approaches for lignin extraction from biomass with the aid of green solvents had prompted the research and development in biorefinery process as an effort towards apprehending the Sustainable Development Goals (SDGs) (Yiin et al., 2021). Efficient biomass conversion needs a deep understanding of the materials involves especially the lignin, solvent and any other medium used in the process. Several conventional pretreatment methods exist, but they have notable disadvantages. Acid pretreatment, for instance, uses concentrated acids that must be recovered to avoid producing acidic wastewater with high acidification, aquatic, and human toxicity potential (Solarte-Toro et al., 2019). Organosolv pretreatment, which employs low-boiling organic solvents like ethanol, methanol, or acetone, effectively extracts high-purity lignin with low molecular weight and fewer impurities (Del Río et al., 2005). However, it involves high solvent use, requires costly recycling, and generates toxic wastewater from biomass washing (Cheah et al., 2020; Wildschut et al., 2013).

SCW-SCCO₂ HTL also offers a promising method for the conversion of lignin into valuable chemical products such as biofuel. This technology is valuable for industries seeking to transition from fossil fuels to renewable energy. However, the process is sensitive to various operational parameters, such as temperature, pressure, and reaction time, leading to inconsistent product yields and making it difficult to scale up for industrial use (Postma

et al., 2022). For example, A prior HTL studies found that at higher pressure, a 30-minute reaction yielded more bio-oil than 60 minutes (Feng et al., 2021; Jia et al., 2021). A lack of understanding of critical parameters increases the risk of process failures, such as inconsistent product quality, equipment malfunctions, or unexpected chemical reactions. These risks can lead to increased downtime, maintenance costs, and potential safety concerns, further discouraging adoption (Sharifian et al., 2021).

Lastly, to develop an efficient and scalable lignin conversion process, we need to understand the influence of process parameters and the reaction kinetics involved. The complexity of lignin's structure and its transformation under supercritical conditions makes it challenging to predict product yields without a robust kinetic model (Yoo et al., 2020). For example, Changi et al. (2015) reviewed reaction mechanisms of biomolecules in microalgae during HTL, while Hao et al. (2021) focused on biomass reactions and catalytic hydrogenation for biocrude upgrading. However, a comprehensive review linking HTL kinetic models, reaction pathways, and process parameters for overall optimization is still lacking (Ahmad et al., 2025). This uncertainty poses a significant risk for industries investing in bio-refineries, as unpredictable outcomes can result in financial losses and inefficiencies (Dessbesell et al., 2018).

1.3 Hypothesis

Delignification of oil palm biomass using LTTMs will yield lignin with distinct physicochemical properties, such as lower molecular weight, higher purity, and improved functional group availability compared to lignin extracted via conventional pretreatment methods.

Besides that, improving the efficiency and scalability of lignin conversion in SCW-SCCO₂ hydrothermal liquefaction can be achieved by carefully optimizing key process parameters such as temperature, pressure, and reaction time. Adjusting these factors can greatly boost the amount and quality of the chemical products we want, making the whole process more dependable and cost-effective for large-scale use.

Lastly, developing a detailed reaction Arrhenius kinetic model accompanied by Modified Reverchon-Sesti Osseo equation for the SCW-SCCO₂ HTL of lignin will significantly enhance the predictability and control of the process outcomes. The activation energy (E), pre-exponential factor (A) and bio-oil yield will be known which will make future processes more predictable and consistent, lowering the risks and costs.

1.4 Research Questions

- i. How do LTTMs influence the physicochemical properties of lignin extracted from oil palm biomass?
- ii. What are the key operational parameters that impact product yields in SCW-SCCO₂ HTL of lignin?
- iii. How can a robust reaction kinetics model be developed to accurately predict the reaction pathways and product yields in SCW-SCCO₂ HTL of lignin?

1.5 Research Objectives

- i. To investigate the physicochemical properties of lignin derived from oil palm biomass through delignification with LTTMs.
- ii. To investigate the influence of different process parameters of SCW-SCCO₂ HTL in conversion of lignin into bio-oil.

- iii. To investigate the reaction kinetics of SCW-SCCO₂ HTL in converting lignin while producing a suitable kinetic model.

1.6 Scope of Work

In this research, the scope is focused on these elements:

- i. The biomass used is EFB which was obtained from Masranti Plantation and oil palm mill at Serian, Kuching. Fourier-Transform Infrared Spectroscopy (FT-IR) was used for structural analysis and recoverability of LTTMs. The reaction time (1-5hrs), recycled LTTMs and constant temperature of 90°C are the parameters in delignification of biomass using LTTMs, magnetic stirrer and oil bath. Thermogravimetric analyser (TGA), FT-IR, differential scanning calorimetry (DSC), powder X-ray diffractometry (XRD), Scanning Electron Microscopy (SEM), and Matrix-Assisted Laser Desorption/Ionization-Time Of Flight (MALDI-TOF) mass spectrometry (MS) are used to investigate the thermal stability, purity, heat of reaction, possibility of crystalline phases formation, particle size and purity of lignin extracted from EFB.
- ii. The elements of SCW-SCCO₂ HTL such as temperature (250, 275 & 300 °C), pressure (20, 25 & 30 MPa), lignin-to-water ratio (1:2, 1:3 & 1:5) are the parameters to show the effects towards the mechanisms and yield of bio-oil. GC-MS was used to investigate the composition of bio-oil.
- iii. Based on the experimental findings, the kinetic data of bio-oil yield with respect to reaction time were fitted into the Arrhenius kinetic model and modified Reverchon-Sesti Osseo equation to predict the activation energy (E), pre-exponential factor (A) and product yields from SCW-SCCO₂ HTL process.

CHAPTER 2

LITERATURE REVIEW

2.1 Potential and Challenges of Biomass

The significant potential of biomass arises from its global availability and demand. According to the International Energy Administration's report, the demand for biofuels is anticipated to grow by 4% annually until 2026, reaching 186 billion liters, a 41 billion-litre increase from 2020. Brazil and the United States remain the primary biofuel markets, experiencing the highest demand surge in the next five years. By the end of the projected period, ethanol and biodiesel are expected to contribute to 87% of global biofuel consumption, marking an eight-percentage point decrease from the current levels. Market dynamics exhibit variations based on geography and fuel types. By 2024, Asia is poised to surpass Europe, becoming the third-largest regional demand center. The global supply and demand overview is presented in Figure 2.1.

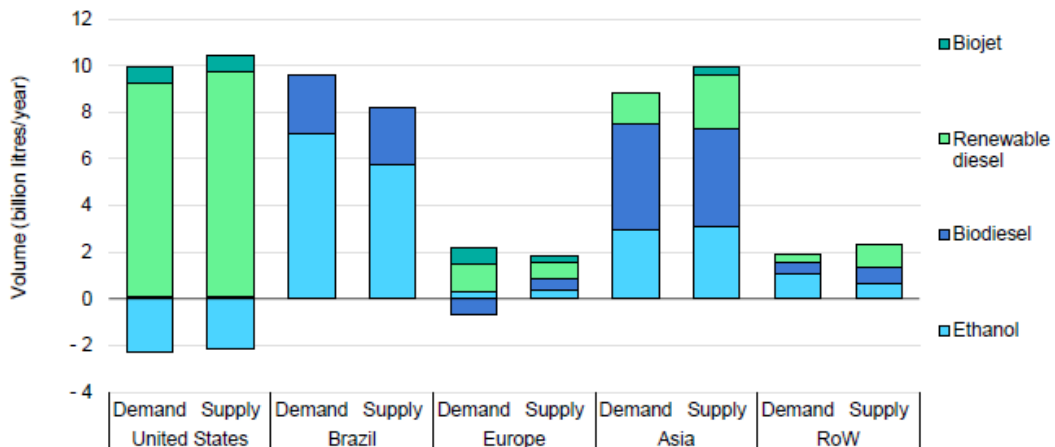


Figure 2.1: Summary of Supply and Demand (IEA, 2021)

According to Figure 2.1, Malaysia possesses a total bioenergy resource potential of 3.6 GW, encompassing biomass, biogas, and WTE (waste-to-energy). Among these,

biomass stands out as the most abundant resource, with an estimated potential of 2.3 GW. The distribution across regions reveals that Peninsular Malaysia leads with 1.3 GW, followed by Sabah and Sarawak with 561 MW and 448 MW, respectively. The collective biogas resource is 736 MW, inclusive of landfill gasification. In this category, Peninsular Malaysia holds the majority with 453 MW, trailed by Sabah and Sarawak with 158 MW and 125 MW, respectively. WTE combustion, utilizing solid waste, contributes 516 MW to the bioenergy resource, with Peninsular Malaysia contributing 443 MW, Sarawak with 43 MW, and Sabah with 30 MW, as depicted in Figure 2.2.

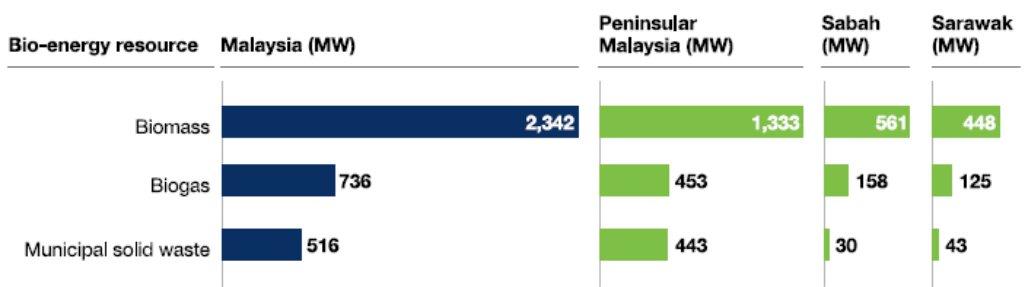


Figure 2.2: Overview of Bioenergy Resource Availability in Malaysia (SEDA Malaysia, 2021)

Despite biomass’s considerable potential for generating greater yields compared to other renewable energy sources, it faces challenges such as irregular feedstock and pricing issues. The inconsistency in both the price and quality of feedstock, including factors like water content, adversely impacts the operational efficiency of biomass power plants in Malaysia. A significant contributing factor is the lack of interest and hesitation among palm oil millers to invest in and develop biomass power facilities for processing their waste and generating renewable energy (Mahidin et al., 2020). This disinterest translates to a lack of motivation to maintain stable feedstock prices and provide high-quality feedstock (SEDA Malaysia, 2021).

Globally, meeting the rising demand for biofuels hinges on robust policies addressing cost, sustainability, and technical constraints. Countries like India, the EU, the US, China, and others are considering stricter biofuel regulations. However, the main challenge in most markets is the higher cost of biofuels compared to conventional fuels, hindering both government goals and biofuel competitiveness. Technical complexities and uncertainties in sustainable feedstock availability are additional significant hurdles (IEA, 2021).

In conclusion, the potential of biomass power generation faces significant challenges due to the irregular and unreliable supply of local and global feedstock caused by factors such as seasonal variations, weather patterns, and market dynamics, making it difficult for palm oil millers to invest in and develop sustainable biomass power facilities. Additionally, technologies are lagging behind in meeting the demand for biomass, impacting their utilization. Consequently, there is a pressing need for increased research on biomass, including materials like EFB in Malaysia.

2.2 EFB Application in Green Chemistry

The interest in using EFB for applications in a wide array of applications has been increasing due to its availability and characteristics. The amount of EFB is larger in recent years, which has caused some negative effects on the environment. Recycling and make use of EFB is encourage especially in Malaysia. In this section, the availability of EFB in Malaysia and its characteristics are discussed.

2.2.1 EFB Availability in Malaysia

Malaysia is the 2nd largest contributor in producing oil palm in the world. New developments such as palm oil mills and plantation have been experiencing an increase in progress through large government parties such as FELDA, FELCRA and RISDA. The field

of oil palm development has also been invested by private companies such as Sime Darby, Genting Plantations, and IOI Plantations. Table 2.1 shows the amount of palm oil plantations ownership across the world. Figure 2.3 on the other hand, shows the amount of ownership of palm oil plantation in Malaysia.

Table 2.1: Major Centres of Global Oil Palm Cultivation in 2020 (Goggin et al., 2020)

Rank	Country	Palm oil production	
		Million tonnes (Mt)	Percentage (%)
1	Indonesia	42.5	58.8
2	Malaysia	18.5	25.6
3	Thailand	2.8	3.9
4	Colombia	1.5	2.1
5	Nigeria	1.0	1.4
	Others	5.9	8.2
	Total	72.3	100

Malaysian Oil Palm Producers by Category (as at December 2019)

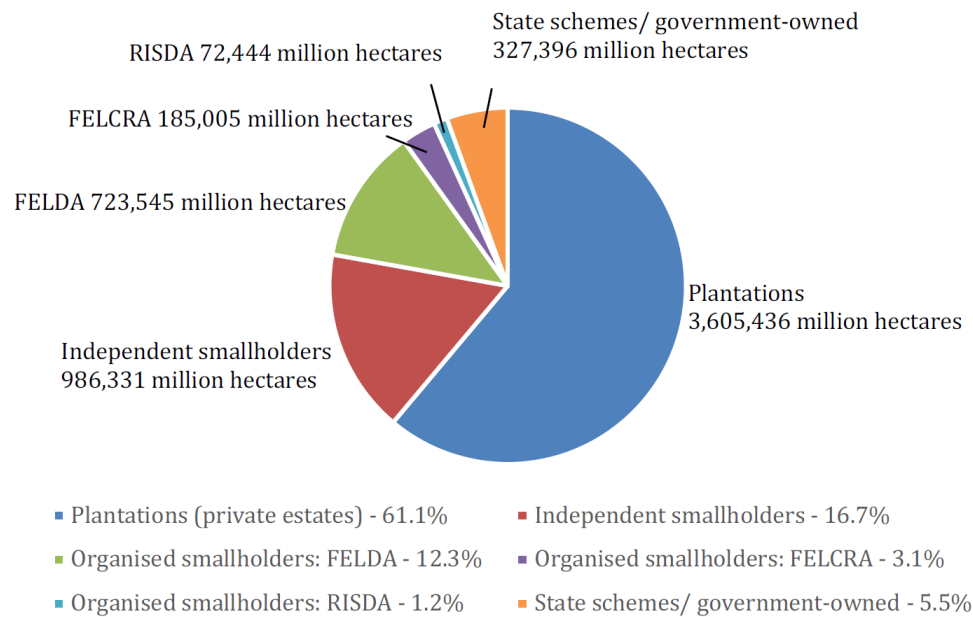


Figure 2.3: Malaysian Oil Palm Producers by Category (MPOB, 2022)

Government agencies are formed and support these oil palm plantation companies which contribute to the success now. Key government bodies involved include the Malaysian Palm Oil Board (MPOB), Malaysian Palm Oil Council (MPOC), Palm Oil Research Institute of Malaysia (PORIM), and Forest Research Institute Malaysia (FRIM). Their ongoing success significantly contributes to the economic growth of the country.

The waste by-product from palm oil extraction process which consist of oil palm trunks (OPT), oil palm fronds (OPF) and empty fruit bunches (EFB) can be 70–80 million tons per annum (Roslan et al., 2014). The production of palm oil only consists of only 10% of biomass while the other 90% are left as discarded wastes which produces more operating cost with disposal difficulties such as recycling (Awalludin et al., 2015). These waste can be put to more use as the potential of OPT, OPF, and EFB can be utilized for bioenergy production, biomaterials, fertilizers, activated carbon, biochar, biochemicals, livestock feed, and reinforcements in textiles and composites (Ng et al., 2022).

2.2.2 Characteristics of EFB

The EFB is produced by removing the treated fruit by a rotary thresher drum. The final stage of the EFB will be bulky and voluminous size, brown colour, 3.5 kg in weight and 130 mm in thickness (Sung et al., 2010), they range in length from 170 to 300 mm and width from 250 to 350 mm. (Kerdsuwan & Laohalidanond, 2011). Based on other research, Table 2.2 shows the physical properties of EFB.

Table 2.2: Physical Properties of EFB (Law et al., 2007)

Property	EFB Fiber
Length-weighted fiber length, mm	0.99
Fiber diameter (D), μm	19.1
Cell-wall thickness (T), μm	3.38
Fiber coarseness, mg/m	1.37
Fines (<0.2 mm), % (arithmetic mean)	27.6
Rigidity index, $(T/D)3 \times 10^{-4}$	55.43

Based on Figure 2.4, it shows various cross-sectional of EFB. Based on observation, there are three large vessels at the core region of a vascular bundle (170X magnification) and shows how it is pitted in a longitudinal view (200 μm). The characteristic of having long vessels also causes a high tear index (Law et al., 2007). It is also shown the presence of granules of starch which is identified using an iodine solution (50 μm).

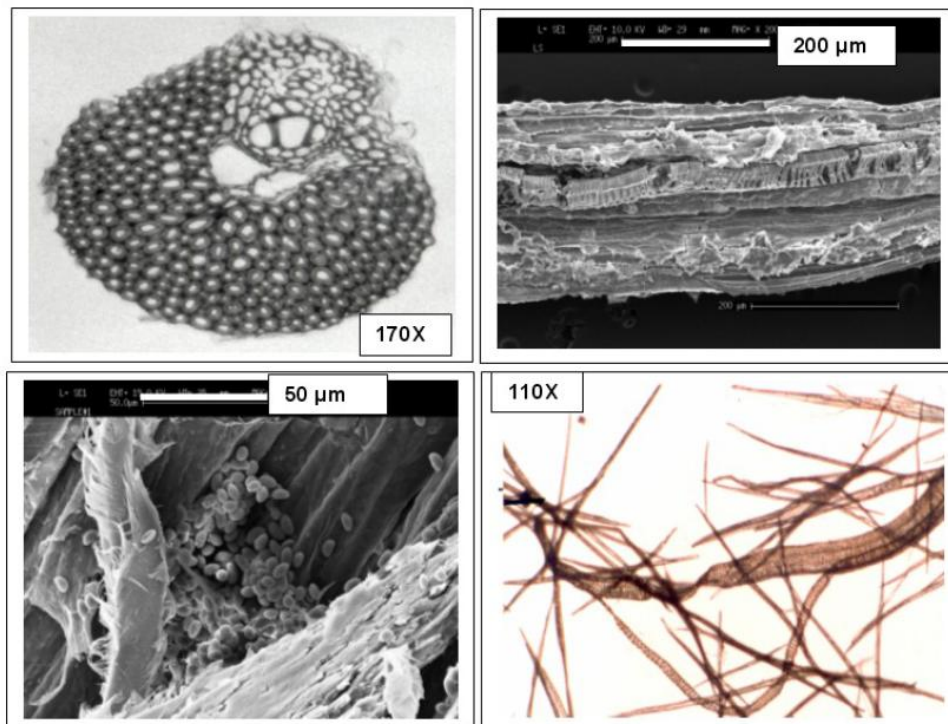


Figure 2.4: Cross-section View of a Fibrous Strand (left, top, 170X), Longitudinal View (right, top), Interior View Showing Starch Granules (left, bottom), and Fibrous Elements (right, bottom, 110X) (Law et al., 2007).

Table 2.3: Mechanical Properties of Oil Palm Residue

Fibres	Tensile strength (Mpa)	Young's modulus (Gpa)	Elongation at break (%)	References
Oil Palm EFB	50-400	0.57-9	2.5-18	(Sreekala & Thomas, 2003); (Bismarck et al., 2005); (Kalam et al., 2005); (Bakar et al., 2006))
Oil Palm Frond	20-200	2.0-8	3.0-16	(Abdul et al., 2012)
Oil Palm Trunk	30-600	8.0-45	5.0-25	(Z. Ahmad et al., 2010); (Lim & Khoo, 1986))

Based on various research conducted, the mechanical properties of different parts of oil palm such as tensile strength, young's modulus and elongation at break have been determined by multiple works which can be shown at the Table 2.3.

Moreover, Table 2.4 presents the rich inorganic elements found in EFB, detailing proximal and ultimate analyses, along with the chemical composition of EFB fibers. Proximate analysis quantifies moisture, volatile matter, fixed carbon, and ash contents in EFB fibers, offering insights into the ratio of combustible to incombustible substances, crucial for determining their energy content. On the other hand, ultimate analysis assesses the quantities of carbon, hydrogen, oxygen, nitrogen, and sulfur, providing essential information for calculating air requirements during EFB fiber combustion, as well as the composition and volume of gases released in the process.

The proximate analysis shows that EFB fibres comprise Ash (up to 13.65%), followed by moisture (up to 14.28%), fixed carbon (up to 18.3%), and predominantly volatile matter (up to 83.86%), make up its composition, as indicated in Table 2.4. The high volatile matter concentration of EFB fibres indicates their ease of burning, with an ignition temperature of roughly 190 °C (Omar et al., 2011), whereas a significant amount of fixed carbon suggests a significant amount of heat that might be released when EFB fibres are burned. In contrast, ash is the solid remnant of EFB that remains after combustion. Calcium oxide (0.13%), potassium oxide (2.4%), magnesium oxide (0.23%), silica (0.19%), and phosphorus pentoxide (0.18%) make up most of it. (Yahya et al., 2010). Owing to high volatile matter and fixed carbon in EFB fibers, they have a significant combustible to incombustible ratio, resulting in a high heating value (HHV) of 17.02-19.35 MJ kg⁻¹ (Omar et al., 2011).

EFB fibers, akin to numerous other natural fibers, consist primarily of rigid, crystalline cellulose microfibrils enveloped within a pliable, non-crystalline matrix comprising lignin and hemicellulose (Hassan et al., 2010). The chemical makeup of EFB fibers, illustrated in Table 2.4, reveals cellulose as the primary constituent, comprising up to 65%, followed by lignin (up to 29.2%), hemicellulose (up to 28.8%), and extractives (up to 3.7%). Lignocellulose components include cellulose, hemicellulose, and lignin, whereas the extractive from EFB fibers consists of minerals (potassium (2.24%), nitrogen (0.44%), magnesium (0.36%), calcium (0.36%), phosphorus (0.144%)), proteins, pectic acids, fatty acids, phenols, oil, and wax (Menon et al., 2020). Because of their complicated and little-known architectures, the lignocellulose components of EFB fibres have rendered them resistant to various physico- and biochemical conversion processes. Hemicellulose is a complex polymer composed of diverse 5- and 6-carbon saccharides like xylose, arabinose, mannose, glucose, and galactose, exhibiting a branched structure. On the other hand, lignin is a intricate polymer formed from phenylpropane units, featuring an aromatic backbone (Rubin, 2008). Hydrogen linkages established between separate layers of cellulose chains, along with the crosslinking of lignin with both cellulose and hemicellulose, create a intricate network of connections. This network not only imparts structural strength to EFB fibers but also presents a challenge in terms of degradation (Dashtban et al., 2010).

Table 2.4: Chemical Properties of EFB (Chang, 2014)

Properties	EFB	References
Proximate Analysis (wt. %) ^a		
Moisture	2.40-14.28	(Kerdsuwan & Laohalidanond, 2011); (Sreekala et al., 1997) ;(Omar et al., 2011); (Yahya et al., 2010); (Sukiran et al., 2011); (Ruengvilairat et al., 2012); (Abdullah et al., 2011); (Mohammed et al., 2012); (Khor et al., 2009); (Shinoj et al., 2010)
Ash	1.30-13.65	
Volatile Matter	70.03-83.86	
Fixed Carbon	8.97-18.30	
Ultimate Analysis (wt. %) ^b		
Carbon	43.80-54.76	(Kerdsuwan & Laohalidanond, 2011); (Sreekala et al., 1997); (Omar et al., 2011); (Sukiran et al., 2011); (Ruengvilairat et al., 2012); (Abdullah et al., 2011); (Mohammed et al., 2012); (Khor et al., 2009);(Baharuddin et al., 2009; Schuchardt et al., 2002; Suhaimi & Ong, 2001)
Hydrogen	4.37-7.42	
Nitrogen	0.25-1.21	
Sulphur	0.035-1.10	
Oxygen ^c	38.29-47.76	

Table 2.4 continued

Chemical Composition (%)		
Cellulose	23.7-65	(Sreekala et al., 1997); (Omar et al., 2011); (Abdullah et al., 2011); (Mohammed et al., 2012); (Khor et al., 2009); (Shinoj et al., 2010); (Law et al., 2007); (Abdul Khalil et al., 2008); (Baharuddin et al., 2009)
Hemicellulose	20.58-33.52	
Lignin	14.1-30.45	
Extractive	3.21-3.7	(Khor et al., 2009); (Law et al., 2007); (Abdul Khalil et al., 2008);
^a weight percent on a dry basis, ^b weight percent on a dry ash-free basis, ^c by difference		

2.2.3 Characteristics of Lignin

Lignin is one of the most abundant biopolymers, second only to cellulose. Found in plant cell walls, lignin is a highly branched polymer composed of three main phenylpropanoid monomers: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Wang et al., 2023). The figure for these monomers is shown in figure 2.5. The proportions of these monomers vary among plant species, categorized into hardwood, softwood, and grass types of lignin. This variation directly influences the lignin's thermal stability, solubility, and reactivity (Río et al., 2021). For instance, softwood lignin predominantly contains guaiacyl units, hardwood lignin contains both guaiacyl and syringyl units, and grasses have all three, including significant *p*-hydroxyphenyl units (Karthäuser et al., 2021). Lignin's structure forms from radical polymerization, creating complex linkages like β -O-4 (the most abundant), β -5, and 5-5 bonds. This heterogeneity gives lignin its amorphous nature and resistance to hydrolysis (Yang et al., 2021).

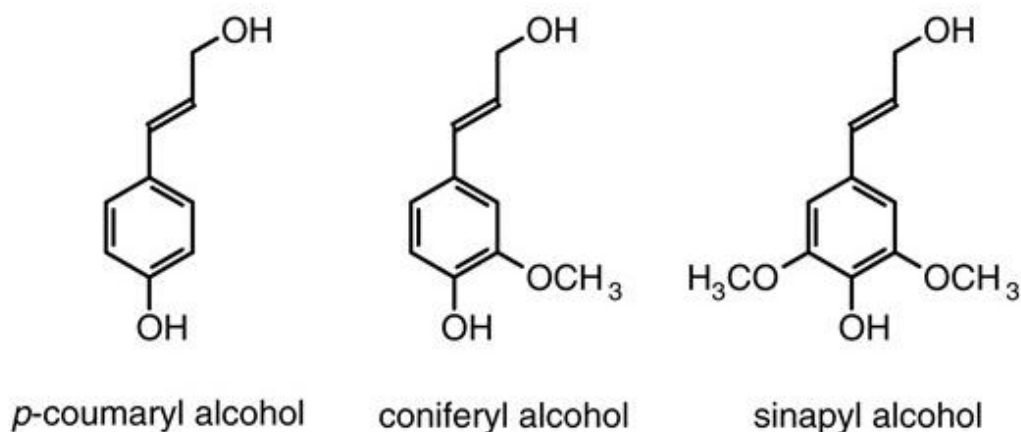


Figure 2.5: Three main phenylpropanoid monomers of lignin (Hatfield & Vermerris, 2001)

The unique physicochemical properties of lignin distinguish itself from other biopolymers. As an amorphous polymer, lignin lacks a regular crystalline structure, leading to a complex, irregular morphology that makes it harder to process compared to cellulose. For example, Cellulose has a more regular structure, making it easier to break down into sugars for biofuel production. In contrast, lignin's irregular and highly cross-linked structure makes it more resistant to hydrolysis, requiring harsher conditions such as higher temperatures or more aggressive chemicals (Bhatia et al., 2020).

Its hydrophobic nature, due to non-polar aromatic rings, limits its compatibility with aqueous environments but is valuable for water-resistant materials, composites, and coatings. An example of lignin's hydrophobic nature being valuable is its use in water-resistant coatings for wood by enhancing the water resistance of surfaces, reducing absorption and prolonging durability (Herrera et al., 2023).

Thermally stable, lignin decomposes between 200°C and 500°C depending on its source and extraction method, making it suitable for applications in thermoplastics and bio-based adhesives. These lignin-based adhesives provide heat resistance and durability, making them ideal for use in high-temperature environments, such as construction materials exposed to fluctuating temperatures (Zhang, et al., 2020).

Lignin, though insoluble in water, dissolves in organic solvents like acetone or ethanol, especially after modifications such as sulfonation or acetylation. Its solubility depends on factors like molecular weight and bonding patterns, which is important for industrial uses. For example, modified lignin dissolves better in ethanol and can be used to bind dyes to textiles, improving color uniformity and durability while utilizing a natural, sustainable material (Samanta, 2020).

Overall, lignin's physicochemical properties such as its amorphous nature, hydrophobicity, thermal stability, and solubility highlight its versatility and potential across a range of applications, from advanced materials to bio-based chemicals.

2.3 Conventional Pretreatment Approaches in Extraction of Lignin from Biomass

Mechanical pre-treatment methods including milling, microwave irradiation, ultrasound irradiation, and extrusion are commonly used to increase the surface area of the lignocellulosic materials by reducing and minimising the particle sizes. This method usually leads to reduction in degree of polymerisation and crystallinity. In general, mechanical pre-treatment methods alone are insufficient and ineffective to hydrolyse hemicellulose and extract lignin from the lignocellulosic biomass. Thus, they are normally incorporated with chemical pre-treatment methods to enhance the overall downstream conversion and yield (Tu & Hallett, 2019).

Chemical pre-treatment methods such as acid pre-treatment, alkaline pre-treatment and organosolv pretreatment are dependent on the superior lignin dissolvability of the organic or inorganic chemicals. The utilization of the organic and inorganic solvents helps to dislocate and loosening the recalcitrant structure of the lignocellulosic materials with the chemical interactions between the intrapolymer or interpolymer bonds of lignin, hemicellulose, and cellulose (Vásquez-Garay et al., 2021). Physiochemical pre-treatment methods like steam explosion, ammonia fiber explosion and carbon dioxide explosion are usually required a high control of operating conditions as these reactions occur at extreme pressure and temperature, which causes both physical parameters, chemical bonding, and intermolecular interactions to change. It has been reported that the chemical pre-treatment methods tend to generate undesirable inhibitors which need to be removed regularly. Both

kraft and sulfite pulping are two of the most conventional lignin extraction processes applied widely in many industrial chemical pulping processes. One of the biggest issues of extraction of lignin via sulfite treatment is the generation of large number of inorganic contaminants including sulfur which covalently linked to lignin in thiols form (Graglia et al., 2015). Other examples of inorganic contaminants include calcium, magnesium, and sodium, which can form salts like calcium sulfate, sodium sulfite, and magnesium sulfate (Choi, 2022). Such contaminants can act as an inhibitor to the subsequent heterogeneous catalytic lignin upgrading processes such as hydrogenolysis, hydrodeoxygenation (HDO), pyrolysis, aromatic monomer production.

In general, chemical pre-treatment processes can be divided into three types: acid pre-treatment, alkaline pre-treatment and organosolv pre-treatment. Acid pre-treatment exploits the catalytic functionality of acidic catalysts to hydrolyse and solubilize the biomass hemicellulose into its building monomers by destructing the polymeric bonds and depolymerizing lignin structure and subsequently improve the accessibility of enzymatic substrates and biodegradability for further enzymatic treatment process. Despite concentrated acid is well reported to be effective in hydrolyse cellulose, the inherently corrosive characteristic of the acidic solvent demands the reactor equipment to be fabricated from corrosive resistant materials which make it expensive. The highly concentrated acidic solvent usually also needs to be recovered after the pre-treatment step. Otherwise, highly acidic wastewater is generated with a high acidification potential, aquatic toxicity potential and human toxicity potential (Solarte-Toro et al., 2019). Thus, diluted acid pre-treatment appears to be a more favourable alternative than concentrated acid pre-treatment method as it can be performed at milder operating conditions and requires less costly chemicals. However, this diluted acid pre-treatment method has its own downfalls including low

conversion rate and formation of inhibitory by-products such as hydroxymethylfurfural (HMF) under strong acidic conditions for the subsequent fermentation process (Nazari et al., 2018). The generation of inhibitors would require further extensive washing and neutralization before the downstream processing steps to avoid inhibitory effect. In a similar way of acid pretreatment, alkaline-based pretreatment methods usually involve the removal of lignin by the cleavage of the ester linkages and glycosidic side chains, which causes cellulose swelling and partial cellulose recrystallization (Ndwandwa et al., 2023).

Organosolv pretreatment has also been demonstrated to be an efficient strategy to extract lignin from lignocellulosic biomass by using low boiling point organic solvents including methanol, ethanol, acetone, ethylene glycol, formic acid, acetic acid, or in aqueous form which can be easily removed and recovered. Del Río et al. (2005) demonstrated that using ethanol/water mixtures for organosolv pretreatment effectively extracts high-purity lignin from hardwood biomass, yielding lignin with lower molecular weight and fewer impurities, making it ideal for biochemical and material applications. The main concern of this method is the cost and chemical usage which requires a further solvent recycling step and demands a higher operating cost (Cheah et al., 2020). At the same time, the process also suffers poor lignin yield via transformation of hemicellulose and cellulose monomers to their degradation monomers and generates a large amount of toxic wastewater due to the water washing of pre-treated biomass pulp (Wildschut et al., 2013). The current conventional chemical treatments methods still have more disadvantages when compared to green solvents/LTTMs as summarized in Table 2.5.

Table 2.5: Advantages and Disadvantages of Conventional Pretreatment Approaches and Green Solvents in Extraction and HTL of Lignin

Chemical Pretreatment Methods	Advantages	Disadvantages
Acid pretreatment	High lignin yield; Improve biomass porosity; Good enzymatic hydrolysis performance.	Recovery of toxic acids via recycling; Expensive solvent cost, Equipment corrosion; Formation of potential inhibitors by-products such as hydroxymethylfurfural (HMF) at strong acidic conditions; Generation of highly acidic wastewater; Neutralization and salt disposal.
Alkali pretreatment	Major removal of lignin and a part of hemicellulose; Selectively break down the lignin-carbohydrate bonds; Reduction in polymerization degree and crystallinity	Low digestibility in softwoods; Formation of salts of calcium and magnesium; Wastewater production and require downstream treatment; Long pretreatment time; High chemical recovery cost.
Organosolv pretreatment	Highly flexible with a wide selection of organic solvents; Allowed it to be tailored for a wide range of operating temperatures; Effective for lignin and hemicellulose hydrolysis; Useful for lignin recovery; Pure lignin can be obtained.	High pretreatment temperature; High solvent cost; Requires high pressure equipment due to the inherently high volatility nature of the solvent; Solvents inhibit enzymatic hydrolysis costly; Solvent needs to be drained and recycled back to the system.
Green solvents	Cheaper and environmentally benign alternatives; Easily recyclable by distillation	Poor stability and prone to contaminants

2.4 General Definition of DESs/LTTMs

In definition of Francisco et al. (2013) the term Low Transition Temperature Mixtures (LTTMs) is used to describe the synthesization of solvents By combining two or more solid elements that can form hydrogen bonds, the outcome is liquid solvents characterized by a significantly lower melting point compared to any of their individual components which shows a glass transition temperature instead of a eutectic (melting) point. However, most research or literature still use the term Deep Eutectic Solvents (DESs) as it was originally named before.

The definition of DESs is the interaction between two solid starting materials which produces eutectic mixture that remains as liquid form at ambient temperature (Abbott et al., 2003). The constituents of the eutectic mixture do not interact individually to form a new entity but impede the crystallization process of one another and consequently resulted in the depression of melting/freezing point to lower than that of any of its individual constituents.

In the preparation of LTTMs, it is done by mixing both material in solid state, followed by heating and melting them with a temperature that changes on the type of mixtures, such as lactic or oxalic acid mixture are heated at 60 °C while for nicotinic and malic acid mixtures are heated at 130 °C (Francisco et al., 2012). Based on observation, the mixture will melt at a lower temperature than their own melting point while increasing the temperature increases the melting rate. After, it will produce a clear and transparent liquid with no solid particles. Figure 2.6 shows the Hydrogen Bond Donor (HBD) and Hydrogen Bond Acceptor (HBA) which produce the formation of stable, homogeneous solutions, ultimately resulting in the production of clear liquids.

In theory, a near infinite number of combinations can be produced due to the numerous HBA and HBD available. However, the practice of mix-and match approach is not guaranteed.

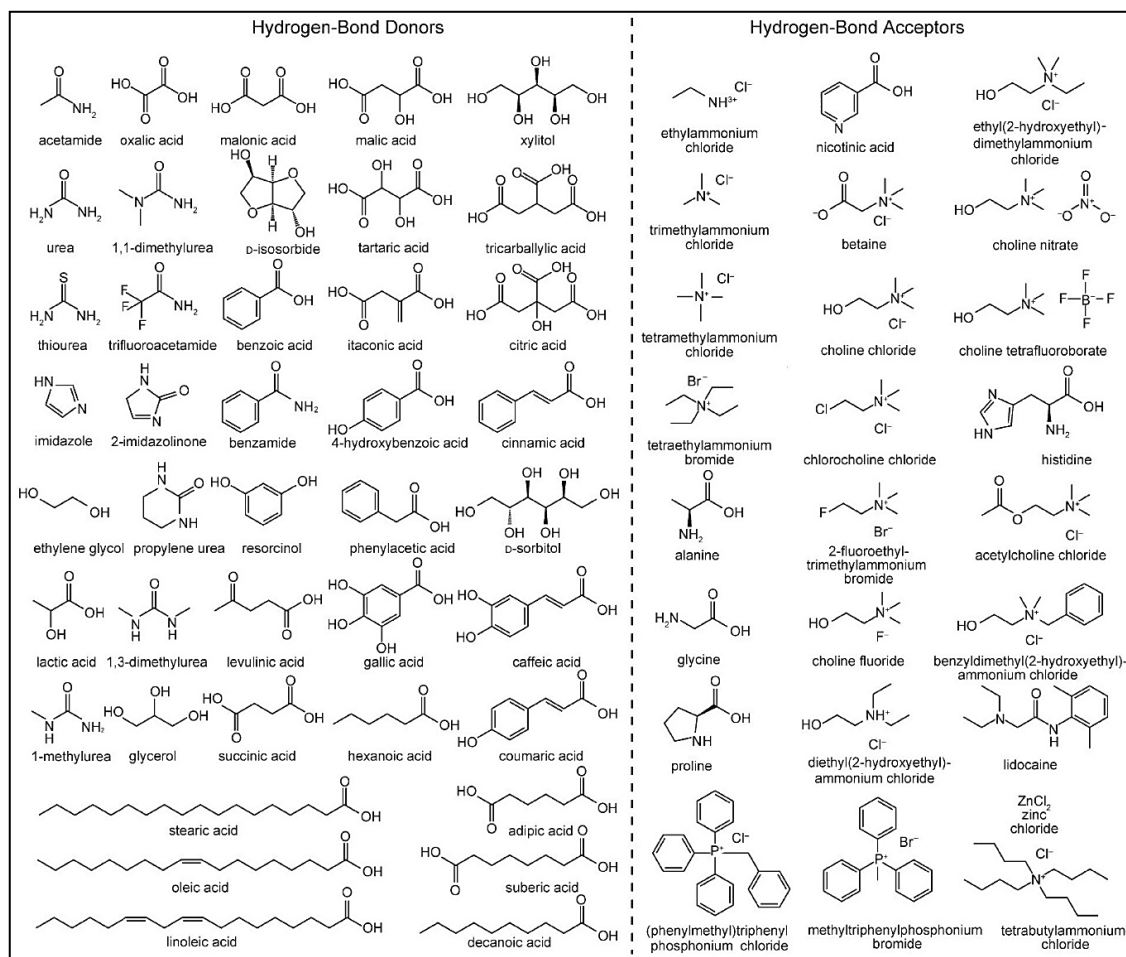


Figure 2.6: Molecular structures of HBA and HBD for the synthesis of DESs or LTTMs (Francisco et al., 2013)

2.5 Characterisation of LTTMs

LTTMs have been produced and experimented many times to search for a viable characteristic as a green solvent. The physicochemical properties need to be supported by availability of accurate and well-grounded research to fully utilise their properties in the green chemistry world. This has caused the studies to have scarce information on their

physiochemical properties even though the importance and significance of the research field.

In this section, the various characterisations of ChCl-based LTTMs are discussed.

2.5.1 Chemistry

The chemistry of LTTMs needs to be understood to further understand the difference between other solvents such as Ionic Liquids (ILs). Figure 2.7 is the schematic diagram which shows the depression of the melting and freezing points.

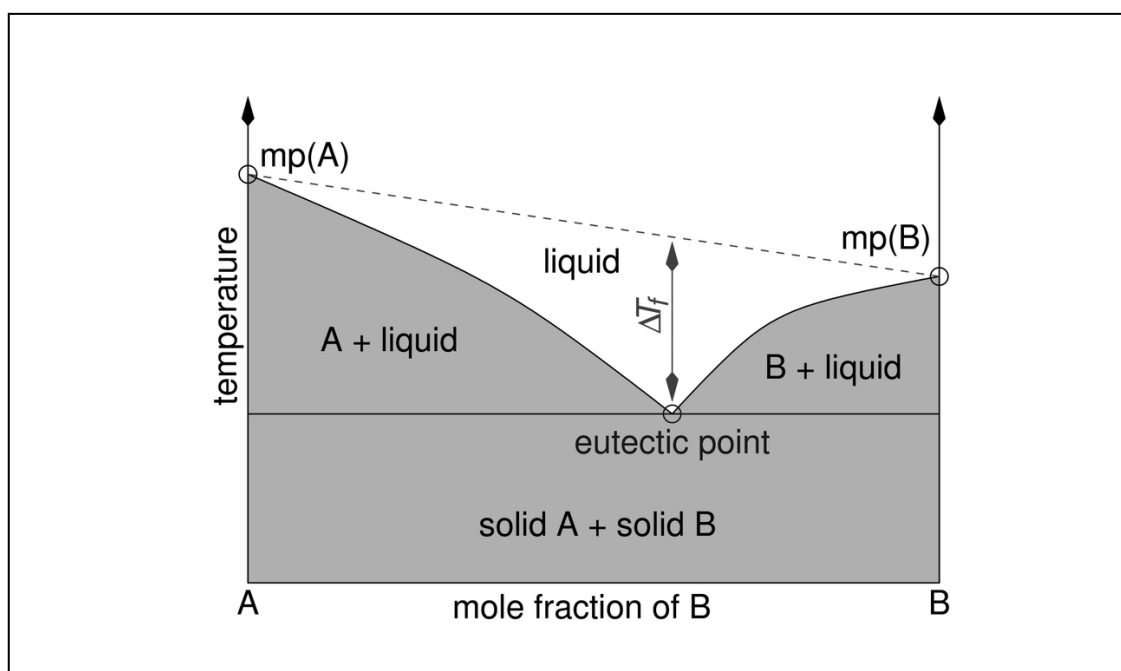
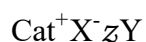


Figure 2.7: Phase Diagram for Eutectic Formation in a Binary System (Smith et al., 2014)

DESs are eutectic mixtures generated by combining an HBA, most commonly quaternary ammonium salts, with an HBD made up of alcohols, acids, amines, and carbohydrates, among other things. DESs are generally described by the following Equation 2.1 (Smith et al., 2014).



Equation 2.1

where Cat^+ refers to any ammonium (NR_4^+), phosphonium (PR_4^+), or sulphonium cation (SR_3^+)

X is a Lewis base, generally a halide anion (F^- , Cl^- , Br^- , I^- , etc.)

Y is either a Lewis or Brønsted acid

z refers to the number of molecules Y that interact with the anion

A complex anionic species emerges between the halide anion X and another Lewis or Brønsted acid Y, leading to charge delocalization between the anion and the HBD compounds. The formation of the eutectic mixture is believed to be driven by hydrogen-bonding interactions between a compatible pair of HBA and HBD (Francisco et al., 2013). Table 2.6 displays four main types of deep eutectic solvents (DESs) based on the nature of their constituents, with the recent addition of Type V DESs.

Table 2.6: Classification of Eutectics Based on the Nature of the Complexing Agent and Their Respective General Formulas (Kalhor & Ghandi, 2019; Smith et al., 2014)

Type	General Formula	Terms
I	$\text{Cat}^+\text{X}^-z\text{MCl}_x$	$\text{M} = \text{Zn, Sn, Fe, Al, Ga, In}$
II	$\text{Cat}^+\text{X}^-z\text{MCl}_x \cdot y\text{H}_2\text{O}$	$\text{M} = \text{Cr, Co, Cu, Ni, Fe}$
III	$\text{Cat}^+\text{X}^-z\text{RZ}$	$\text{Z} = \text{CONH}_2, \text{COOH, OH}$
IV	$\text{MCl}_x + \text{RZ} = \text{MCl}_{x-1}^+ \cdot \text{RZ} + \text{MCl}_{x+1}^-$	$\text{M} = \text{Al, Zn; and } \text{Z} = \text{CONH}_2, \text{OH}$
V	† Non-ionic DESs	Composed only of molecular substances

† Type V DES: Recently proposed and not well established (Abranches et al., 2019)

Type I eutectics primarily consist of non-hydrated metal halides and quaternary ammonium salts, encompassing diverse eutectic combinations ranging from chloroaluminate or imidazolium to less prevalent ones like 1-ethyl-3-methylimidazolium chloride (EMIC). Research in the 1980s extensively explored these eutectic mixtures with various metal halides (Bernasconi et al., 2017). Since the spectrum of acceptable non-hydrated metal halides with low melting points to make Type I DESs is restricted, numerous

metal salts hydrates were linked with quaternary ammonium salts due to their inertness to air or moisture, resulting in Type II eutectics.

Most LTTMs are based on Type III eutectics, with quaternary ammonium salts like choline chloride (ChCl) and HBDs like glycol, ethylene glycol, urea, carboxylic acids, and amides among the most common starting materials (Zhekenov et al., 2017). Because of their ability to solvate a wide range of transition metal species, including chlorides and oxide derivatives, Type III eutectics have drawn a lot of interest (Smith et al., 2014). These eutectic compositions have shown to be highly inert to water, almost unreactive, making them comparatively simple to make and manage.

While quaternary ammonium salts are used as the cationic component in most IIs and DESs, quaternary ammonium salts are not required to generate eutectics. However, disproportionation methods have demonstrated that a metalliferous solution composed of cations and anions can be formed by mixing metal chloride hydrate with HBDs such as simple amides (-CONH₂) or alcohols (-OH) (Abood et al., 2011). Type IV eutectics are the most recent family of DESs to be firmly established, consisting of metal chloride salts and HBDs without organic quaternary ammonium cations.

Type V DESs, which are made up of non-ionic species, are the most recent breakthrough among the four major categories of DESs. These non-ionic hydrophobic eutectics overcome the drawbacks of quaternary ammonium salt-based hydrophobic eutectics, such as higher cost, hydrophobicity, and viscosity, and have also showed potential for DES recovery and regeneration via evaporation, owing to their non-ionic nature (Abranches et al., 2019). Type V DESs, on the other hand, are a very new field of study, and so are not yet developed enough to support many scientific studies.

DESs are categorised according to the components utilised in the solvent's manufacture. The majority of LTTMs are based on the Type III eutectics fundamental, in which the starting materials are a quaternary ammonium salt and neutral organic HBDs with functional groups such as amines, amides, carboxylic acids, alcohols, and so on. In comparison to their metallic analogues, Type III DESs have various advantages, including a lower cost, ease of manufacturing, and excellent water inertness. Furthermore, many of them are frequently recognised as biodegradable and non-toxic green solvents, owing to their starting constituents, which are organic HBDs generated from natural biomass (Longo & Craveiro, 2018). The creation of hydrogen bonds between its elements is essential for the synthesis of LTTMs. Abbott et al. (2003) hypothesised the synthesis of LTTM through hydrogen bonding interactions between the HBA and HBD in their attempt to synthesise an LTTM with ChCl as the HBA and urea as the HBD in Figure 2.8.

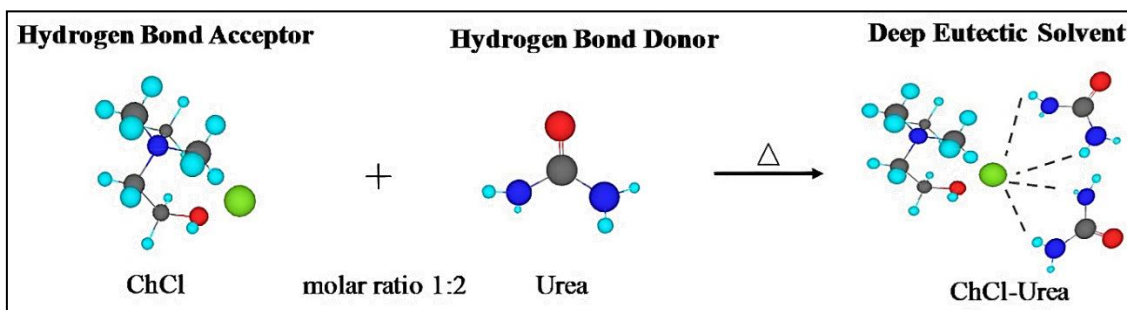


Figure 2.8: Schematic Representation of the Hydrogen Bonding Interaction Between Urea and ChCl to Form LTTM (Tomé et al., 2018)

LTTMs form a category of eutectic blends that are easily customizable to meet specific needs, attributed to the abundant presence of hydrogen bond donors (HBDs) in the mixture (Bernasconi et al., 2017). While the molecular-level processes governing the creation and operation of these solvents remain incompletely comprehended, the presence of hydrogen bonds between the two components in LTTMs can be confirmed using techniques such as proton nuclear magnetic resonance (^1H NMR) spectroscopy or FT-IR.

(Yiin et al., 2015; Zhekenov et al., 2017). Thus, significant interaction of hydrogen bonding is responsible for the reduction in the melting/freezing point of LTTMs.

2.5.2 Density

The importance of solvent density in process design is a hot topic right now. In this context, thermodynamic modelling using appropriate mathematical connections such as equations of state (EoS) contributes significantly to the computation of thermodynamic parameters that are commonly used in industrial process design. This necessitates the initial establishment of a detailed description of the relationship between temperature and pressure with density (P-V-T behaviour) of LTTMs (García et al., 2015). In LTTMs, density can be modified by elements of various natures and molar compositions, with the same effect as a change in mass and volume, which defines density as an attribute of matter. As the ratio of quaternary ammonium salt to HBD increases, the density of LTTMs decreases, leading to a stronger structuring effect on the liquid and consequently reducing the free volume (Francisco et al., 2013).

The density of the LTTMs can still be determined using an analytical procedure and manual calculation (Degam, 2017). The density of multiple ChCl-based LTTMs was determined via gravimetric analysis, which involved using a calibrated pipette with a capacity of 1.00 mL to transfer exactly 1.00 mL of each LTTM to ascertain the mass of that amount of liquid, followed by manual calculation (Degam, 2017). Similarly, filling a 10 mL volumetric flask with the LTTM until the calibration mark is reached, then measuring the weight of the LTTM in the volumetric flask at 25°C to calculate the density by simple computation. The density was determined using the Equation 2.2 in both circumstances (Shafie et al., 2019).

$$\text{Density, } \rho = \frac{m}{V} \quad \text{Equation 2.2}$$

where m is the weight of the LTTM in the volumetric flask (in g)

V is the volume of the LTTM in the volumetric flask (in cm³)

The density of the LTTMs is strongly reliant on the molar compositions and process circumstances, particularly the temperature, as seen by its P-V-T behaviour, which shows a strong interconnection between density and temperature fluctuations. When previously stated, the density of LTTMs reduces as the molar ratio of salt to HBD increases, increasing the alkyl chain length of the LTTM components, and the same is true for temperature increases due to molar volume expansion at elevated temperatures, where molecular motion increases (Francisco et al., 2013).

The effect of water on the density of the LTTM is of special interest in this study. Water is universally acknowledged to have a density of 0.997 g cm⁻³ at 25°C, while most of the LTTMs exhibited densities in the range from 1.0 to 1.35 g cm⁻³, although LTTMs composed of metallic salts such as ZnCl₂ have slightly higher densities in the 1.3 to 1.6 g cm⁻³ range (García et al., 2015). This is further supported by (Jablonský et al., 2019) that mentioned the typical range of DES densities from 1.04 g cm⁻³ to 1.63 g cm⁻³. Because water is less dense than most LTTMs, adding water to them reduces their density. As a result, increasing the water content of LTTMs results in lower densities. This shows that while LTTMs offer unique benefits, their high viscosity compared to other ILs or organic solvents can impact their performance, particularly in applications requiring rapid ion or molecule movement (Bernasconi et al., 2017).

2.5.3 Viscosity

Another important attribute of LTTMs is viscosity, which is known to be high due to the extensive hydrogen bond network between each component in the LTTM, which reduces the mobility of free species inside the LTTM (Dai et al., 2013). As a result, lower molecular mobility equals higher viscosity. The charge transport capacity of DES is influenced by its viscosity, which affects other transport parameters such as conductivity, diffusion coefficient, charge transfer rate, and so on (Yuan et al., 2018). Due to the lengthy solvent transfer and slow molecule diffusion, the high viscosities commonly observed by LTTMs may limit their potential for wider applications. As a result, the increased liquid viscosity contributes to higher energy expenditures associated with the usage of viscous LTTMs in industry or commerce. The most outstanding LTTMs in favour for practical applications are those with reduced viscosities, particularly near to those of the existing benchmark organic or water-based solvents (Bernasconi et al., 2017).

The LTTM's viscosity is determined by their intermolecular interactions, which can be influenced by a variety of parameters including the nature of the constituents, the molar ratio of HBA to HBD in the LTTM, temperature, and water content (Smith et al., 2014). As the temperature rose, the internal resistance of the LTTM decreased, making the LTTM less viscous and easier to flow (Shafie et al., 2019). Water, on the other hand, has a lower viscosity than LTTMs, meaning that increasing the water content will reduce the LTTM's viscosity (Francisco et al., 2013).

2.5.4 Conductivity

The conductivity of DES is a key physicochemical property that helps reveal how DES interact with other properties in practical applications such as electrolytes for energy

storage devices. For example, Millia et al. (2018) showed that high-conductivity DES improved lithium-ion battery performance by enhancing ion transport, thereby increasing charge-discharge efficiency and energy storage capacity. It also plays a significant role in the selection and design of green solvents, guiding the development of more effective and sustainable alternatives. The Walden rule, which explains the linear relationship between conductivity and the fluidity of the DES or as the reciprocal of viscosity, has been validated by numerous studies (Reuter et al., 2021). The synthesis of several tetrahydroisoquinolines employing DES and copper (II) oxide impregnated on magnetite as the catalyst, for example, was described, and the results revealed that product yield is directly proportional to conductivity (Clarke et al., 2018; Marset et al., 2016). DES were classified as ionic solvents, and it was suggested that they could be used for electrochemical applications such as electrolytes in batteries and solar cells, metal electrodeposition, and electropolishing of metal surfaces, with the electrical conductivity of the DES becoming a key parameter (Reuter et al., 2019).

2.5.5 Biopolymer Solubility

Biopolymers are natural polymers made by living creatures' cells, and they are made up of repeated monomeric units that are covalently bound to form larger molecules. Collagen, silk fibroin, gelatine, starch, cellulose, and alginate are some of the most prevalent biopolymers. In Malaysia, where lignocellulosic biomass is abundant, but pre-treatment options are limited, the solubility of biopolymers in LTTMs is of particular interest. For example, studies shown the dissolution of oil palm biomass in a variety of LTTMs and found that choline chloride-based DESs were effective in dissolving cellulose, hemicellulose and lignin (Silveira et al., 2015). The analysis of biopolymer solubility offers information on the LTTMs' dissolving capabilities and selectivity for certain biopolymers in the solute, such as

cellulose, hemicellulose, lignin, and other polysaccharides in lignocellulosic biomass shown in Figure 2.9.

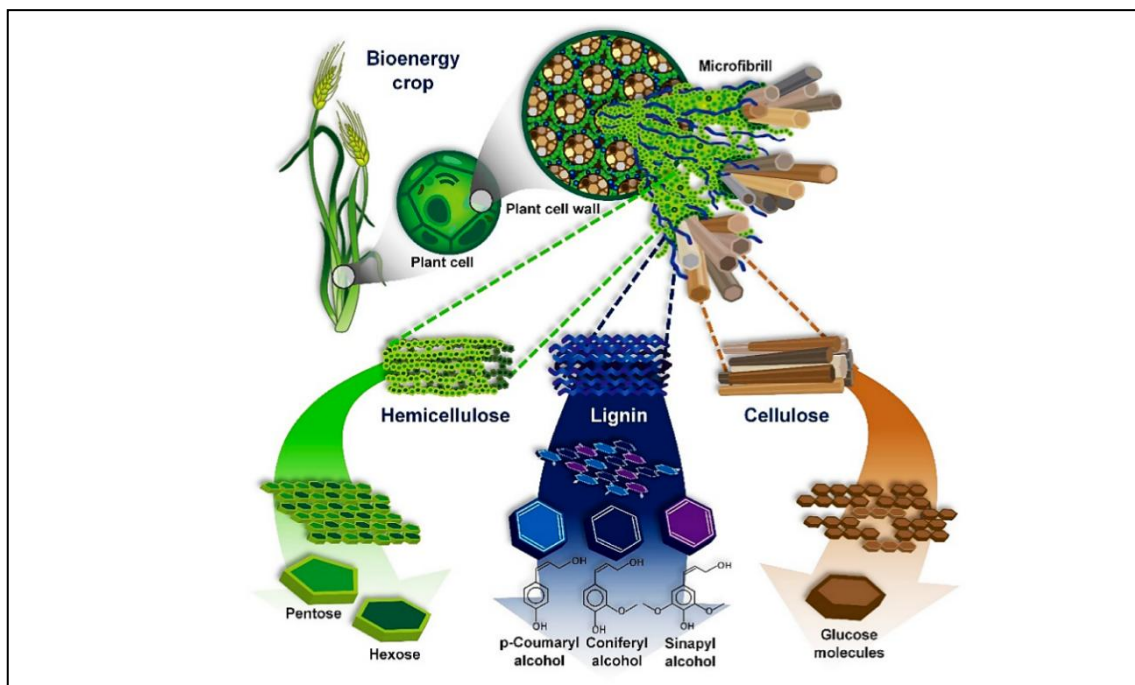


Figure 2.9: Composition of Biopolymers and Corresponding Monomers in Typical Lignocellulosic Biomass (Hernández-Beltrán et al., 2019)

Following the protocols, the solubility of three biopolymers contained in lignocellulosic biomass, notably lignin, starch, and cellulose, was screened using the cloud point method. 2 g of LTTMs were placed in vials and heated in an oil bath to a constant temperature of 60°C, after which small amounts of samples (0.2 to 1 mg) were continually added while rapidly stirring (Francisco et al., 2012). The dissolution of the biopolymers was visually checked, and the samples were stored for 24 hours after entire dissolution of the solutes in the LTTMs was observed (Yiin et al., 2015). Similar procedure was reported by Liu et al. (2019), adding that consecutive additions of solute by 10 mg to 50 mg of solute into reaction system until the existence of particles were noticeable, in case if the sample was completely miscible at first (Liu et al., 2019).

The separation of the LTTM and the solutes was used to assess the solubility of biopolymers in the LTTM. If the solutes did not dissolve into the solvents after 24 hours, the biopolymer solubility was recorded (Yiin et al., 2017). The formula to calculate biopolymer solubility is given as follow (Wang et al., 2018; Zhang et al., 2020):

$$\text{Biopolymer solubility (wt\%)} = \frac{W_0 - W_1}{W_0} \times 100\% \quad \text{Equation 2.3}$$

where W_0 represent the weight of biopolymers before the dissolution

W_1 represent the weight of biopolymers after the dissolution (24 hours)

The solubility of biopolymers can be visually screened, with an apparent suspension of particles without a reduction in the number of solutes indicating that the solute is immiscible in the solvent, and no observable particles indicating that the solute is totally miscible in the solvent. Partial miscibility in the solvent is shown by a reduction in solute mass, and the actual solubility in weight percent can be calculated using Equation 2.3.

2.6 Application of Green Solvents (LTTMs) in Extraction of Lignin from Biomass

LTTMs serve as cost-effective and environmentally friendly alternatives to replace traditional solvents in processes such as extraction, purification, and other separation procedures. Moreover, LTTMs find applications in various areas, including chemical and polymer synthesis, metal electrodeposition, nanomaterials, CO₂ capture, biomass and biofuels processing, biomedicine, pharmaceuticals, food processing, cosmetics, and more (Marcus, 2019; Silva et al., 2019; Ünlü & Takaç, 2020).

Bioenergy development is one of the key area of research that make use of LTTMs. Kalhor & Ghandi (2019) proposed two feasible routes capable of valorising lignocellulosic biomass for bioenergy applications, namely, (i) conversion of sugars from polysaccharides

(cellulose and hemicellulose) in lignocellulosic biomass into biofuels; or (ii) production of bio-oil and biogas by means of hydrothermal liquefaction and gasification. All these methods are similar in such a way that pre-treatment and solvation steps are essential and the use of LTTMs to substitute for hazardous solvents marks a significance at this point. For instance, biodiesel is a renewable diesel substitute that valorises an increasingly diverse mix of resources such as vegetable oils, animal fats, and waste oils, as the promising alternative to depleting sources of fossil fuels. In this context, some of the benefits reported from the use of LTTMs as co-solvents in the transesterification process for biodiesel production are increased yield, less soap formation, and simpler purification process (Taslim et al., 2017).

Closely linked with biofuels research, the application of LTTMs in biomass treatment caught remarkable attention worldwide due to the fact that lignocellulosic biomass is underutilized despite being the most abundant natural sources in the world. Most of the lignocellulosic biomass are disposed or burnt without prior treatment, mainly attributed to the high cost of conventional biomass pre-treatment options, or the ineffectiveness of the existing alternatives. These lignocellulosic wastes have harmful environmental impacts due to their high Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD). Both COD and BOD are key indicators of water quality, measuring the amount of oxygen needed to break down the organic matter present in water. The application of LTTMs in biomass treatment involves the extensive use of LTTMs in the fractionation of lignocellulosic wastes. At this point, the ability of LTTMs in the pre-treatment and selective dissolution of the constituents in lignocellulosic biomass, specifically cellulose, hemicellulose, and lignin (Kalhor & Ghandi, 2019). Apart from that, ongoing researches on the extraction and recovery of bioactive compounds from biomass waste indicated high

possibilities of converting biomass to value-added products such as biofuels, organic acid, enzymes, biopolymers, chemical additives, solvents, etc. (Ünlü & Takaç, 2020).

Both in Malaysia and globally, LTTMs for the valorisation of biomass is of great interest due to the abundance of lignocellulosic biomass. The obstacles and complexities hindering the effective utilization of lignocellulosic biomass are primarily attributed to the resistance of plant cell walls to biochemical and biological breakdown. This resistance is caused by the heterogeneous polyphenolic structure of lignin which refers to its complex and irregular composition, primarily made up of various phenolic compounds. Hence, the study on the biopolymer solubility of LTTMs is of appreciable importance in order to close up the gap between LTTMs and conventional solvents. A major leap in the application of LTTMs for biomass pre-treatment and further processing will open up limitless opportunities in this field. Since then, there is a momentous growth of studies which investigating the delignification of lignocellulosic biomass as shown in Table 2.7.

This research use the same composition of LTTMs of ChCl/L-Malic acid/Water 2:4:2. Yiin et al. (2017) research that cactus malic acid can attain a considerable performance in lignin removal compared to L-malic acid, with lignin removal at 41.94% by using ChCl/L-Malic acid/Water while its cactus malic acid variant attained 37.22%. This proves that the efficiency of the LTTMs composition is higher than most in Table 2.8 and is suitable for this research.

Table 2.7: Summary of Biomass Delignification using Green Solvents

Biomass	DESs	Key findings	References
Keratinous waste biomass	• ChCl/Oxalic acid 3:1, 2:1, 1:1, 1:2, 1:3	• Destruction of the crystalline structure of the wool have been achieved. • Dissolution affected the amino acid composition. • The optimized dissolution conditions are ChCl/Oxalic acid molar ratio 1:2, 5 % wool-to-solvent (w/w) and temperature at 110–125 °C for 2 h.	(Wang & Tang, 2018)
Rice husk, rice straw and wheat straw	• ChCl/Oxalic acid-Butanol (2:1)	• Delignification using DES-OL system [DES (CO)-Butanol (2:1), 1h, 15 % S/L] showed 50 % higher efficiency than that of pure DES treatment. • The optimized temperature for delignification is 120 °C.	(Kandanelli et al., 2018)
Pure lignin and wheat straw biomass	• ChCl/Phenol (ChCl-Ph) • ChCl/α-naphthol (ChCl-Npt) • ChCl/resorcinol (ChCl-Res) • ChCl/maleic acid (ChCl-Mal)	• ChCl-Res demonstrated the highest solubility of lignin at 48.15 w/w%, with ChCl-Ph following closely at 40.43 w/w%, ChCl-Mal at 38.13 w/w%, and ChCl-Npt at 23.91 w/w% • Delignification of wheat straw biomass using ChCl-Res resulted in a lignin solubility of 41.67 w/w%.	(Malaeke et al., 2018)
Switchgrass, corn stover and <i>Miscanthus</i>	Microwave-assisted ChCl:Lactic acid	• The pretreatment only required 45 s and highly effective for lignin and xylan removal. • Recovered lignin of switchgrass: (48.39$\pm$0.72) % yield and (87.42$\pm$0.09) % purity. • Recovered lignin of corn stover: (70.84$\pm$1.88) % yield and (84.96$\pm$0.52) % purity. • Recovered lignin of <i>Miscanthus</i>: (42.67$\pm$1.21) % yield and (86.01$\pm$1.08) % purity.	(Chen & Wan, 2018)

Table 2.7 continued

Empty Fruit Bunch (EFB)	• ChCl:lactic acid (1:5) • D(+)-glucose:lactic acid (1:5) • ChCl: D(+)-glucose (1:1) • ChCl: glycerol (1:2) • ChCl: urea (1:2) • potassium carbonate: glycerol (1:6)	• Organic acid-based DES is proven to have potential for biomass processing. • ChCl:lactic acid (1:5) showed the best result with 88 % delignification and solid recovery of $(53.1 \pm 0.5)\%$. • The energy requirement levels exhibit marginal variation across DES pretreatments	(Tan et al., 2018)
Oil palm frond	• ChCl/Urea	• The effectiveness of lignin removal through DES was notably improved by ultrasonic treatment, increasing from 14.02% with DES treatment alone to a range of 17.73-36.42% with ultrasound combined with DES treatment.	(Ong et al., 2019)
Oil palm fronds	• Alkaline hydrogen peroxide + ChCl:Urea	• Combining AHP (0.25 vol%, 90 min) at room temperature with DES (ChCl:Urea) at fixed conditions (120 °C, 4 h) achieved the highest delignification (18.99%), surpassing DES-alone pretreatment (12.16%). • Increased in glucan content from 48.23 (raw) to 54.40%. • The xylan content decreased to 21.67%, in comparison to the original oil palm frond (OPF) content of 21.86%.	(Ho et al., 2019)
Wood-apple pulp	• ChCl/Oxalic acid 1:1, 1:2, 2:1	• The best solvation effect was demonstrated by ChCl/Oxalic acid 1:1 with addition of 25 % water (v/v) and extraction temperature of 80 °C demonstrated extraction yield and capacity (> 60%). • Better cavitation process allowed the formation of stronger hydrogen bonding between the starting materials.	(Saha et al., 2019)

Table 2.7 continued

Moso bamboo	• ChCl/Lactic acid 1:9	• Pretreatment at 120 °C for 3 hours with a solid-to-liquid ratio of 1:25 resulted in the removal of over 94% of the lignin. • The self-standing films made by DES-n showed exceptional mechanical characteristics due to their great aspect ratio and high DP value (tensile strength reached 213 Mpa).	(Liu et al., 2019)
Beech wood and wheat straw	• Lactic acid:alanine 9:1 • Lactic acid:glycine 9:1 • Lactic acid:betaine 2:1 • ChCl:ethylene glycol 1:2 • ChCl:glycolic acid 1:3	• The density and viscosity of eutectic solvents decreased with increasing temperature, but conductivity increases in the opposite direction. • The most effective delignification solvents for wheat straw are lactic acid:alanine (9:1) and ChCl:glycolic acid (1:3) which removed 23.7 % and 16.6 % of lignin, respectively. • The most effective delignification solvent for Beech wood is lactic acid:alanine (9:1) and ChCl:glycolic acid (1:3) which removed 14.4% and 15.4% of the lignin respectively.	(Jablonsky et al., 2019)
Raw corn straw and lactic acid (Lac) pretreated corn straw	• ChCl/Lac 1:2 • Betaine/Lac 1:2	• Lignin isolated by DESs showed higher purity (86.43 – 89.15 %) compared to the lignin obtained through enzymatic hydrolysis (47.85 – 74.65 %). • Prior to DES (ChCl/Lac) treatment, acid pretreatment created lignin with a simplified structure, lower molecular weight, improved thermal stability and increased reactivity.	(Liu et al., 2020)
Miscanthus and birchwood	• ChCl/Acetic acid 1:2 • ChCl/Formic acid 1:2 • ChCl/Glycerol 1:2 • ChCl/Lactic acid 1:2 • ChCl/Malic acid 1:1	• ChCl/Oxalic acid and ChCl/Formic acid demonstrated the highest delignification efficiency for birchwood and miscanthus respectively. • ChCl/Glycerol DES was documented to yield the smallest quantity of recovered lignin.	

Table 2.7 continued

	• ChCl/Oxalic acid 1:1	• A UV–V method was established for lignin quantification, with the absorbance maximum at 785 nm proving to be more effective for accurate lignin measurement.	(Kohli et al., 2020)
Pretreated bamboo and untreated bamboo	• ChCl/ ethylene glycol (EG)/p-TsOH • Tetrabutylammonium chloride (N4Cl)/EG/p-TsOH • tetrapropylammonium chloride (N3Cl) /EG/ p-TsOH	• p-TsOH-based DESs were utilized to fractionate woody biomass and disrupt the resistant structure of the plant cell wall under mild conditions. • ChCl-EG-p-TsOH (molar ratio of 1:0.5:1) emerged as the most efficient, achieving removals exceeding 93.36% for xylan and 90.32% for lignin. Notably, a significant portion of cellulose (86.73%) was retained in the pretreated bamboo within a brief reaction time of 10 minutes at 100 °C and a 10% solid loading. • The extracted lignin exhibited high purity, a comparatively low molecular weight, a lower PDI, and a well-preserved structure, including features like β-O-4 bonds. • After four recycling cycles, the DES maintained high fractionation efficiency and yielded excellent enzymatic hydrolysis of CRS.	(Zhai et al., 2020)
<i>Bambusa bambos</i> stem (BS)	• ChCl:oxalic acid (CO) (1:2) • ChCl:urea (CU)(1:2)	• Optimal delignification of BS was achieved at 120 °C for 4 hours using DESs. • The crystallinity index rose from 43.8% in raw BS to 44.3% in CUT-BS and further to 46.4% in COT-BS. • The delignification using CO system (25.4 %) was easier to dissociate the BS biomass compared to CU system (19.4 %). • The impurities in the recovered DESs reduced the efficiency of recycle process.	(Ramesh et al., 2020)
Watermelon rinds	• ChCl:lactic acid (1:6)	• Maximum lignin removal of 43.56 % was achieved using combination pretreatment of DESs and ultrasound with variables of 180 W of ultrasonication power, 60 kHz of ultrasonication frequency, 40 min of ultrasonication time, 120 °C of reaction temperature and 180 min of reaction time. • Stand-alone DESs pretreatment achieved only 17.23 % of removal while ultrasound pretreatment achieved 35.62 % of removal.	(Fakayode et al., 2020)

Table 2.7 continued

Dried bagasse biomass	• ChCl/Ethylene glycol 1:2 • ChCl/Glycerol 1:2 • ChCl/Lactic acid 1:2 • ChCl/Oxalic acid 1:1 • ChCl/Urea 1:2	• While the solubility of lignin in ChCl/Oxalic acid was the highest at 47.85%, it led to the carbonization of the bagasse during the pretreatment. • ChCl/Lactic acid was the most ideal solvent for the separation and extraction of bagasse cellulose. • ChCl/Oxalic acid separated lignin and hemicellulose, ChCl/Lactic acid was suitable for cellulose separation, and ChCl/Ethylene glycol, ChCl/Glycerol, and ChCl/Urea showed selectivity for lignin separation.	(Li et al., 2021a)
Bamboo <i>Dendrocalamus yunnanicus</i>	• ChCl/Oxalic Acid 1:1	• The highest lignin yield reached 50% at 120 °C. • Regenerated DES lignin samples displayed a purity of up to 90%. • Lignin samples demonstrated enhanced thermal stability and excellent antioxidant activity, showcasing significant potential for lignin valorization.	(Li et al., 2021b)
Rice straw	• Tetra-n-butylammonium bromide: 2-aminoethanol (1:2) + tetrahydrofuran (6-part DESs and 4-part tetrahydrofuran)	• 46 % delignification with higher recovery of cellulose (~ 91 %) and hemicellulose (~ 67 %). • The novel solvent system maintained consistent efficiency across 10 consecutive reuse cycles • The pretreated biomass could be readily hydrolyzed by cellulases, even at lower dosages.	(Thulluri et al., 2021)
Flash dried kraft pulp	• Choline chloride:lactic acid (1:10)	• Mechanical stirring method produced lignin content of 10.83 % while rotary evaporator method yielded lignin content of 13.07 % with constant liquor-to-wood ratio of 27:1, temperature of 120 °C and 1 h of cooking. • Time between 30 to 45 min resulted in a pulp yield of about 50 % and a fiber length of 0.6 mm.	(Pérez et al., 2021)

Table 2.7 continued

<i>E. globulus</i> wood	• ChCl: LA (1:10) • Urea:Propionic Acid (1:2) • ChCl:<i>p</i>-toluenesulfonic acid monohydrate (1:1) • ChCl:Urea (1:2) at 50 wt% water content	• Urea:Propionic Acid (1:2), ChCl: LA (1:10), and ChCl:Urea (1:2) aqueous solutions yielded high solid fractions (above 70 wt%) and low precipitated lignin (below 3 wt%), indicating low efficiency in <i>E. globulus</i> wood delignification with these solvents. • The ChCl:PTSA (1:1) aqueous solution achieved higher wood delignification, with a solid fraction yield of 46.41 ± 0.88 wt% (containing residual Klason lignin content of 10.69 ± 0.16 wt%). A recovered lignin fraction of up to 15.38 ± 0.59 wt% was obtained, representing over 75 wt% of the initial lignin content in wood. However, the high acidity led to the destruction of some original cellulose content.	(Soares et al., 2021)
Sugarcane bagasse	• ChCl:Gly • ChCl:Urea	• The optimization demonstrated that pretreatment using ChCl-Gly and ChCl-Urea at ideal conditions could remove 81.1 % (13.12 h, LSR 23.4:1 and 160 °C) and 82 % (14.04 h, LSR 17:1 and 160 °C) of the lignin in sugarcane bagasse, respectively. • It is feasible to convert 50-80 % of the cellulose in sugarcane bagasse through DES treatment.	(Varilla-Mazaba et al., 2022)
Coconut coir	• ChCl: LA (1:4)	• ChCl: LA (1:4) showed the highest lignin yield of 82 % with >95 % purity. • H factor for process was 55.5 due to efficient microwave heating at 150 °C with reaction time of 20 min. • CTH of extracted lignin showed bio-oil yield of 38.8% using Ru/C and isopropanol.	(Mankar et al., 2022)
Poplar sawdust	• ZnCl₂:lactic acid	• ZnCl₂-lactic acid DES successfully recovered 95.2 wt% of lignin with a high purity of 92.1%. • The recovered lignin exhibited a low polydispersity of 1.67 and contained a small quantity of β-aryl-ethers.	(Bai et al., 2022)

2.7 HTL of Lignin

HTL is a thermochemical process that efficiently converts organic wet biomass, such as algae, agricultural residues, and lignocellulosic materials into liquid fuels and valuable chemicals. By replicating and expediting the natural formation of crude oil, HTL employs water as a solvent under high temperature and pressure to break down the complex organic structures of lignin, cellulose, and hemicellulose in biomass, transforming them into simpler, energy-dense products (Zhu et al., 2014). The products are biocrude, gases (mainly CO₂), aqueous phase products containing organic acids, sugars, and alcohols, and solid residues like biochar. With biocrude yields ranging from 30% to 70%, HTL offers a high conversion efficiency compared to pyrolysis or gasification. The biocrude can be upgraded through catalytic refining to produce transportation fuels such as gasoline and diesel, positioning HTL as a promising technology for sustainable biofuel production and biomass valorization (Zhu et al., 2021).

In HTL process, various parameters play crucial influence on the conversion efficiency of lignin and subsequently dictating the various reactions' rates during HTL and the bio-oil yield and composition. Parameters commonly explored and optimized in the context of lignin/biomass hydrothermal liquefaction (HTL) encompass temperature, pressure, lignin-to-water ratio, reaction/residence time, and catalyst type and loading (Mishra et al., 2022). In this section, the effect of these parameters/factors towards the conversion of lignin and bio-oil yield/composition are critically elucidated. Table 2.8 summarizes some recent findings on HTL conversion of lignin to bio-oil.

Table 2.8: Summary on HTL Studies of Lignin Conversion to Bio-oil and Value-added Chemicals.

Lignin type (source)	Temperature (°C)	Pressure (Mpa)	Lignin:water ratio (wt:wt)	Catalyst and loading	Reaction time (min)	Lignin conversion (%)	Bio-oil yield (wt%)	Major compounds in bio-oil	References
Alkali lignin	260 – 300	-	1:6	Activated carbon (AC), Ni/AC, Co/AC, Ni-Co/AC (5-20 wt%)	15	58.8 – 61.9	24.1 – 26.7	Vanillin (32.1%), Phenol (12.0%)	(Biswas et al., 2021)
Kraft lignin (wheat straw)	280	-	1:10	Ni-Al/MCM-41 (10 wt%)	60	66.8	39.6	Phenol (12.0%)	(Feng et al., 2021)
Kraft lignin (wheat straw)	280	10 – 18	1:10	Co/CNT (20 wt%)	30	67.8	40.6	-	(Jia et al., 2021)
Kraft lignin (sinocalamus oldhami)	180–280	-	1:10	NaOH + Na ₂ SO ₃ + Ni-W ₂ C/AC (2.5-25%)	120-420	87-94.4	9.35-17.18	Phenol (9.87%), Phenol, 4-ethyl- (2.94%)	(Lin et al., 2021)
Kraft lignin	200–350	-	1:10	KCl, AlK(SO ₄) ₂ , ZrOCl ₂ , CaCO ₃ , and K ₂ CO ₃ (10 wt%)	40	59.5-72.8	37.7–48.5 (K ₂ CO ₃)	Guaiacol (19.14%), Homovanillic acid (10.42%)	(Rana et al., 2019)

Table 2.8 continued

Kraft lignin	250	-	1:50	GO, N ₂ -doped (N-GO), solvothermal carbon (STC), SO ₃ -STC, N-STC (10 wt%)	60-540	55.20	~4.1-7.6 (N-STC)	Guaiacol (~6% of lignin), Catechol (~1% of lignin)	(Totong et al., 2019)
Kraft lignin	200–350	-	1:10-1:80	-	0–60	59.5-72.6	28.9–44.7	Pyrocatechol (1.88% of lignin), Guaiacol (1.18% of lignin)	(Islam et al., 2018)
Kraft lignin	450	10 (H ₂)	-	Ru/C, RuAl ₂ O ₃ , Pt/C, Pt/Al ₂ O ₃ , Pd/C, Pd/Al ₂ O ₃ , Rh/C, Rh/Al ₂ O ₃ (5 wt%)	240	67.2-83.5	21.5-36.3 (Rh/Al ₂ O ₃)	Alkylphenolic (15.3%)	(Hita et al., 2018)
Kraft lignin (softwood)	350	-	1:30	MoO ₃ /SBA-15 (10%)	60	79-88.2	44.6-56.4	1,2-benzenediol (42.07%), Phenol, 2-methoxy- (19.5%)	(Rana et al., 2018)

Table 2.8 continued									
Kraft lignin	300	19.5	1:16.6	K ₂ CO ₃ (1.6 wt%)	15	45.6	33.9	Phenol (0.187 wt%)	(Arturi et al., 2017)
Soda lignin Organosolv lignin (almond shell and olive tree pruning)	300	9	1:20	NaOH (4 wt%)	80	~47-61	~11.5-23.5	Catechols (7.78%)	(Fernández-Rodríguez et al., 2017)
Organosolv lignin (beech wood)	270-350	-	1:40	-	10-120	~27-68.5	8-14.6	Syringol (22.8%), 3-Methoxycatechol (21%)	(Hashmi et al., 2017)
Lignin (corncob)	210-290	-	1:10	-	0-40	52-62	~31-38.5	Benzene, 1,3-dimethyl- (14.5%), Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl) (7.6%)	(Yang et al., 2015)

Table 2.8 continued

Kraft lignin (bamboo)	130-230	-	1:6	K ₂ CO ₃ (1.6 wt%)	15-60	33.9	45.6	Guaiacol (77.58%), 4-Hydroxy-3,5-dimethoxyphenyl ethanone (16.38%)	(Zhou 2014)
Lignin	345	30	1:10	Al-Ni alloy (10 wt%), Mg, Al, Zn, Fe (0.05 mol)	30	-	44.53 – 49.83 (Fe/Fe+ Al-Ni)	1,2-benzenediol (93.14%) (Al-Ni)	(Wang et al., 2022)
Lignin (<i>Spartina alterniflora</i>)	300 – 360	-	1:10	-	20 – 60	-	8.1 – 22.3	Phenolic compounds (82.89 wt%)	(He et al., 2020)
Lignin (herbaceous plant)	350	-	1:10	-	60	53.62 – 59.69	12.18 – 17.98	Phenol, 2-methoxy- (15.34%), Phenol, 2,6-dimethoxy- (14.08 %)	(Chen et al., 2019)

2.7.1 Temperature

Temperature is a critical operating parameter that is often examined in the context of thermochemical conversion (pyrolysis, liquefaction, gasification) of biomass or wastes to value-added products, due to the overall endothermicity nature of the involved reactions. Generally, higher temperature provides the necessary activation energy to decompose and crack the lignin macrostructure in the presence of water during the HTL process (Chan et al., 2018). Other than that, the desirable physicochemical properties of water at elevated temperature, such as low dielectric constant, weak hydrogen bond, high diffusivity, compressibility, and reactivity, favors the dissolution and degradation of lignin to various bio-oil compounds via radical reactions (Chan et al., 2019).

Lignin is a complex, irregular molecule made up of different types of monomers linked together in various ways which create different levels of polymerization, hence exhibiting a wide range of decomposition temperature (120 – 700 °C) (Amit et al., 2021). As shown in Table 2.9, most HTL studies were conducted at 280 – 350 °C, at which water is in the subcritical condition capable of liquefying lignin to bio-oil containing primarily of various organic aromatic/phenolic compounds. He et al. (2020) systematically investigated the effect of temperature and other process parameters on the bio-oil yield from HTL of high-purity lignin (>90 wt%) extracted from *Spartina alterniflora* powder (He et al., 2020). The optimum reaction temperature of 360 °C produced highest bio-oil yield of 22.3 wt%, with phenolic compounds constituted ~83% of the bio-oil components. Comparable trends were also exhibited in other lignin HTL studies summarized in Table 2.9. In addition, similar trend was also reported by Lin et al. (2021), in which the phenolic hydroxyl (an intermediate compound indicative of the extent of lignin depolymerization) content of the bio-oil first increased with temperature, then decreased when temperature was further increased.

Generally, the effect of reaction temperature on bio-oil yield from lignin HTL is similar to that of biomass HTL. Higher HTL temperature would result in increment of the bio-oil yield, and upon reaching an optimum temperature, further rise in temperature would reduce the bio-oil yield (Xu & Li, 2021). Higher temperature favors the decomposition of lignin but is not recommended as it produces a broader range of organic compounds, including smaller molecules and gases (El-Sayed & Mostafa, 2020). However, as the temperature goes beyond the optimum temperature for a specific feedstock, repolymerization and secondary decomposition dominate and transform the liquid bio-oil compounds into solid products and non-condensable gases, as evident from increased solid and gas yields at unfavorably high reaction temperatures (Fernandes et al., 2021).

2.7.2 Pressure

Pressure is crucial in maintaining the single-phase reaction media, avoiding large enthalpy inputs in the case of phase change of the solvents (Akhtar & Amin, 2011). Besides, the density of liquefaction solvent, which directly influences its solvation power, is also dependent on pressure. In certain instances, an increase in pressure was found to positively impact bio-oil yield, while in other cases, the opposite effect was observed. Elevated pressure enhances solvent density, thereby increasing penetration power and promoting the decomposition and depolymerization of lignin macromolecules. However, once the supercritical condition is attained, additional increases in pressure have minimal or negligible effects on bio-oil yield due to the limited influence of pressure on solvent properties (Cao et al., 2017). In some cases where solid catalysts were used, increasing pressure decreased bio-oil yield, most probably due to catalyst coking, while other cases showed an increase in bio-oil yield. While increased pressure enhances the overall density of the solvent, it can also result in localized increases in solvent density, creating a cage

effect around the C-C bonds in the biomass macromolecules. Due to the prominence of this cage effect, free-radical reactions are slowed down and the cleavage of C-C bonds is inhibited, leading to decrease in bio-oil yield (Kruse & Dinjus, 2007). In addition, High pressure conditions additionally promote the water-gas shift reaction and decrease the rate of lignin decomposition (Jindal & Jha, 2016). In-depth elucidation of the effect of pressure on liquefaction of lignin to bio-oil (such as the kinetics and reaction mechanisms) is lacking in the literature. As shown in Table 2.9, only a few studies reported the pressure at which HTL was performed, in which they were conducted mostly at a fixed subcritical pressure of <20 MPa, which is below the critical pressure of water, i.e., 22 MPa.

2.7.3 Lignin-to-water Ratio

Lignin-to-water ratio is one of the critical variables in the context of lignin HTL. As the process requires water to liquefy and decompose the lignin, sufficient water concentration plays a significant role in converting lignin to bio-oil efficiently and thus enhancing the overall process efficiency. At high lignin-to-water ratios, lignin conversion and bio-oil yield are lowered, as the lignin cannot form a well-mixed suspension with water, which hinders the mass and heat transfer, thus limiting the hydrolysis and liquefaction reactions (Jindal & Jha, 2016). On the other hand, if excessive amount of water is used (low lignin-to-water ratio), it would incur extra operating cost for the downstream wastewater treatment (Jindal & Jha, 2016). Hence, it is vital to determine the optimum lignin-to-water ratio for a particular lignin HTL process.

Most of the lignin HTL studies reviewed employed a fixed lignin-to-water ratio, with lignin-to-water ratio of 1:10 being the commonly employed setting for a majority of lignin HTL works, while few studies tested the lignin HTL at a higher lignin-to-water ratio of up

to 1:80, and some tested at a slightly lower lignin-to-water ratio of 1:6. Islam et al. (2018) varied the lignin-to-water ratio from 1:10 to 1:80, and reported that increasing water concentration (decreasing lignin-to-water ratio) beyond 1:20 impacted the bio-oil yield negatively, while the aqueous phase (light oil) increased due to the enhanced secondary degradation of phenol-formaldehyde resins contained in the bio-oil (Islam et al., 2018).

2.7.4 Catalysts

The types of catalyst used for HTL of lignin is employed to selectively cleave the interunit linkages in its complex structure include base, acid, salts, metals, zeolites, and carbon-based catalyst. Base catalysts, such as K_2CO_3 , Na_2CO_3 , KOH and NaOH, demonstrated good performance in lignin depolymerization to phenolic monomers-rich oil by facilitating hydrolysis and dissolution of lignin (Fernández-Rodríguez et al., 2017; Rana et al., 2018; Roberts et al., 2011; Toledano et al., 2012). The high activity of base-catalyzed solvolysis can also leads to repolymerization of monomers into undesired oligomers (Lin et al., 2021). Aqueous acid or acidic salts have a less pronounce effect on lignin degradation. Acidic medium tends to support condensation reactions which causes increased formation of solids residue (Ibbett et al., 2011; Rana et al., 2019). Recently, lower cost and environmental-friendly carbonaceous material were investigated for hydrothermal treatment of lignin. Totong et al. (2019) incorporated basic active site on the surface of catalyst by doping nitrogen into sulfonated solvothermal carbon (N-STC) to enhance depolymerization activity.

To further boost lignin conversion, metal (e.g., Ni, Al, Co, Mo) supported mesoporous catalyst (e.g., carbon nanotube, activated biochar, MCM-41, SBA-15) were applied to suppress the repolymerization of reactive intermediates (Biswas et al., 2021; Jia

et al., 2021; Rana et al., 2018). Combining composite basic ($\text{NaOH} + \text{Na}_2\text{SO}_3$), metal (Ni) and the Lewis acid (W_2C) sites, higher selectivity of phenolic monomers is attained as hydrogenolysis reactions take place synergistically during rapid thermochemical decomposition of lignin under alkaline conditions (Lin et al., 2021). In general, augmenting the catalyst dosage enhances lignin liquefaction and bio-oil yield, primarily due to an increase in active sites and improved lignin solubility at lower catalyst concentrations. However, further addition of catalyst beyond optimal dose encourages condensation reaction leading to loss of monophenols and more bio-residues formation (Lin et al., 2021; Zhao et al., 2019).

2.7.5 Reaction time

In Hydrothermal Liquefaction (HTL) of lignin, longer reaction times initially increase both lignin conversion and bio-oil yield by breaking down ether bonds into simpler, valuable compounds like vanillin and hydroxylated aromatics (Alhassan et al., 2020). However, extended reaction times eventually lead to the repolymerization of these products into complex structures such as lignin hydrochar, which decreases the overall bio-oil yield (Montesantos & Maschietti, 2020). Thus, while increasing reaction time can enhance conversion, it can also reduce bio-oil yield once an optimal point is surpassed.

An antagonist effect is observed when reaction time is pro-longed. These valuable compounds repolymerize to form lignin hydrochar, hence reducing overall bio-oil yield. The optimum time may vary greatly (from 20 mins to 5 hours) for each lignin HTL process of different catalyst system, temperature and other operation conditions (Islam et al., 2018; Jiang et al., 2016; Lin et al., 2021; Totong et al., 2019; Yang et al., 2015). For example, Du et al. (2018) showed that the optimum reaction time for HTL of sugarcane bagasse was

around 60 minutes, where further increase in time led to a decrease in bio-oil yield due to over-decomposition. Another research shows that the optimal reaction time for HTL of Kraft lignin was only around 15 minutes, further increasing to 30 minutes led to reduction in bio-oil yield (Zhang et al., 2021).

2.7.6 Enzymatic pre-treatment

As lignin is a recalcitrant macromolecule that is difficult to depolymerize during HTL, several studies have attempted the use of enzymes in biomass pre-treatment prior to HTL to enhance the HTL efficiency and the quality of bio-oil produced. Jensen et al. (2018) investigated the HTL of residues from enzymatic hydrolysis and protease treatment of wheat straw and *Miscanthus x giganteus*. The enzymatic pre-treatment resulted in enhanced lignin depolymerization of the residues at optimum HTL temperature of 300 °C. In another study, to overcome the low bio-oil yield from corn stover, Collett et al. (2019) studied the liquefaction of enzyme-treated corn stover with lipid-rich broth derived from corn stover hydrolysate at 350 °C and 20 MPa and reported an optimum bio-oil yield of 40 wt%. When compared with organosolv and kraft lignin, lignin extracted using enzymatic process gives the highest bio-oil yield (70%) from hydrothermal decomposition (Cao et al., 2020). According to Gu et al. (2021), the effect of fungal pre-treatment is less significant on hydrothermal conversion at higher temperature and reaction time, where these two factors became dominant in HTL. To summarize, aside from lignin extraction using green solvents, enzymatic pre-treatment of biomass could be the potential cost-effective alternative for the HTL of lignin-rich residues to bio-oil in an integrated biorefinery concept..

2.7.7 Reaction mechanisms of HTL in converting lignin.

The mechanism of lignin conversion using HTL approach involves the cleavage of aromatic cross-links, which include β -aryl ether, β -O-4, which is the most predominant that accounts for ~50% (Galkin et al., 2015), followed by aryl ether bonds such as, α -O-4 and 4-O-5, and biphenyl linkages that encompass 5-5, β -1, β -5 and β - β (Dunn & Hobson, 2016). Other common end-groups that are recovered in lignin and plausible to be converted during HTL process include coniferaldehyde and vanillin (Lui et al., 2017).

It has been reported that the β -O-4 and α -O-4 bonds are the more easily chemically cleaved linkage, while others typically biphenyl linkages are more resilient to degradation (Dunn & Hobson, 2016; Wu et al., 2013). The possible reaction mechanisms of HTL in breaking down lignin under specified operating conditions and the plausible generated products are summarized in Table 2.9. In general, from the review, it is found that the lignin conversion process is challenging owing to the various model compounds and a wide range of molecular weight distributions that may potentially exist, which pose multiple variations, possibilities, conversions, yields, and products. The complexity of HTL is influenced by the physicochemical properties and operating conditions of the medium. Different studies using various model compounds often yield inconsistent mechanisms. However, lignin degradation typically involves two main pathways, fragmentation and alkylation. Fragmentation breaks down ether bonds, producing simpler aromatic compounds such as oligomers, dimers, alcohols, ketones, and aldehydes. In contrast, alkylation modifies aromatic rings, forming heavier condensation products like alkylated aromatic hydrocarbons and di- or tri-benzylated phenols, while the aromatic rings themselves remain intact during hydrothermal reactions.

Table 2.9: Possible Reaction Mechanisms of HTL in Breaking Down Lignin Under Specified Operating Conditions with their Generated Products

Aromatic cross-links	Reaction mechanisms	Operating conditions	Products	References
β -O-4	- Group elimination - Keto–enol tautomerization - Alkylation	- Temperature: 350 °C - Basicity: 0.1 M NaOH	- Benzyl alcohol - Styrene glycol - Acetophenone - Alkylated products, e.g., 2-benzylphenol, 4-benzylphenol, di- and tri-benzylated phenols	(Lui et al., 2017)
	“Base-catalyzed” dehydration from autoprotolysis of water “Acid-catalyzed” elimination that involves a series and oxidation/reduction and dehydration from autoprotolysis of water - Hydrolysis - Alkylation	- Temperature: 350 °C - pH: neutral	3,4-dimethoxyacetophenone - Enol ether 3,4-dimethoxyphenylacetaldehyde - Phenol - Alkylated products, e.g., 2-benzylphenol, 4-benzylphenol, di- and tri-benzylated phenols	(Lui et al., 2017)

Table 2.9 continued

α -O-4	• “Acid-catalyzed” hydrolysis from autoprotolysis of water • Alkylation	• Temperature: 250 °C	• Benzyl alcohol • Phenol • 2-benzylphenol • 4-benzylphenol • Alkylated products, e.g., 2-benzylphenol, 4-benzylphenol, di- and tri-benzylated phenols	(Lui et al., 2020; Siskin et al., 1990)
4-O-5	• “Acid-catalyzed” hydrolysis from autoprotolysis of water • Alkylation	• Temperature: 120 °C • Pressure: 6 bar H₂ in the aqueous phase • Catalyst: Ni/SiO₂	• Phenol • Benzene • Alkylated products, e.g., 2-benzylphenol, 4-benzylphenol, di- and tri-benzylated phenols	(He et al., 2012)
Coniferaldehyde	• “Acid- and base-catalyzed” hydrolysis from autoprotolysis of water • Keto–enol tautomerization • Retro-aldol reactions	• Temperature: 350 °C • pH: neutral	• Benzaldehyde • Acetaldehyde	(Lui et al., 2017)

Table 2.9 continued

Coniferaldehyde/Vanillin	• Hydrolysis • Oxidation • Reduction • Dehydration • Group elimination • Alkylation	• Temperature: 350 °C • Pressure: 160–170 bar • pH: basic	• Benzoic acid, e.g., veratric acid and vanillic acid • Benzyl alcohol, e.g., veratryl alcohol, guaiacol and catechol • Benzene, e.g., veratrole • Alkylated products, e.g., 2-benzylphenol, 4-benzylphenol, di- and tri-benzylated phenols	(Lui et al., 2017)
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2.7.8 Kinetic modelling of HTL

The hydrothermal conversion of lignin presents significant challenges due to the complex and heterogeneous nature of lignin. However, various modelling efforts have been made to quantify the performance of lignin degradation and conversion. One of the efforts is the Arrhenius equation which belongs to empirical kinetic models and is used within various types of mechanistic and complex kinetic models to describe how the rate constant of a chemical reaction depends on temperature (Khan et al., 2020). A common and widely accepted approach is the assumption of first-order reaction kinetics, which has been found effective in capturing the key trends and outcomes of lignin conversion. These models employ formal kinetic rate coefficients for the degradation of lignin, denoted as k_j , for a given j . The temperature dependence has been captured via Arrhenius correlation, as summarized in Equation 2.4.

$$k_j(T) = A_j \exp \left(-\frac{E_{A,j}}{RT} \right) \quad \text{Equation 2.4}$$

In which, A_j is the apparent Arrhenius factor for reaction j and R is the ideal gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$). The Arrhenius equation illustrates that the reaction rate k_j increases exponentially with temperature, which is crucial for hydrothermal processes where high temperatures drive lignin degradation and conversion. The parameters A_j and $E_{A,j}$ (activation energy) vary based on the lignin type, reaction medium, and conditions. Summary of kinetics parameters for hydrothermal decomposition of lignin extracted from relevant studies using Arrhenius correlation have been summarized in Table 2.10 for comparison.

To accompany the kinetic model, the Modified Reverchon-Sesti Osseo equation complements kinetic models in systems involving simultaneous chemical reactions and mass transfer. It integrates solid-fluid mass transfer principles with diffusion through the material matrix, addressing both external and internal resistances. This model is frequently used for extracting natural products like essential oils and bioactive compounds using supercritical CO₂ as the solvent. The Modified Reverchon-Sesti Osseo equation is shown in Equation 2.5.

$$C(t) = C_0 \cdot (1 - e^{-k_e t}) + \left(\frac{D_e A}{L^2} \right) \cdot (1 - e^{-D_e t / L^2}) \quad \text{Equation 2.5}$$

In which k_e is the external mass transfer coefficient, D_e is the effective diffusion coefficient inside the solid matrix, A is the surface area available for mass transfer, L is the characteristic diffusion length (e.g., particle radius) and t is time.

The Modified Reverchon-Sesti Osseo equation is essential for modelling supercritical fluid extraction processes, particularly for materials like plant substances, polymers, and lignin. Enhanced versions of the model, which account for factors such as particle swelling, significantly improve the accuracy of predicting extraction rates and yields (Rai et al., 2014). It facilitates process optimization by allowing adjustments to key parameters, including pressure, temperature, particle size, and CO₂ flow rate. The model has been successfully applied to characterize the extraction of soybean oil (Melo et al., 2014) and to optimize the extraction of bioactive compounds from plant materials like rosemary and olive leaves (Patel et al., 2011). Additionally, it helps differentiate between rapid surface extraction and slower, diffusion-controlled phases, providing valuable insights into extraction kinetics.

Table 2.10: Comparison of Different Kinetic Studies of Lignin Degradation using HTL

Lignin/Model compounds/Reactants	T (K)	k_j (min ⁻¹)	$E_{A,j}$ (J/mol)	$\text{Log}(A/A')$ ^a	References
Alkali-lignin from Pine, 10 wt. %	573–683	$2.00 \times 10^{0\text{ b}}$	NA	NA	(Zhang et al., 2008)
Catechol, 1.1 wt. %	643–663	$2.40 \times 10^{-4\text{ b}}$	5.10×10^4	0.60	(Sasaki & Goto, 2009)
Guaiacol, 1.24 wt. %	653–673	$1.80 \times 10^{-2\text{ b}}$	3.90×10^4	1.50	(Wahyudiono et al., 2011)
Lignin from spruce by enzymatic hydrolysis, 9 wt. %	603–633	$1.50 \times 10^{-2\text{ b}}$	1.70×10^5	12.00	(Forchheim et al., 2012)
Organosolv-lignin, 2.3 wt. %	623–693	$3.00 \times 10^{-2\text{ b}}$	7.90×10^4	2.90	(Takami et al., 2012)
Alkali-lignin from spruce, 0.1 wt. %	663–733	$2.20 \times 10^{2\text{ b}}$	3.40×10^4	3.40	(Yong & Matsumura, 2012)
Anisole	533–563	$3.83 \times 10^{-5\text{ c}}$	1.50×10^5	0.46	(Wu et al., 2013)
Benzyl phenyl ether	533–563	$3.50 \times 10^{-2\text{ c}}$	1.50×10^5	0.58	(Wu et al., 2013)
Phenethyl phenyl ether	533–563	$7.67 \times 10^{-5\text{ c}}$	1.43×10^5	0.45	(Wu et al., 2013)
Lignin from spruce by enzymatic hydrolysis, 11.5 wt. %	593–653	$3.60 \times 10^{-2\text{ b}}$	3.20×10^4	1.20	(Forchheim et al., 2014)
Methoxyphenols	593–653	$1.10 \times 10^{-2\text{ b}}$	8.50×10^4	5.00	(Forchheim et al., 2014)

Table 2.10 continued

Catechols	593– 653	$2.90 \times 10^{-4}{}^b$	5.50×10^4	1.00	(Forchheim et al., 2014)
Solid to Aqueous (Alkaline lignin model)	523– 623	$7.92 \times 10^1{}^d$	4.90×10^3	72.00	(Obeid et al., 2019)
Renewable crude to aqueous (Alkaline lignin model)	523– 623	$2.29 \times 10^2{}^d$	3.90×10^4	516.00	(Obeid et al., 2019)
Aqueous to renewable crude (Alkaline lignin model)	523– 623	$3.90 \times 10^1{}^d$	2.76×10^4	288.00	(Obeid et al., 2019)
Renewable crude to gas (Alkaline lignin model)	523– 623	$2.88 \times 10^1{}^d$	7.60×10^3	42.00	(Obeid et al., 2019)
Kraft lignin	643– 673	$4.00 \times 10^2{}^e$	NA	NA	(Abad-Fernández et al., 2020)
Oligomer	643– 673	$4.99 \times 10^1{}^e$	NA	NA	(Abad-Fernández et al., 2020)

2.8 Bio-Based Fuels Produced from Hydrothermal Liquefaction

2.8.1 Characteristics of Bio-Oil

Bio-oil, a renewable liquid fuel, is easily stored and transportable. It can replace fuel oil or diesel in stationary applications like boilers, engines, and turbines. Alternatively, crude bio-oil is used for adhesives, resins, wood flavors, and other products. After further

processing and separation, several specialised compounds derived from bio-oils are also feasible. Figure 2.10 shows examples of bio-industrial oil's applications.

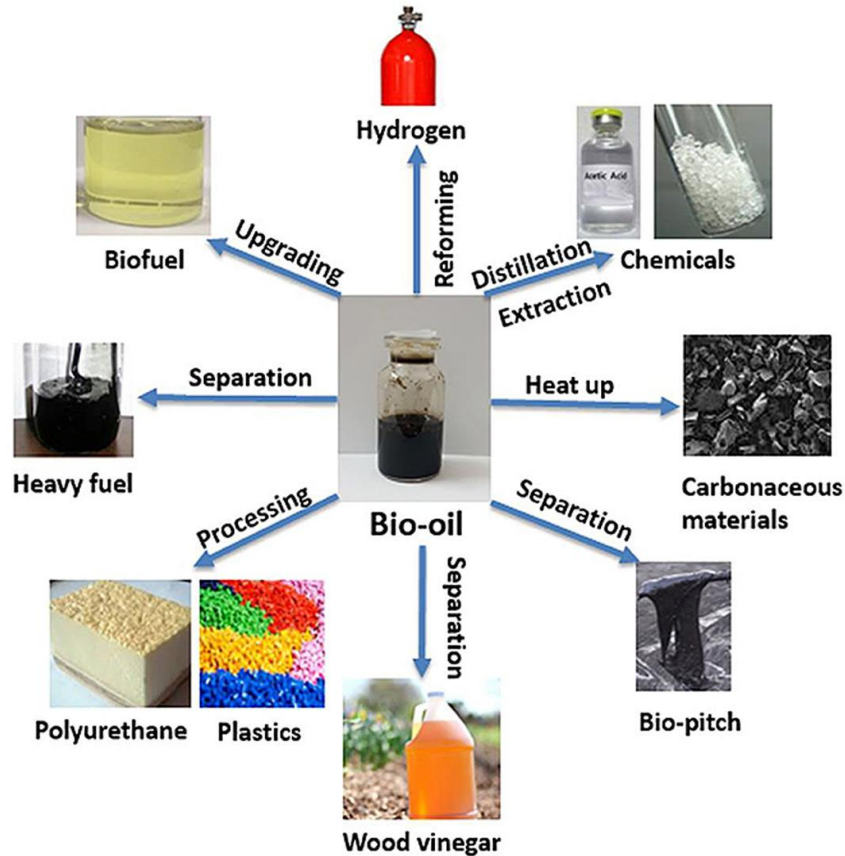


Figure 2.10: Application of Bio-oil

Based on the figure, there are numerous amounts of applications for bio-oil. It shows it is a viable and an alternative fuel for transportation or any power generated machine. For the direct combustion of bio-oil in boilers and heavy engines, designing a new burner system is necessary. Key considerations include addressing the high corrosion rate, potential for elevated solid sedimentation, managing the air-to-fuel ratio, and handling a high ash amount in the combustion chamber (Hu & Gholizadeh, 2020).

Bio-oil is also used as a feedstock in the hydrogen manufacturing process. The free literature offers a lot of information about steam reforming of bio-oil or the model

compounds of bio-oil. The fundamental issue with this procedure, however, is catalyst deactivation, a process by which a catalyst loses its ability to effectively accelerate a chemical reaction over time (Jiang et al., 2020). Due to the high tendency of the primary organic components to polymerize at the enhanced reaction temperature, process design modification can reduce coke production but not completely remove it. Due to the organics in bio-oil have many reaction paths for conversion and the organics with different structures have different reactivity toward steam reforming, the selectivity of hydrogen needs to be raised even more (Kumar et al., 2017).

Additional thorough scientific, technical, and economic investigations are required to achieve practical applications of bio-oil. Bio-oil has a long way to go before it can be used as a feedstock for the manufacture of fuels, chemicals, and carbon materials. Other technical routes are being investigated to produce value-added products from bio-oil, in addition to the processes reviewed for bio-oil application. This is important not only for finding an outlet for bio-oil application, but also for realising the commercialization of pyrolysis technology to make the best from biomass that is currently largely regarded as a waste.

Bio-oils are often dark brown, free-flowing liquids with a smokey aroma. Several papers explain the physical properties of bio-oils. The chemical makeup of bio-oils differs greatly from that of petroleum-derived oils, resulting in a variety of physical qualities (Xiu & Shahbazi, 2012). On another description, Bio-oil is a black, viscous, and energy-dense liquid made from the HTL of biomass ingredients (cellulose, hemicellulose, lignin, lipids, and proteins), with an energy content of 70–95% that of petroleum fuel oil (Jindal & Jha, 2016). The physical and chemical qualities of bio-oil are frequently influenced by the feedstock and production circumstances. Bio-constituents' oils are extremely complex,

having a wide variety of molecular weights that can be partially described by gas chromatography. The majority of the heavy compounds, however, are unable to be eluted into the column and remain unidentified (Cao et al., 2016).

Acids, alcohols, aldehydes, esters, ketones, phenols, and lignin-derived oligomers are only a few of the hundreds of organic chemicals found in bio-oil. Some of these chemicals are directly linked to bio-unfavorable oil's qualities. Table 2.11 compares basic statistics for liquefied bio-oils from swine manure, pyrolysis bio-oil from wood, and conventional petroleum fuels. In comparison to oils from quick pyrolysis, liquefied oils have substantially lower oxygen and moisture concentrations, and thus a much higher energy value, as indicated in Table 2.12. In comparison to oils from quick pyrolysis, liquefied oils have substantially lower oxygen and moisture concentrations, and thus a much higher energy value, as indicated in Table 2.12. The HHV of liquefied oil from swine dung is 36.05MJ/kg, which is almost 90% of the HHV of heavy fuel oil (40MJ/kg). Bio-oil from both methods has characteristics that are vastly unlike heavy petroleum fuel oil. Bio-oils present less favorable qualities for fuel applications compared to heavy petroleum fuel oil. These include high-water content, elevated viscosity, increased ash content, higher oxygen content (resulting in a lower heating value), and heightened corrosiveness (acidity).

The spectrum of bio-oil applications has been limited thus far due to these undesirable qualities. The product yield and composition of bio-oils fluctuate significantly due to differences in processing conditions and feedstock. Intensively studied the fuel parameters of rapid pyrolysis oils and explained how these properties affect the usage of bio-oils based on recent research (Lu et al., 2009).

Table 2.11: Comparison of Selected Properties of Bio-oils Produced by HTL of Swine Manure and Pyrolysis of Wood and Heavy Fuel Oil.

Properties	Liquefied bio-oil from swine manure (Xiu et al., 2010)	Pyrolysis bio-oil from wood (Zhang et al., 2007)	Heavy petroleum fuel oil (Oasmaa & Czernik, 1999).
Moisture content (wt%)	2.37	15-30	0.1
pH	-	2.5	-
Specific gravity	1	1.2	0.94
Elemental composition (wt%)			
C	72.58	54-58	85
H	9.76	5.5-7.0	11
O	13.19	35-40	1
N	4.47	0-0.2	0.3
Ash	0.78	0-0.2	0.1
HHV (MJ/Kg)	36.05	16-19	40
viscosity (at 50°C) cP	843	40-100	180
Solids (wt%)		0.2-1	1
Distillation residue (wt%)	63	up to 50	1

2.8.2 Other Types of Biofuels

As there are many products gained through hydrothermal liquefaction of lignocellulosic biomass, there are several more biofuels that can be obtained through lignocellulosic biomass but with different processes.

Bioethanol or ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) is a colorless, volatile, and flammable liquid, with molecular weight of 46.07 g and density of 789 kg/m^3 at 294 K. It has a smokeless blue flame that is almost imperceptible in standard light. The auto-ignition temperature is the lowest temperature at which ethanol can spontaneously ignite in a standard environment, without the need for an external ignition source like a flame or spark (Baeyens et al., 2015). The five methods for bioethanol production are Simultaneous Saccharification and Fermentation (SSF), Simultaneous Saccharification and Co-Fermentation (SSCF), Consolidated Bioprocessing (CBP), Integrated Bioprocessing (IBP), and Separate Hydrolysis and Fermentation (SHF) (Jagmann & Philipp, 2014). Because of its low cost and high product yield, SSF is the most promising of these technologies. Another interesting method is IBP, which includes treating each stage with microorganisms in a single step. However, no research on IBP pretreatment has been published (Chandel et al., 2015).

Biohydrogen is a viable alternative carrier to fossil fuels. Thermochemical (gasification and pyrolysis) and biological processes can be used to manufacture biohydrogen from lignocellulosic biomass. Hydrogen can be created using pyrolysis, either rapid or flash pyrolysis (Putro et al., 2016). Gasification, which involves partial oxidation and steam reformation followed by a water-gas shift reaction, can create hydrogen. Photo fermentation, which is light dependent, and dark fermentation, which is light independent, are two biological mechanisms for producing biohydrogen (Sivagurunathan et al., 2016).

Even though biogas and syngas have similar chemical compositions (CO_2 , CH_4 , H_2 , and N_2), they are created in two different ways. Biogas is produced through anaerobic digestion, involving four steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Taherzadeh & Karimi, 2008), whereas syngas is made through gasification at a lower

temperature due to the high reactivity of biomass (Taherzadeh & Karimi, 2008). There are three types of biomass gasification processes:

- Pyrolysis: Anaerobic decomposition of biomass at high temperatures.
- Partial oxidation: Requires a reduced amount of oxygen compared to standard oxidation.
- Steam gasification: Involves the reaction of water with biomass.

2.9 Chapter Summary

The chapter begins with the potential and challenges of biomass. The comparison of different type of biomass in their availability shows that EFB is the most promising biomass in Malaysia. The comparison of different kinds of pretreatment methods for delignification is presented and discussed. DESs and LTTMs stand out to be the most promising options compared to conventional pretreatment methods such acid pretreatment, alkali pretreatment and Organosolv pretreatment. The characterisation of LTTMs such as chemistry, density, viscosity, conductivity, FTIR analysis and biopolymer solubility are also discussed. The optimization of synthesizing LTTMs is presented and reviewed. Next, the parameters for HTL of lignin such as temperature, pressure, lignin-to-water ratio, catalysts, reaction time, enzymatic pre-treatment, reaction mechanisms and kinetic modelling are discussed and presented. Finally, this chapter presents the bio-based fuels produced from HTL along with their characteristics of bio-oil and comparison with other types of biofuels are discussed and reviewed.

CHAPTER 3

METHODOLOGY

3.1 Introduction

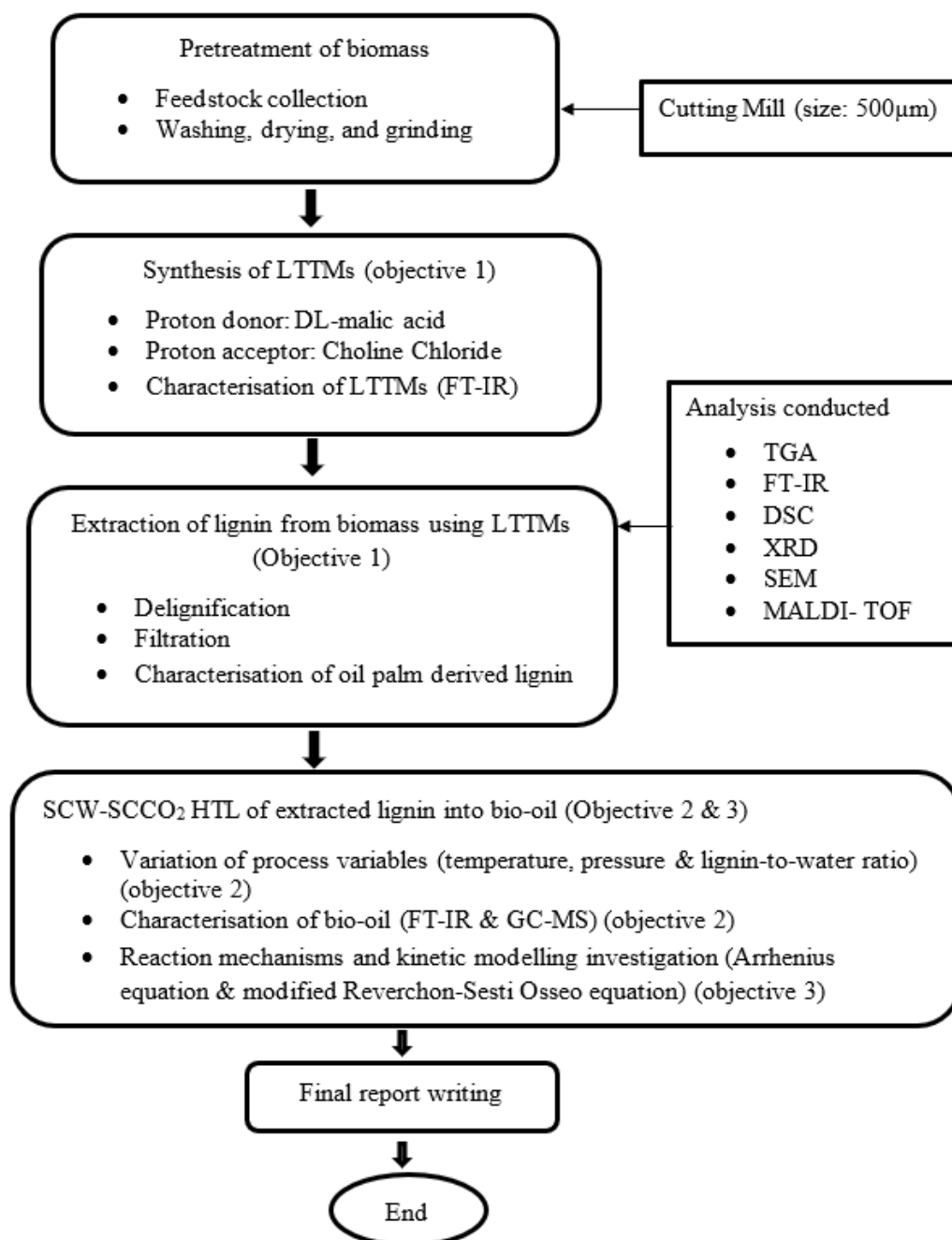


Figure 3.1: Research Methodology Flow Chart

This chapter consists of the materials prepared for usage and methodologies used for collection and characterisation of LTTMs, lignin and bio-oil. The materials prepared were used for the synthesis of LTTMs which were later used for the delignification of pretreated biomass. The extracted lignin was then undergone SCW-SCCO₂ HTL using multiple manipulated variables to investigate the reaction mechanisms and kinetics. The data was also collected for the characterisation of the LTTMs, lignin and bio-oil. Figure 3.1 shows the flow of overall research methodology based on the activities conducted from the beginning to the end of the research.

3.2 Materials

Analytical reagent (AR) grade choline chloride 99% (CAS Registry No.: 67-48-1) and DL-Malic acid 99+% (CAS Registry No.: 6915-15-7) were obtained from Sigma-Aldrich and a HBA and HBD respectively. EFB was obtained from a local palm oil mill. Distilled water was produced as required in the laboratory by using FAVORIT W4L water stills.

3.3 Experimental Procedures

3.3.1 EFB Pretreatment and Lignin Content Analysis

The source of oil palm biomass was obtained from palm tree plantation areas, which are Masranti Plantation and oil palm mill at Serian, Kuching. The untreated EFB was washed and dried in an oven at 100 °C for 3 consecutive days. The dried biomass was then chopped and cut into smaller pieces. Using the FRITSCH Cutting Mill, the dried biomass was grounded and sieved to ensure that the particle size is no larger than 500 µm. Then, the EFB was washed again to remove dust particle attached to the EFB fibers and later dried again. Figure 3.2 depicts the overall process of EFB pretreatment.

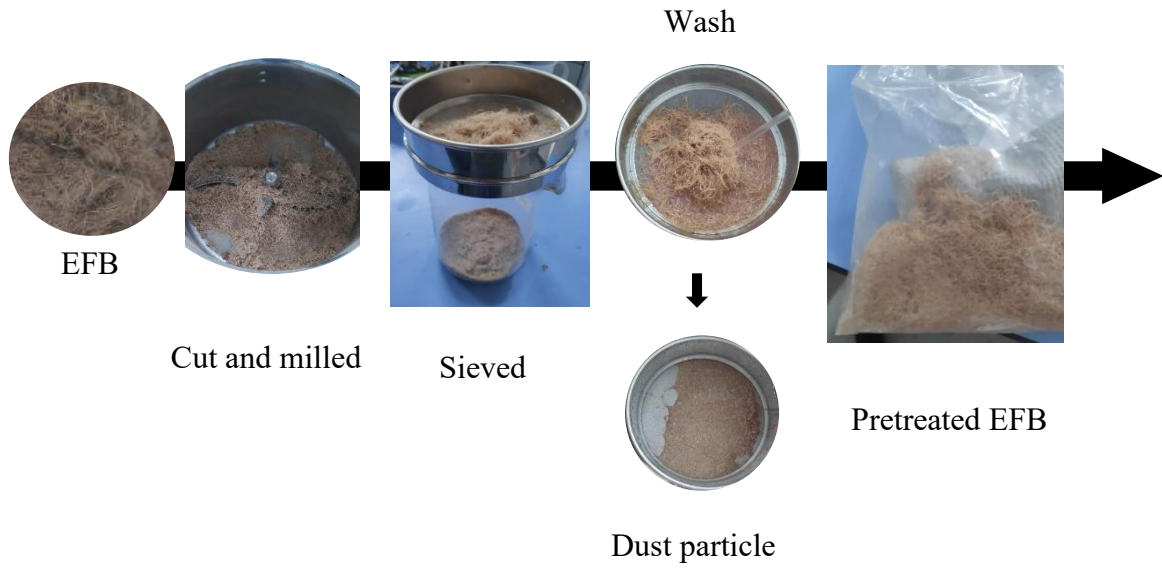


Figure 3.2: Workflow of Biomass Pretreatment

The EFB was analysed by using the Klason method to assess its lignin content. The EFB went through treatment with 72% sulfuric acid (H_2SO_4) at room temperature for 2 hours. Subsequently, the hydrolyzed sample was diluted to 3% H_2SO_4 using distilled water and boiled under reflux conditions for 4 hours. The acid insoluble lignin (AIL) was then separated from the solution and dried at 50°C . The remaining acid soluble lignin (ASL) in the 3% H_2SO_4 solution was quantified using a UV/Vis spectrophotometer (Perkin Elmer Lambda 35) and calculated based on Equation 3.1.

$$\text{Acid soluble lignin} = \text{Equation 3.1}$$

$$\frac{\text{Absorbance at } 205 \text{ nm}}{\text{Cell path length} \times \text{Absorptivity}} \times \text{dilution factor}$$

The ASL value was calculated using a 3% H_2SO_4 reference blank, a dilution factor of 20, a 1 cm cell path length, and a lignin absorptivity of 110 L gcm^{-1} at 205 nm (Wen et al., 2022).

3.3.2 LTTMs Synthesis

In a beaker, the starting materials (HBA and HBD) were thoroughly mixed with magnetic stirring to allow contact between the solid crystals. Then, LTTMs were synthesised from the mixture of DL-malic acid-choline chloride-water with a molar ratio of 2:4:2 (w/w/w). Using magnetic stirring, the mixture was gradually heated in an oil bath and stirred until a transparent liquid mixture devoid of any solid particles was formed.

3.3.3 Characterisation of LTTMs

A JASCO FT-IR 4100 spectrometer was used to determine the existence of hydrogen bonding in the LTTMs based on shifting of FTIR spectra and monitored using the Spectra Manager TM II spectrometer in the range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1} .

3.3.4 Recoverability of LTTMs

The recoverability of LTTMs was also investigated using a rotary evaporator as shown in Figure 3.3. The recovered solvent was obtained using heating bath temperature of 50 °C, vacuum of 72 mbar and rotation of 40 rpm. The rotavapor successfully produced the 1st and 2nd recovered solvent by using used fresh solvent and 1st recovered solvent respectively. Then it was used for the delignification of biomass.



Figure 3.3: Rotavapor R-300

3.3.5 Delignification of Biomass using LTTMs

The processed biomass was pretreated using LTTMs with a ratio of 1:20 (w/w) at a temperature of 90 °C over a multiple period of time, 1–5-hour period as a parameter in an oil bath with magnetic stirring. Then, the delignified biomass was washed with distilled to separate lignin from the biomass. To separate the precipitated lignin and delignified biomass from the supernatant, A Grade 5C Advantec ashless quantitative filter paper ($< 5 \mu\text{m}$) was used. The extracted lignin was dried with 50°C overnight whereas the delignified EFB was disposed. The dried lignin was grinded into powder form which is shown in Figure 3.4. This was repeated using 1st and 2nd recovered solvent which was obtained using the parameters in section 3.3.4.



Figure 3.4: Dried Lignin in Powder Form

3.3.6 Characterisation of Extracted Lignin

To obtain a deeper understanding of its thermal stability, purity, heat of reaction, possibility of crystalline phases formation, lignin sequencing and purity of lignin, respectively the lignin extracted from the biomass was analysed using Thermogravimetric analyser (TGA), Fourier-Transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), powder X-ray diffractometry (XRD) and Matrix-Assisted Laser Desorption/Ionization-Time Of Flight (MALDI-TOF) mass spectrometry (MS).

3.3.6.1 Fourier-Transform Infrared Spectroscopy (FT-IR)

The sample was prepared by finely grinding it and mixing it with potassium bromide (KBr) in a 1:100 ratio to create a pellet. The Perkin Elmer FT-IR spectrometer was configured to scan in the range of $500\text{--}4000\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . The prepared lignin sample was then placed into the sample holder, and the scan was initiated to collect the FT-IR spectra. The resulting spectra were analyzed to identify characteristic peaks corresponding to lignin's functional groups, such as phenolic -OH, methoxyl -OCH₃, and aromatic C-H stretches. These were compared with known reference spectra for verification. The figure of the equipment is shown in Figure 3.5.



Figure 3.5: FT-IR Frontier Perkin Elmer

The FTIR technique is employed to obtain the infrared spectrum of absorption or emission from a solid, liquid, or gas. The FTIR spectra of the individual starting material and the LTTM can be analysed and compared to prove the creation of hydrogen bonds between the constituents of the LTTM, which can be used for the detection and quantitative measurement of hydrogen bonding between the starting materials (Yiin et al., 2015).

The absorption bands in FTIR spectra are caused by changes in the vibrational states of bonds in the compound, and the frequency range from which the bond is absorbed is assigned to a specific group or class of compounds and is influenced by the bond's strength. Fourier transform infrared (FTIR) spectroscopy with attenuated total reflectance (ATR) is often used to detect the different functional groups present in the LTTM and to examine the interactions between the HBA and HBD (Shafie et al., 2019). The number of molecules whose vibrational states change as a result of infrared radiation is measured by the absorbance of a band. The proof for the existence of hydrogen bonds between the constituents in the LTTM is the shift in the stretching frequency of the X-H bond.

The importance of studying hydrogen bonding interactions between the HBA and HBD in the LTTM cannot be overstated. Due to the LTTM's remarkable sensitivity to changes in microstructure, the FT-IR spectrum is frequently used to explore the interactions

of different functional groups to analyse and identify the structure of a material, particularly for analysing hydrogen bond interactions. To summarise, the primary goal of FT-IR analysis for physicochemical characterisation of LTTM is to demonstrate the creation of hydrogen bonds between the HBA and HBD, which is required for LTTM synthesis to be successful. Redshifts, band broadening, and peak alterations in the FT-IR spectra could all be indicators of the presence of hydrogen bonds (Zhu et al., 2016).

3.3.6.2 Thermogravimetric analyser (TGA)

Approximately 7 mg of lignin sample was measured and deposited into a conventional ceramic crucible. This crucible was then positioned in a TG/DTA 6200 system, as depicted in Figure 3.6. The heating process involved ramping from room temperature to 1100 °C at rates of 10, 30, 50, and 100 °C min⁻¹. The entire test was conducted in a nitrogen atmosphere with a flow rate of 20 mL min⁻¹. The resulting curve depicted the relationship between weight loss and temperature.



Figure 3.6: TG/DTA 6200 system

3.3.6.3 X-ray diffractometry (XRD)

XRD patterns were obtained using a MiniFlex 600 diffractometer (40 kV, 40 mA) with a Ni filter, employing Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) as shown in Figure 3.7. Scans

ranged from 10° to 50° with 0.02° increments at 2 seconds per step. Compound identification utilized PDXL 2 software.



Figure 3.7: Rigaku MiniFlex 600 Diffractometer

3.3.6.4 Differential scanning calorimetry (DSC)

DSC analysis of lignin samples was conducted using a Hitachi DSC-7020 system, and the results were processed as illustrated in Figure 3.8. Each sample (2 to 5 mg) was positioned in a standard aluminum pan (40 μ L) and subjected to heating under a nitrogen atmosphere at a flow rate of 50 mL/min. The sample underwent an initial heating phase up to 200 °C at a rate of 10 °C/min, followed by cooling to -10 °C at a rate of 30 °C/min. Subsequently, the sample was reheated to 200 °C at a rate of 10 °C/min. The initial heating and cooling cycle aimed to eliminate the thermal history, removing endothermic enthalpy relaxation that could influence T_g determination (Poursorkhabi et al., 2013; Rials and Glasser, 1984). The T_g value for each sample was derived from the last heating cycle



Figure 3.8: Hitachi DSC-7020 System

3.3.6.5 Matrix-Assisted Laser Desorption/Ionization-Time of Flight (MALDI-TOF)

A matrix solution of 2,5-dihydroxybenzoic acid (2,5-DHB) was formulated by combining 0.1 vol.% trifluoroacetic acid in acetonitrile with a concentration of 20 mg/ml, in a ratio of 7/3 (v/v) (TA 30). Sodium trifluoroacetic acid (NaTFA) was blended with TA 30 to create a cation agent solution (2 mg/ml). Separate 1000 ppm sample solutions were prepared by dissolving the extracted lignin into TA 30. For the generation of 2,5-DHB dried droplets on a ground steel target plate, a molar ratio of 5:1:1 (2,5-DHB:sample: cation agent) was utilized. Analysis was performed using matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS). Each sample (0.5-1 μ l) was spotted in duplicate on the plate and dried at room temperature for 30 minutes. A Shimadzu Biotech AXIMA Performance instrument was employed to capture high-resolution mass spectra, as illustrated in Figure 3.9. The detector range was configured from 0 to 1000 Da in linear positive (LP) mode. MALDI-TOF-MS was performed across 10 different sample deposit zones for each lignin sample, with a total of 10 shots delivered.



Figure 3.9: Shimadzu Biotech AXIMA Performance System

3.3.6.6 Scanning Electron Microscopy (SEM) Analysis

Lignin samples were first dried in a vacuum oven at 40–60°C for several hours to remove residual moisture. The dried powder was then mounted on standard aluminum SEM stubs using double-sided conductive carbon tape. To counteract lignin's non-conductive nature and minimize charging under the electron beam, samples were sputter-coated with a ~10 nm gold layer using a vacuum coater. The microstructural morphology of the lignin was analyzed using SEM (JEOL JIB-4601 F), as depicted in Figure 3.10, under high-vacuum conditions, with an accelerating voltage of 5–20 kV and a working distance of ~10 mm. A Secondary Electron Detector (SED) was employed to capture detailed surface morphology. The lignin was observed at magnification of 2500x, 7000x and 30000x.



Figure 3.10: JEOL JIB-4601 F Multibeam System

3.3.7 Reaction Mechanism of SCW-SCCO₂ HTL of Extracted Lignin

The extracted lignin of 0.25g and distilled water, at a specified biomass to water ratio, is loaded into the reactor. To perform the liquefaction of the extracted lignin, a 6 mL Inconel batch reactor is placed into a reactor furnace that is set to have mechanical stirring with a cyclic horizontal swing span of 2 cm, at a frequency of 60 cycles per minute as illustrated in Figure 3.11. After the reaction, the liquefaction product was washed and extracted thoroughly using toluene. Then, the liquid bio-oil was obtained after evaporation of toluene at 88 hPa and 57 °C water bath. This process was carried out by Jennie Siew Zhen Ngu and Prof. Dr. Armando T. Quitain from Kumamoto University (KU) as part of a collaborative effort. An examination was conducted on the effects of process parameters such as temperature (250-300°C), pressure (20-35MPa), lignin to water ratio (1:2, 1:3 & 1:5) and time (30-240 min) on hydrothermal liquefaction of lignin.

Gas chromatography-mass spectrometry (GC-MS) and Fourier-Transform infrared spectroscopy (FT-IR) was used to analyse the chemical composition of the bio-oil to quantify the semi-volatile oxygenated compounds that are present. To analyze bio-oil using GC-MS, electron ionization at 70 eV was used, then the mass spectrometer detected the separated compounds, generating mass spectra for identification. A temperature program from 50°C to 300°C helped elute all components, and a mass spectral library was used for compound identification. Semi-volatile oxygenated compounds such as phenols, ketones, and acids were quantified by comparing their peak areas with an internal standard. Also, the bio-based fuels' physical properties were studied. The conversion of lignin and bio-oil yield was calculated using Equations (3.2) based on the literature Chan et al. (2018) and Equation (3.3) based on the literature Sasaki & Goto, (2009).

$$Bio - oil\ yield(wt\%) = \frac{Bio - oil\ obtained\ (g)}{Mass\ of\ lignin\ used\ (g)} \times 100 \quad \text{Equation 3.2}$$

where bio-oil obtained (g) is after HTL while mass of lignin used (g) is before HTL, respectively.

$$\text{Conversion: } X = 100 - \text{Yield}$$

Equation 3.3

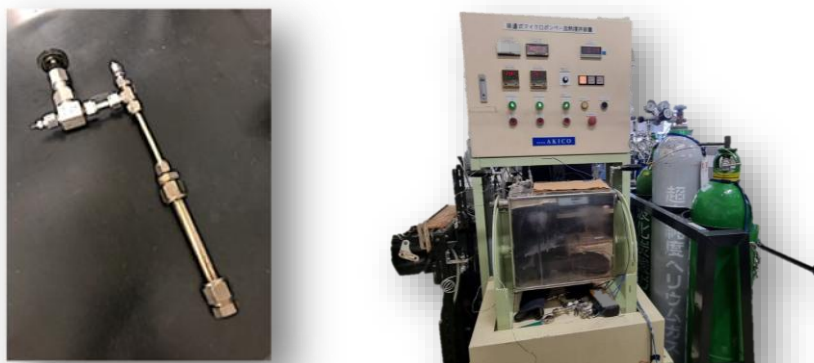


Figure 3.11: Depiction of the Batch Reactor (left) Inside the Reactor Furnace (right)

3.3.8 Investigation on Kinetics of SCW-SCCO₂ HTL

The research then focuses on the subcritical water's basic physical and chemical properties, hydrothermal liquefaction studies of lignin and their reaction paths and products. This is undertaken to acquire additional insight into the underlying reaction mechanisms and key experimental variables involved in hydrothermal liquefaction.

Due to the complex nature of the reaction network of lignin, studying the kinetics of liquefaction based on individual reaction pathways is challenging. Therefore, in this study, the overall kinetics of lignin liquefaction were explored by examining the changes in overall conversion (X) of the lignin with respect to time. The rate of conversion of lignin can be represented as a function of the apparent rate constant (k), apparent reaction order (n), and a temperature-independent function of conversion ($1-X$). For a batch reactor process, the kinetic equation is expressed as follows:

$$\frac{dX}{dt} = k(1 - X)^n \quad \text{Equation 3.4}$$

Taking the natural logarithm, Equation (3.4) can be expressed as:

$$\ln\left(\frac{dX}{dt}\right) = \ln k + n \ln(1 - X) \quad \text{Equation 3.5}$$

The apparent rate constant (k) is defined by the Arrhenius equation as:

$$k = Ae^{\frac{-E}{RT}} \quad \text{Equation 3.6}$$

where A, E, R and T represent the apparent pre-exponential factor (s⁻¹), apparent activation energy (J/mol), molar gas constant (8.314 J/mol.K) and temperature (K), respectively.

Equation (3.6) can be further expressed as:

$$\ln k = \ln A - \frac{E}{R} \left(\frac{1}{T} \right) \quad \text{Equation 3.7}$$

The Modified Reverchon-Sesti Osseo equation, widely employed for modelling the extraction of value-added biochemicals from various plants and herbs, has seen limited application in modelling bio-oil production. The derivation of this modified equation (Equation 3.8) has been documented in previous literature (Mićić et al., 2015; Yim et al., 2017; Chan et al., 2019).

$$Y = 100(1 - e^{-t/(t_i)}) \quad \text{Equation 3.8}$$

Where Y, t_i and t represent normalized bio-oil yield (%), internal diffusion time (s) and extraction time (s). To simplify the complex equation, t_i can be assumed as constant and the term $-t/t_i$ can be represented by linear Equation 3.9.

$$-\frac{t}{t_i} = at + b = Z \quad \text{Equation 3.9}$$

Where a and b are constant and correction term, respectively. Combining Equations 3.8 and 3.9, the term Z can be written as Equation 3.10.

$$Z = \ln\left(1 - \frac{Y}{100}\right) \quad \text{Equation 3.10}$$

The modified Reverchon-Sesti Model can be further simplified as Equation 3.11.

$$Y = 100(1 - e^{at+b}) \quad \text{Equation 3.11}$$

In this study, to compare the experimental data of bio-oils form with modified Reverchon-Sesti model, the normalized bio-oil yield (Y) is calculated following Equation 3.12 (Chan et al., 2019).

$$Y = \frac{y}{y_{max}} \quad \text{Equation 3.12}$$

where y and y_{max} represent the bio-oil yield (wt%) and maximum bio-oil yield (wt%) for a specific temperature, respectively. Equation 3.12 represents experimental data (graph of Y versus reaction time) while a best-fit curve was drawn to evaluate the viability of this kinetic model as a model prediction. A graph of the Z constant versus reaction time was also presented to assess the accuracy of the kinetic data in relation to the model by analyzing the R^2 value of the graph.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter illustrates and elaborates the results and findings obtained throughout the study which include the following sections: (i) characterisation of LTTMs, (ii) delignification of biomass using LTTMs, (iii) characteristics of EFB derived lignin, (iv) The effect of process parameters of HTL of lignin, and lastly (v) kinetic study of HTL of lignin. Each section is related and aims to achieve the objective such as proving the stability of LTTMs, the efficiency of LTTMs for delignification, the authenticity of extracted lignin, the reaction mechanism of lignin and accuracy of product yield prediction respectively.

4.2 Characterisation of LTTMs

Prior research has emphasised the importance of hydrogen bond formation between the respective hydrogen bonding constituents (i.e., HBA and HBD) as a sign of successful LTTM formation. The fundamental knowledge of the LTTM at the molecular level depends heavily on how each component interacts with one another as well as how varying water contents affect the water-LTTM relationship. FT-IR is a crucial tool for detecting structural changes inside the LTTMs as well as conformational alterations that signify hydrogen bonding interactions.

In general, the widening or narrowing of peaks involving OH groups, the shift of the C-H and C=O peak of carboxylic acids (malic acid), or the disappearance of certain IR peaks from the original materials is a key sign in FT-IR analysis when examining the hydrogen bonding interactions involving LTTMs or DESs (Mulia et al., 2015). As shown in Figure

4.1, the majority of the hydrogen bonding interactions occur between the hydroxyl groups of the HBD and the anion of choline chloride.

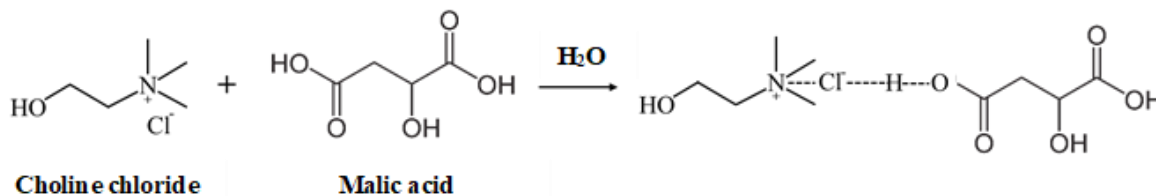


Figure 4.1: Hydrogen Bonding Mechanism of ChCl and Malic Acid to Form LTTM

Although LTTMs is regarded as a reasonably affordable, environmentally friendly solvent, it still needs to have its recyclability addressed in order to further increase its economic worth in low-cost, high-volume industrial applications. LTTMs are more easily regenerated than other solvents, according to Xu et al. (2017), because the regeneration process does not include any additional chemical interactions. In this study, the LTTMs were extracted utilising a rotary evaporator with a straightforward separation process with an inconsistent recovery of $\geq 90\%$ (1st recovery = 93.8% & 2nd recovery = 91.1%). The EFB was then pretreated with the recovered LTTMs, and the delignification level was assessed again. The fresh solvent, 1st recovery and 2nd recovery solvent are shown in Figure 4.2.



Figure 4.2: From left; Fresh solvent, 1st Recovery and 2nd Recovery Solvent

4.2.1 Structural Analysis of LTTMs

Figure 4.3 illustrates the analysis of the FT-IR spectra of choline chloride and malic acids to determine the atoms and the nature of the interactions. The OH stretching zone was seen in FT-IR spectra analysis with a wavelength range of 3700 to 2500 cm^{-1} . In the OH stretching region of malic acid, broad overlapping bands with a centre at 3400 cm^{-1} suggested the formation of dimer rings via strong hydrogen bonding networks. The distinct overlaid bands of the initial components were no longer visible in the fresh solvent because of the transition from solid to liquid mixes in terms of physical state (Yiin et al., 2017). In that range contained the hydroxyl peak associated with $\text{OH}-\text{Cl}^-$ of ChCl is attributed to the strong and broad peak in the 3700 cm^{-1} to 3200 cm^{-1} range that is centred around 3220 cm^{-1} (Saha et al., 2019). The LTTMs spectra showed a noticeable reduction in the distinctive ChCl hydroxyl peak at 3220 cm^{-1} shown in Figure 4.3, indicating that the original $\text{OH}-\text{Cl}^-$ bonds in ChCl were significantly broken up to form a hydrogen bond with the hydroxyl group of the malic acid (Yiin et al., 2023). Due to the widespread hydrogen bond formation between ChCl and malic acid as a result, the absorbance associated with the ChCl hydroxyl stretching vibration within the range of 3700 cm^{-1} to 3200 cm^{-1} considerably broadened and strengthened, indicating successful LTTM production (Peng et al., 2010).

The OH stretching frequency associated with malic acid is allocated to a medium to weak broad band in the absorption range of 3200 cm^{-1} to 2500 cm^{-1} . The LTTMs showed less OH stretching absorption when carboxylic acid was present, indicating that the fresh solvent had much less free carboxylic acid than malic acid, which served as its starting material. Malic acid and ChCl interact, causing the hypochromic effect, which lowers the amount of free malic acid that can be detected.

The C=O stretching region was visible in spectra with a wavelength range of 1800 to 1600 cm^{-1} . The C=O stretch of malic acid, which showed a bathochromic shift (red shift) from 1680 cm^{-1} to 1720 cm^{-1} in the LTTMs relative to the malic acid spectra, is responsible for the abrupt, strong peaks in the C=O stretching zone. Malic acid-based DES showed a similar redshift, which can be interpreted as evidence of the creation of a hydrogen bond, specifically linked to the O=C-O-H-N bond interaction between ChCl and malic acid (Dai et al., 2015).

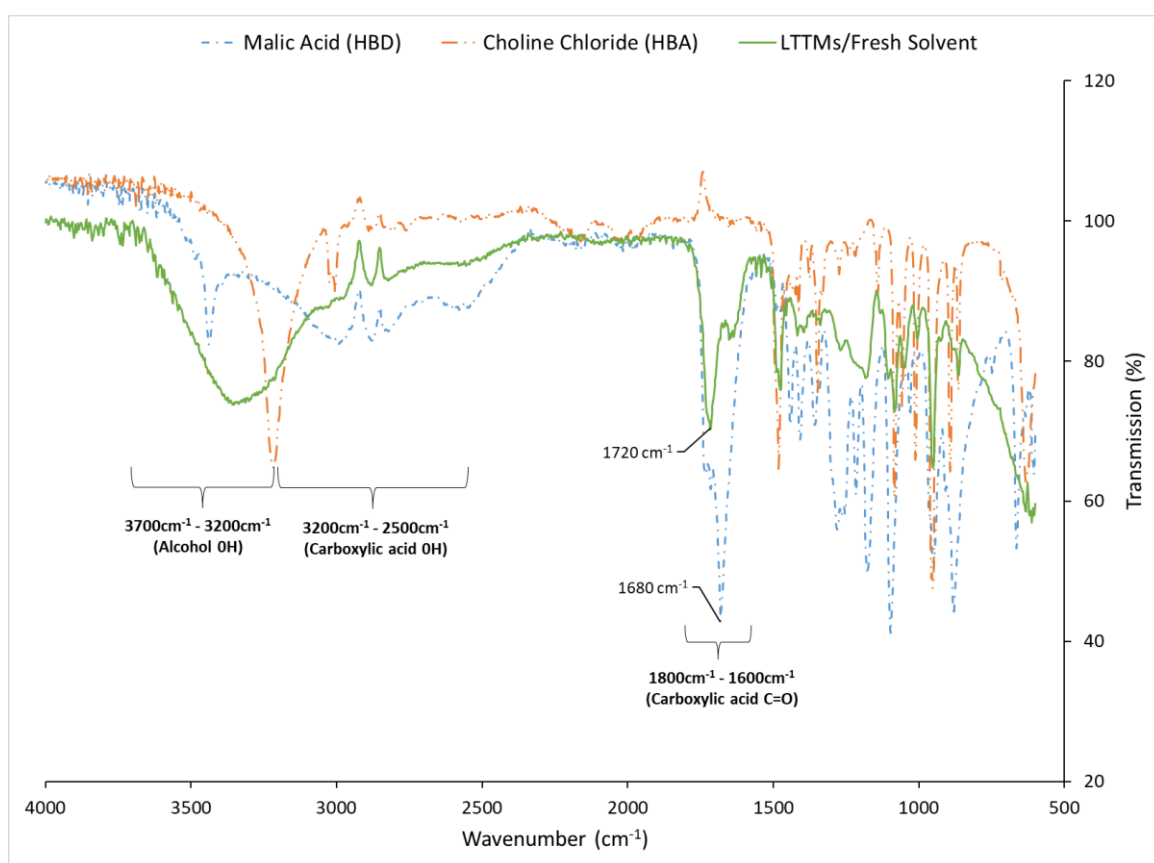


Figure 4.3: FT-IR Analysis of Malic Acid, Choline Chloride and LTTMs/Fresh Solvent

4.2.2 Recoverability of LTTMs

After biomass has been delignified, recoverability of the solvent is preferred. For first screening, water was employed as an anti-solvent (Francisco et al., 2012). The LTTMs in this study were extracted using a rotating evaporator, providing a straightforward separation procedure but resulting in an uneven recovery of $\geq 90\%$. The recovered LTTMs were subsequently subjected to FT-IR analysis to showcase the reusability of the mixtures based on the presence of hydrogen bonding. The carboxylic acid group in the 1800 to 1600 cm^{-1} range (C=O group) and the O-H groups of alcohol and carboxylic acid in the 2500 to 3700 cm^{-1} range persisted in the recovered LTTMs after biomass delignification. The C-O stretching (1080 cm^{-1}) of both recovered LTTMs experienced a shift, likely attributed to the phenolic hydroxyl groups of lignin from biomass (Lisperguer et al., 2009) as shown in Figure 4.4.

A hyperchromic effect (towards higher absorbance) was seen in the alcohol group's related OH stretching with the addition of water in the region of 3700 cm^{-1} to 3200 cm^{-1} because of the increased symmetric and asymmetric H_2O stretching vibration (Yiin et al., 2015). With the addition of water, the malic acid OH stretching intensity showed a minor hypochromic effect (towards lower peak), which led to an increase in the dissociation of the intermolecular OH bond within the carboxylic acid. In addition, the C=O peak about 1720 cm^{-1} associated with the malic acid carboxyl group showed a decreased signal with the addition of water, which is suggestive of reduced free malic acid in the LTTMs (Saha et al., 2019). The LTTMs current hydrogen bond network is deteriorating and disintegrating as a result of the increased availability of alternate pathways for hydrogen bonding interactions between water molecules and the LTTM components (Saha et al., 2019).

Based on Figure 4.4, it shows that the fresh solvent have the lowest while the 2nd recovery solvent contain the highest amount of water based on the peak in the alcohol group. This implies that with each cycle of the recovery process, water content within the recovered solvent is increasing, which also reduces the purity of the ChCl (Abu Hatab et al., 2022). The third recovery solvent was expected to contain the highest amount of water, as repeated use for delignification and the addition of water had increased both the symmetric and asymmetric H₂O stretching vibrations. This was likely due to the inconsistent addition of water (10 mL) after delignification, combined with the varying amounts of water (3-10 mL) extracted using the rotary evaporator.

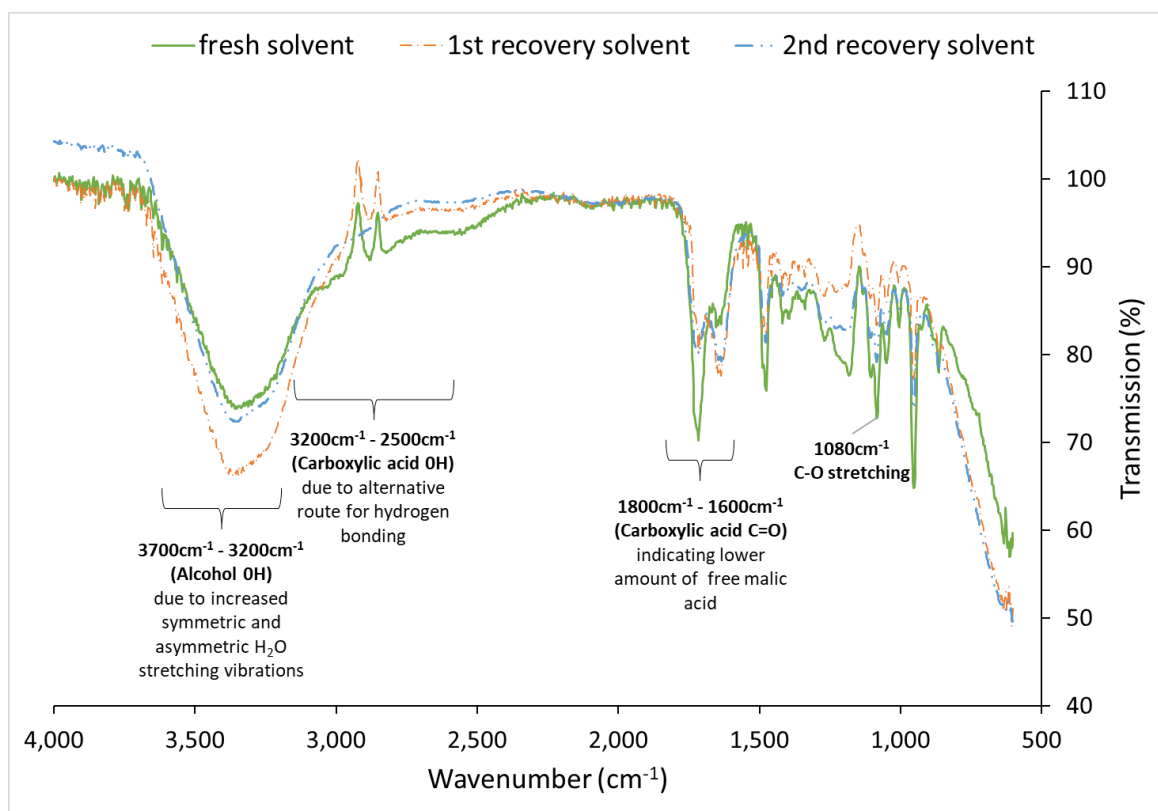


Figure 4.4: FT-IR analysis of Fresh, 1st Recovery and 2nd Recovery Solvent

4.3 Delignification of Biomass using LTTMs

In this study, the physiochemical properties of the solvent used affect the efficacy of the delignification of EFB. To determine the effectiveness of the LTTMs, the reaction time

of delignification of EFB was manipulated and the data is shown in Figure 4.5. The other parameters such as temperature (90°C), amount of EFB used (10g) and amount of LTTMs used (200g) remain constant.

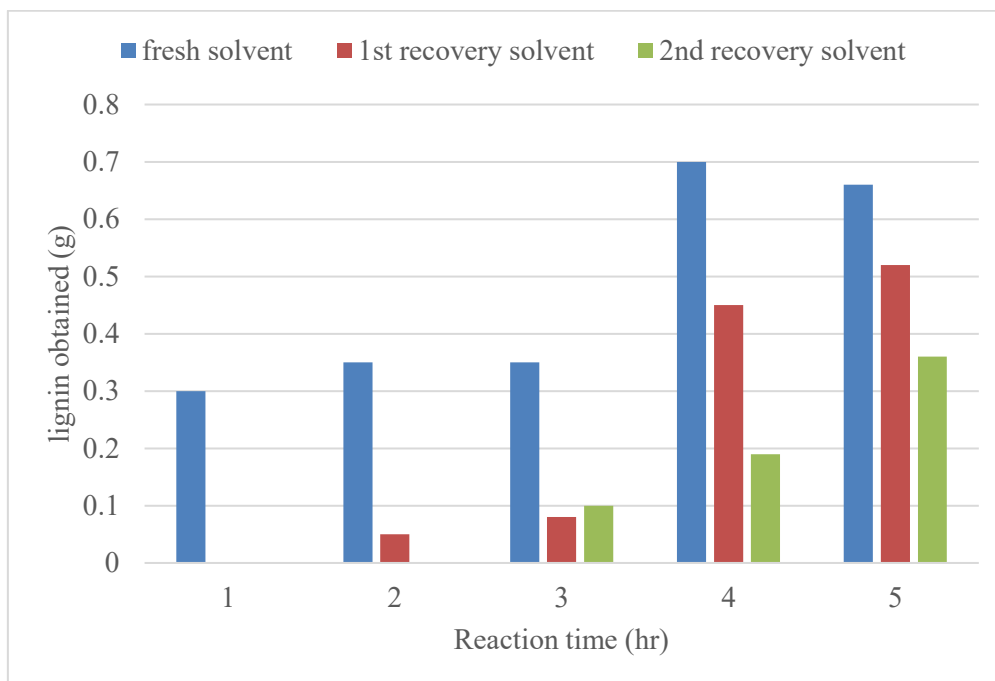


Figure 4.5: Delignification of EFB

Based on Figure 4.5, the time of delignification affects the amount of lignin obtained. Based on the Klason method, the untreated EFB consists of 21.89 wt% of lignin (13.94 wt% AIL and 7.95 wt% ASL). This shows that a maximum amount of lignin (100%) can be obtained from 10g of lignin is 2.18g. The highest amount of lignin obtained was 0.70g out of 2.18g of lignin content (31.98%) at 4hrs while using the fresh solvent. Thus, at 4hrs, 1st recovery solvent obtained 0.45g (20.64% lignin content) and 2nd recovery solvent obtained 0.19g (8.72% lignin content) which shows a decrease in efficiency. It was observed that Choline Chloride-based LTTMs demonstrated superior delignification properties in comparison with other studies. Among them, choline chloride-lactic acid (ChCl-LA) pretreated EFB exhibited the lowest total lignin content in biomass, measuring 18.8%. This was followed by choline chloride-urea (ChCl-U) with 19.4% and choline chloride-glycerol

(ChCl-G) with 21.2% (Quek et al., 2020). This is due to the acidic properties which promotes lignin solubility (Tang et al., 2018).

It is illustrated that the first 3hrs of delignification using fresh solvent was stable and did not affect the amount of lignin until it reached the 4 hrs. Any additional increase of the treatment period had no discernible impact on the yield. These findings suggest that increased biomass solubilization can be achieved with extended treatment. It is also shown that the use of recovered solvent affects the amount of lignin obtained. This confirmed prior work, that showed maximum lignin yield of 86.15 (mg/g of *Bambusa bambos* stem) was obtained in ChCl-U treatment and 103.5 (mg/g of *Bambusa bambos* stem) in Choline Chloride-Oxalic Acid (ChCl-OA) treatment with treatment time of 4-10 hrs (Ramesh et al., 2020).

The recovered LTTMs, 1st recovery and 2nd recovery solvent were also used in the pretreatment of EFB which produced a sharp decline in degree of delignification 1.1g (53.39%) and 0.65g (72.46%) respectively, relative to total yield of fresh solvent (2.36g). These results showed that higher recycling rates result in worse delignification efficiency. This suggests that the EFB derived lignin can be disrupted and dissolved by recycled LTTMs less effectively. Previous research revealed that the recycled LTTMs had a decreased ability to remove lignin as their study concluded the performance of delignification dropped approximately 8% to 11% for all LTTMs after first recycle (Quek et al., 2020). The presence of water and other contaminants like lignin in the regenerated LTTMs caused the degree of delignification in all of them to decrease. In other research, recycled LTTMs's decreased delignification effectiveness was caused by the presence of lignin, which lowered the number of active sites available for reaction (Sattlewal et al., 2018).

Thus, the optimum parameters were obtained to produce more lignin for its analysis and usage for HTL. The extraction of lignin used a temperature of 90 °C with a treatment time of 4 hrs for using fresh solvent and 1st recovery solvent. 2nd recovery solvent is used for analysis purposes. The amount of EFB and LTTMs used is adjusted accordingly to its ratio to increase production of lignin.

4.4 Characteristics of EFB Derived Lignin

4.4.1 Structural Analysis

Fourier Transform Infrared Spectroscopy (FT-IR) was employed to discern the functional groups and structural properties of the extracts. Figure 4.6 depicts the FT-IR spectrum of the sample at wavelength between 600 cm⁻¹ and 4000 cm⁻¹. Functional groups indicating the presence of lignin are hydroxyl and carbonyl group. Two bands at 3292 cm⁻¹ and 3336 cm⁻¹ correspond to O-H stretch of alcohol. The bands at 2850 cm⁻¹ and 2916 cm⁻¹ that belong to C-H stretch of methyl group are found in the spectrum. The band at 1726 cm⁻¹ is due to the non-cellulose compounds such as lignin, pectin, and hemicellulose, referring to Latip et al. (2019). The bands at 1270 cm⁻¹ and 1034 cm⁻¹ belong to the O-H stretch and C-H bend from guaiacyl group (G) while that of 1510 cm⁻¹ and 1609 cm⁻¹ could be caused by the vibration of C=C in aromatic ring skeleton of lignin (Lyu et al., 2019; Liu et al., 2020). The peak at 1462 cm⁻¹ and 1162 cm⁻¹ are attributed to the deformation vibration of CH in -CH₂- group and the vibration of C-O-C stretch of carbohydrate respectively (Liu et al., 2020). Overall, the presence of lignin functional groups shows that lignin extraction was successfully facilitated with the fabricated LTTMs.

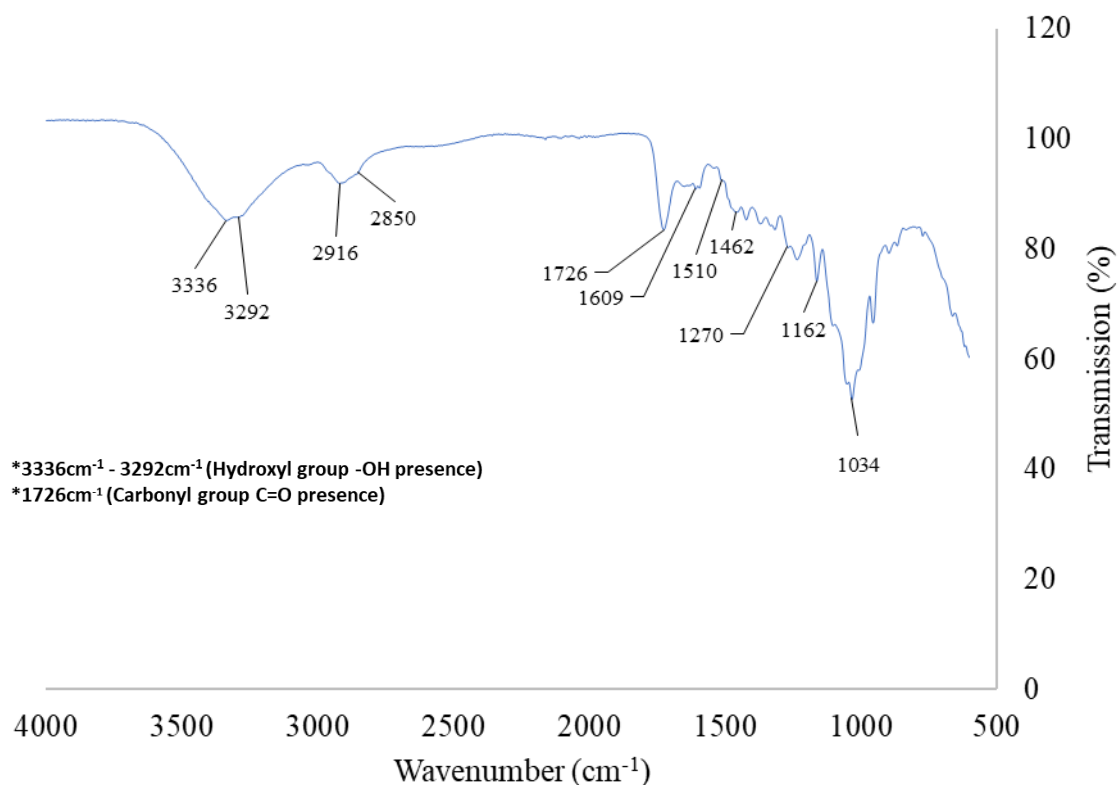


Figure 4.6: FT-IR Spectra Analysis of EFB Derived Lignin

4.4.2 Thermal Analysis

The properties of lignin at various temperatures were investigated using thermogravimetric analysis (TGA), derivative thermogravimetry analysis (DTG), and differential thermal analysis (DTA). The result of TGA, DTG, and DTA between 30°C and 1100°C are represented in Figure 4.7.

TGA curve shows a negligible mass loss of the lignin at the start of the experiment, recorded as approximately 0.247 mg. The mass loss may be caused by the evaporation of water remaining in the sample. The loss of moisture occurs at temperature below 150°C as reported by (Kohli et al., 2020). Based on the DTA curve, the moisture removal process is endothermic.

In the temperature region above 150°C, two sharp peaks are observed at 150°C-296°C and 296°C-450°C in the DTG curve. The former has the largest reduction in mass of approximately 2.381 mg as well as the highest rate of mass loss. The latter has a mass loss of about 1.613 mg. The peaks also appeared in the DTG curves in the research by Lyu et al. (2019). According to them, the breaking of side chains in lignin and the small molecules in solvent-extract mixture occasion the formation of the first peak. On the other hand, the second peak is caused by the breaking of internal linkage presented in the lignin to form small molecular volatiles such as monomeric phenols (Lyu et al., 2019; Kohli et al., 2020). However, the degradation temperatures recorded in this paper are different from the literatures referred which may be attributed to the distinction in thermal stability of the lignin samples. For example, the study from Lyu et al. (2019) uses hardwood type of lignin while this research uses grass type of lignin. The height difference between the two peaks also indicates that the structural components of lignin vary with the type of lignocellulosic biomass sources. The second peak is lower than the first peak because of the smaller rate of decomposition. Two of the stages of lignin degradation are endothermic referring to the DTA curve.

A broad peak is also observed between 450°C and 800°C in DTG curve with a mass loss of about 1.492 mg. Peaks lie in the temperature range exceeding 500°C may be caused by the degradation process of aromatic rings in lignin (Kohli et al., 2020). In this case, the aromatic rings were broken at temperatures above 450°C. After the mass loss of 5.733 mg, the remaining components in lignin undergo condensation to gain stability at temperature above 800°C, indicated by the plateau in the TGA and minimum value in the DTG curves. The remaining components account for 5.33% of the sample and are compatible for biochar

formation. The DTA curve depicts the exothermic behavior of lignin degradation at high temperature.

In summary, thermal stability of the lignin extracted is low at temperatures above 150°C while degradation occurs over a broad range between temperature 450°C and 800°C. These findings are consistent with Kohli et al. (2020), as the maximum weight loss occur between 350–450 °C. In another research degradation occurs at 200-500 °C with a maximum peak of 302 °C (Serrano-Martínez et al., 2024).

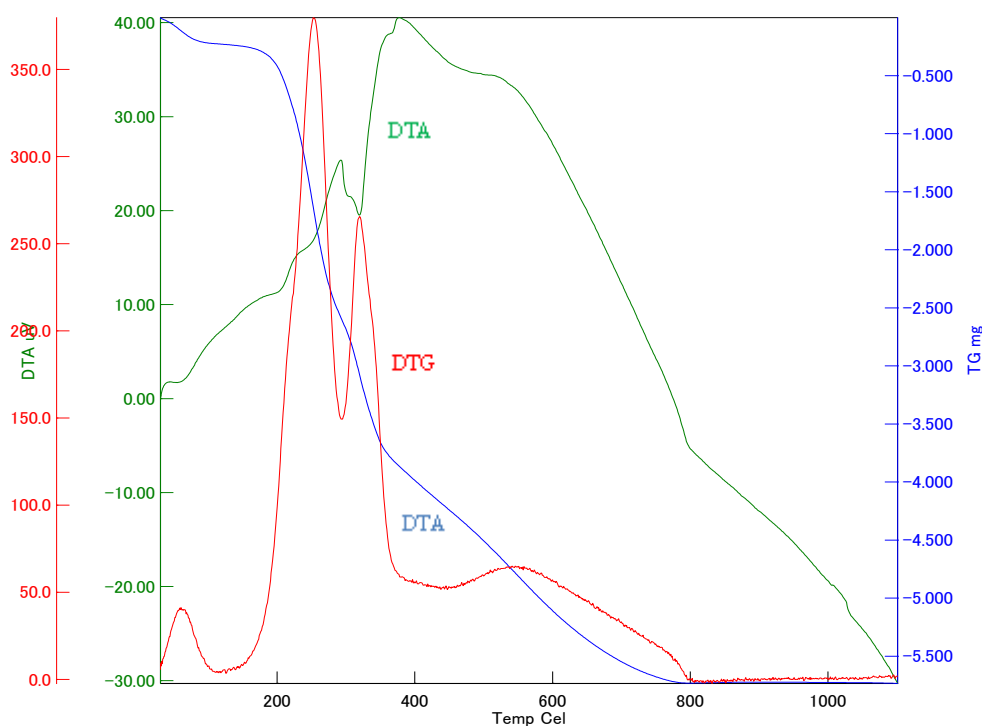


Figure 4.7: TGA, DTG and DTA Analysis of EFB Derived Lignin

4.4.3 Crystallinity

X-ray diffraction (XRD) spectrum of the extracted lignin in Figure 4.8 is obtained to study the crystallinity of the extracted lignin. In the spectrum, Y(obs) represents the observed diffraction intensity, Y(calc) refers to the intensity calculated from the crystal structure model, and Y(bkg) indicates the background intensity from environmental or instrumental

noise. The difference between the observed and calculated intensities, denoted as $Y(\text{obs}) - Y(\text{calc})$, is plotted to visually assess the quality of the fit between the experimental data and the model. The result of the experiment is as shown in the figure. The spectrum of the experiment data has several peaks identified at $2\theta = 16.5^\circ$, 22.3° , and 34.7° . In comparison, the peaks at 16.5° and 34.7° are absent in the calculated plot while the maximum peak is at 22.2° . The peaks overlap, resulting in an overall broad peak in the experiment curve. However, the maximum observed intensity is at 22.3° , majorly contributing the amorphous property of lignin. The peaks at 16.5° and 34.7° were reported as the characteristic peaks of cellulose I structure for plane (110), (200), and (004) respectively according to Khenblouche et al. (2019) and Yang et al. (2022). The peaks of less intensity observed in the experiment curve may be caused by the presence of impurities. These findings are consistent with Kohli et al. (2020), which has a similar sharp peak at $2\theta(22^\circ)$ proven to be the amorphous property of lignin but different diffraction peaks due to different lignin type.

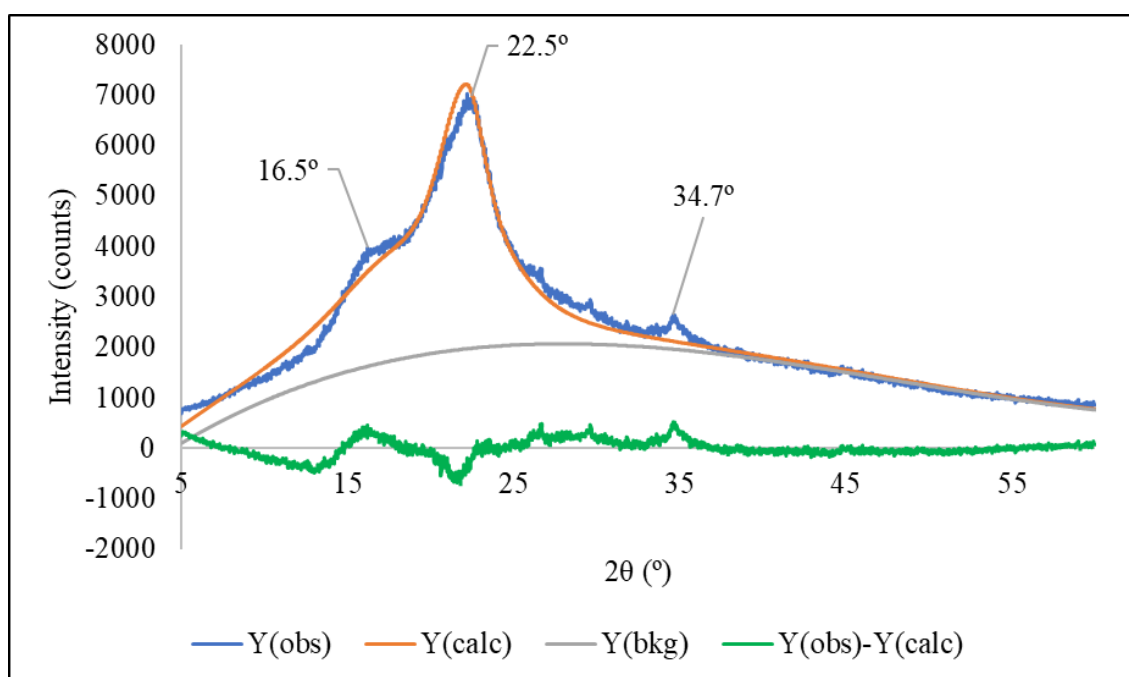


Figure 4.8: XRD Analysis of EFB derived lignin

4.4.4 Glass Transition Behavior

The glass transition temperature (T_g) of lignin is crucial for understanding its thermal behavior, enabling precise control and enhancing bio-oil yield during HTL (Zhang et al., 2021). Differential scanning calorimetry (DSC) and its derivative (DDSC) in Figure 4.9 were used for the determination of thermal transitions of the extracted lignin. The thermogram resembles the result obtained by Ramezani and Sain (2018). The initial DSC curve has a large endothermic peak at 57°C, where the heat flow at the beginning of the experiment was -5.575 mW. DDSC curve shows a sudden increased rate of heat flow at 32°C, attributed to the endothermic reaction. The peak is caused by moisture loss that is feasible at temperatures below 150°C. Continuous heating leads to the formation of another endothermic curve which is caused by the degradation of lignin before the cooling process. Hence, the glass transition temperature is determined as 93°C which is before the formation of the second endothermic peak. According to Ramezani and Sain (2018), phenolic compounds are produced from lignin degradation that remove volatiles components, following the glass transition. Glass transition temperature varies with the physical and structural properties of lignin, including molecular size and weight, phenolic groups bonded to the main chain, crosslinks, intermolecular bonds of hydrocarbon chains, and hydrogen bonds as well as extraction method, lignin conformation, and thermal prehistory (Börcsök & Pásztor, 2021). They also stated that, based on past studies, higher water content reduces glass transition temperature by eliminating intermolecular hydrogen bonds between hydroxyl group in phenolic components, easing lignin fragmentation. Therefore, the low glass transition temperature reported in this study could be contributed by the high moisture content from the extraction method which involves in addition of water that caused the large endothermic curve at low temperature and the structural differences. In the cooling process, heat was released from the

sample owing to the exothermic event and forms positive y-values. These findings differ from those reported of Arfat et al. (2024), who determined a T_g of 186°C , whereas this study observed a T_g of 93°C . Another study reports that Kraft lignin exhibits a T_g ranging from 140°C to 180°C , which differs from the type of lignin analyzed in this research (Henrik-Klemens et al., 2024). This shows that the EFB derived lignin have high moisture content which will lead to easier processing and produce higher bio-oil yield during HTL.

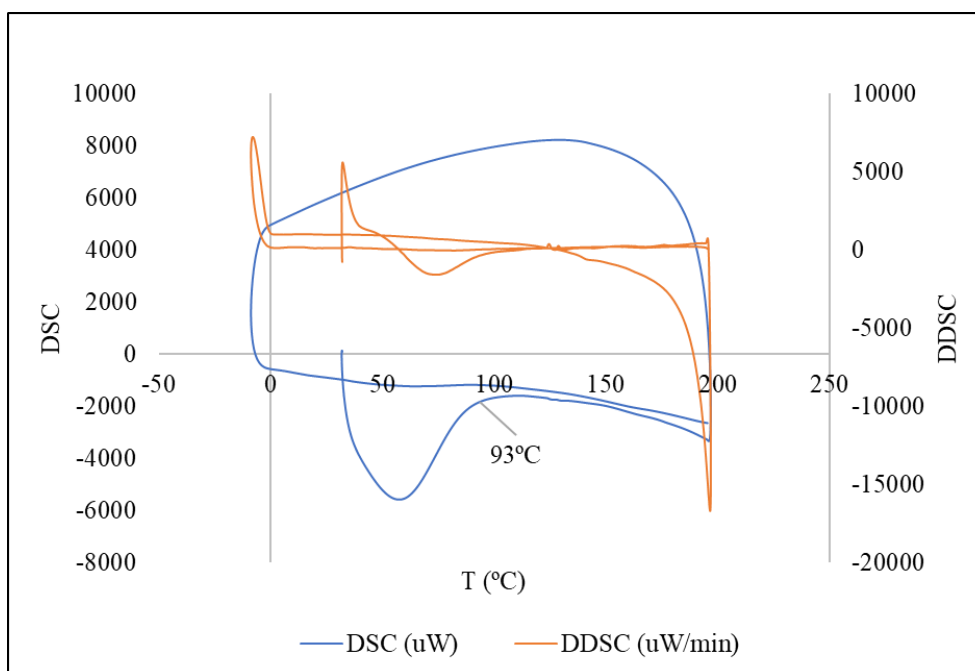


Figure 4.9: DSC and DDSC Analysis of EFB Derived Lignin

4.4.5 MALDI-TOF-MS Analysis

4-hydroxyphenyl (H) group, guaiacyl (G) group, and syringyl (S) group are three primary monomers of lignin that are linked by either ether bond, C-C bond, or complexation (Alzagameem et al., 2019). Estimation of the composition of the monomers as well as the identification of side groups in a lignin sample are feasible with mass spectrometry. Results of matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry (MS) in the range of m/z up to 500 Da (Figure 4.10) and 2000 Da (Figure 4.11) are obtained to identify the structural components of the extracted lignin based on their

molecular weight. Firstly, a weak peak found at 103.75 Da could be caused by fragment ion originated from p-coumaric acid and p-coumaryl alcohol ($C_9H_{10}O_2$) which belongs to H group referring to the results of the past studies (Letourneau & Volmer, 2023). The peak at 152.94 Da is assigned to protonated vanillin that has a chemical formula of $C_8H_8O_3H^+$, and the species originates from coniferyl alcohol, categorized in G group. The strongest peak is found at 175.88 Da, implying the abundance of the species. The peak is assigned to a fragment cation of sinapyl alcohol which is a S group. However, the peak can be partially contributed by the fragment cation of ferulic acid, represented by $C_{10}H_9O_3H^+$ formula as referred to the result presented by Boes et al. (2017). The peak at $m/z = 197.89$ Da can be attributed to the fragment ion originated from the coniferyl alcohol with a formula of $C_{10}H_{12}O_4H^+$ ion based on past studies (Banoub et al., 2015). Fragment ions produced from a dimer of two coniferyl alcohols with 8-5 linkage ($C_{20}H_{22}O_6$) has caused the peaks at $m/z = 153.89$ Da and 339.77 Da. Similarly, the peak at 374.33 Da can be caused by protonated coniferyl alcohol dimers and the fragment ions of sinapyl alcohol-coniferyl alcohol dimer via β -O-4 linkages. On the other hand, tricetin ($C_{17}O_7H_{14}H^+$) is assigned for the peak at $m/z = 331.70$ Da and its fragment ion ($C_{14}H_8O_6H^+$) contributes to the peak at $m/z = 272.19$ Da after the removal of two methyl groups (CH_3) and one carbonyl group ($C=O$). The intensity of the rest of the spectrum is relatively lower in the region of m/z above 400 Da. Overall, the lignin sample majorly consists of S group, followed by G and H groups. Tricetin, ferulic acid, and p-coumaric acid are also found to be the binders of lignin, showing the characteristics of monocots.

Data: h1-linear0003.H1[c] 28 Feb 2023 12:24 Cal: 28 Apr 2016 22:06
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 91, Blanked, P.Ext. @ 600 (bin 59)

%Int. 251 mV[sum= 92168 mV] Profiles 1-367 Smooth Av 100 -Baseline 100

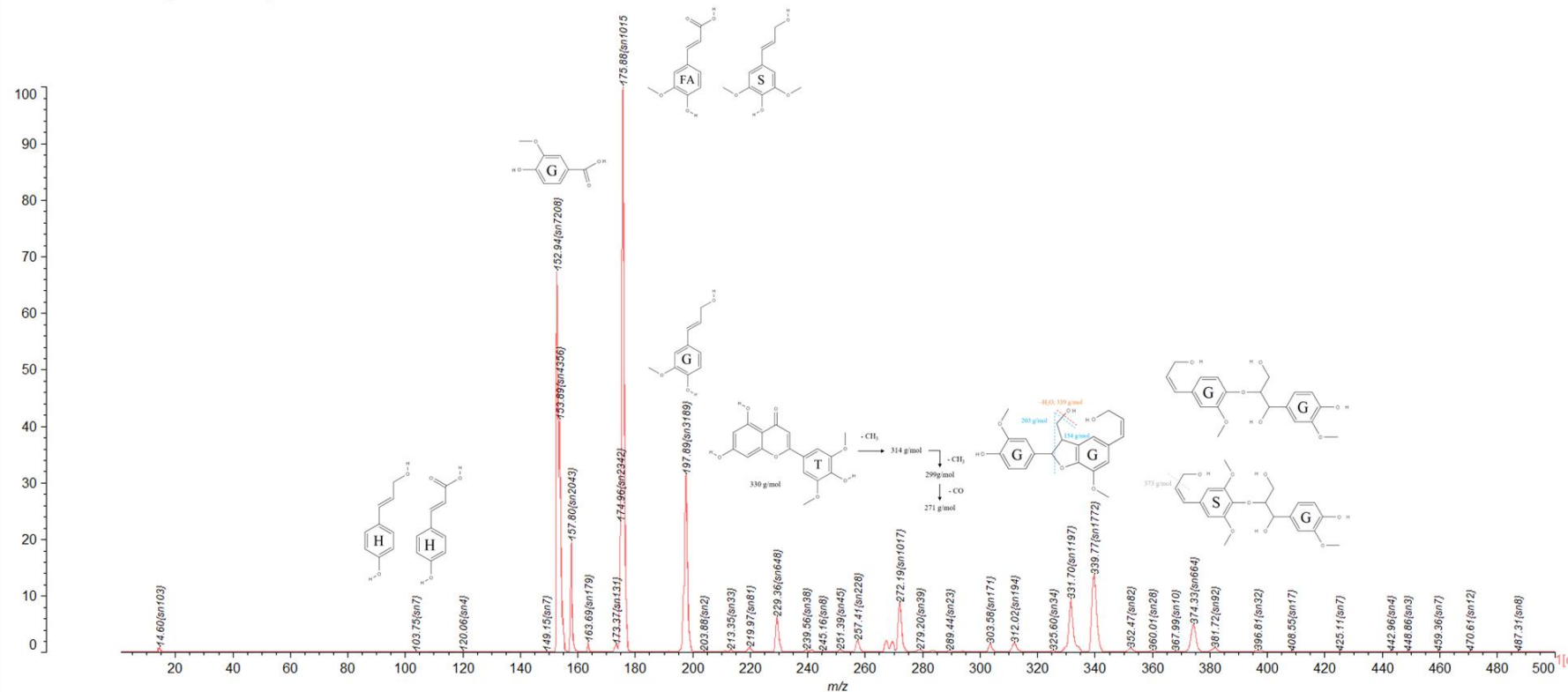


Figure 4.10: MALDI TOF (1-500Da) Analysis

Data: h1-linear0003.H1[c] 28 Feb 2023 12:24 Cal: 28 Apr 2016 22:06
 Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Linear, Power: 91, Blanked, P.Ext. @ 600 (bin 59)

%Int. 251 mV[sum= 92168 mV] Profiles 1-367 Smooth Av 100 -Baseline 100

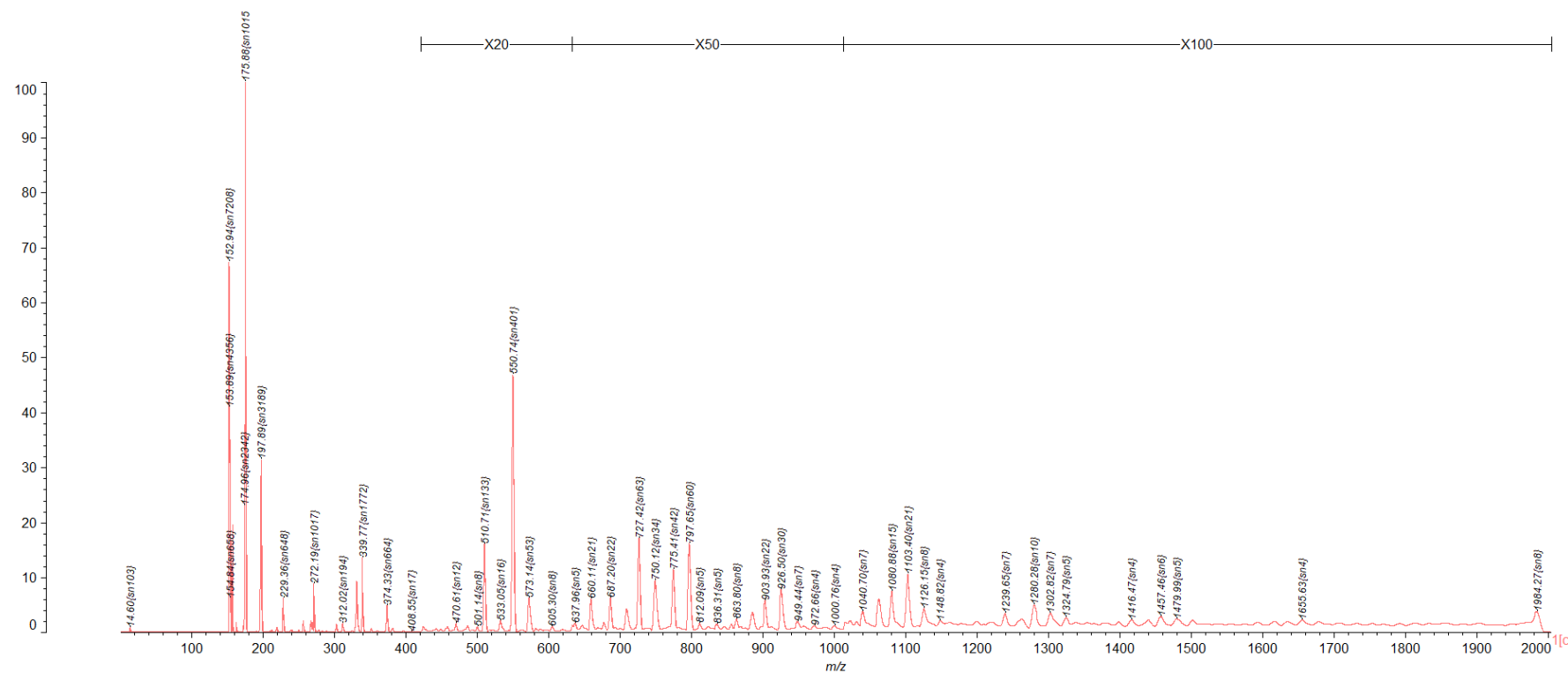


Figure 4.11: MALDI TOF (2000Da) Analysis

4.4.6 SEM Analysis

Scanning electron microscope (SEM) images of the extracted lignin were acquired to study the morphology of the extracts. At a magnification of 2500x (Figure 4.12), lignin extracted with the LTTMs appears as highly dense aggregate with size more than 10 μm . The aggregate has an irregular surface as shown in the figure and becomes more significant at a magnification of 7000x (Figure 4.13). Additionally, particles that have an imperfect globular shape are found to be attached on the surface. The size of the particles is estimated as 800 nm–1000 nm based on the image of 30000x magnification in Figure 4.14. The presence of the particles suggest that lignin aggregation occurs by joining numerous irregular shaped globes in the LTTMs through intermolecular bonding. In the experiment done by Hamzah et al. (2021), ethanol at various operating conditions was used to dissolve lignin and reported the dependence of the aggregation activity on the variables. Referring to them, amorphous properties of lignin contribute to aggregation in solvents where hydrophilic fragments collect to form spheres, and the size of the aggregates can be influenced by the operating conditions and solvent properties that changes the interaction between solutes and solvent molecules. In this case, incomplete fusion to form larger aggregate led to the formation of rough surface and the occasional presence of globular particles. The effect of time and other operating conditions of the LTTMs-based extraction process may be significant on the morphology and aggregation.

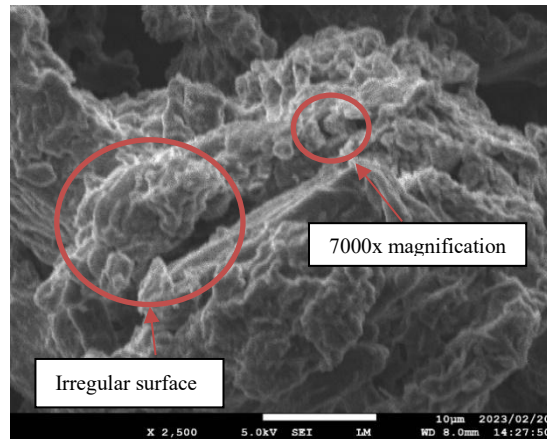


Figure 4.12: SEM Images (2500x) of EFB Derived Lignin

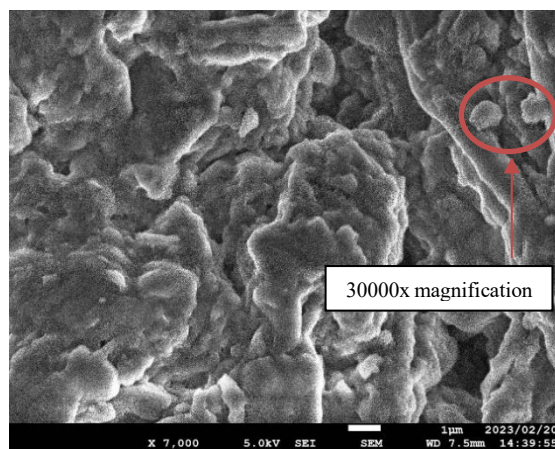


Figure 4.13: SEM Images (7000x) of EFB Derived Lignin

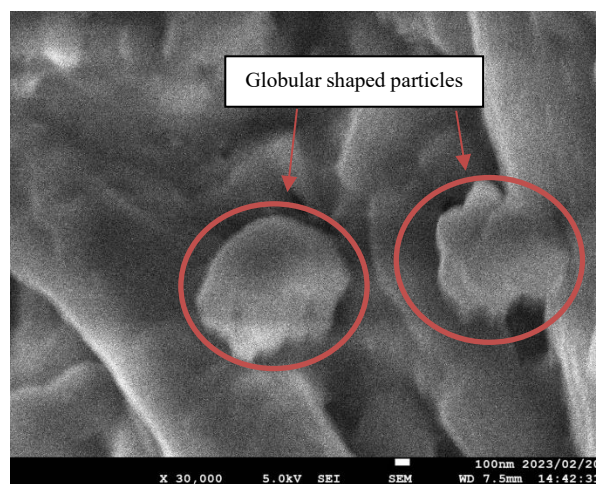


Figure 4.14: SEM Images (30000x) of EFB Derived Lignin

4.5 The Effect of Process Parameters of SCW-SCCO₂ HTL of Lignin

This study explored SCW-SCCO₂ HTL of EFB-derived lignin by varying temperature, pressure, and lignin-to-water ratio, yielding bio-oil with varying amounts and properties. Biomass input was adjusted by ~15% to exclude unreactive components such as ash, gases, and solid residue for more accurate bio-oil yield calculations. Similar exclusions were made in studies such as Chan et al. (2019) and Riaz et al. (2016), which separated ash, residue, and gas to refine yield estimates. Bio-oil properties were analyzed using FT-IR, with yields shown in Table 4.1.

Table 4.1: Summary of Process Parameters of HTL of Lignin

Run No.	Lignin (g)	Mass of biomass (g)	Water (g)	Pressure (MPa)	Temperature (°C)	Time (min)	Mass of bio-oil (g)	Yield (%)
Effect of liquefaction temperature								
1	0.25	0.2125	1.25	20	250	60	0.114	53.65
2	0.25	0.2125	1.25	20	275	60	0.1645	77.41
3	0.25	0.2125	1.25	20	300	60	0.069	32.47
Effect of pressure								
4	0.25	0.2125	1.25	20	250	60	0.134	53.65
5	0.25	0.2125	1.25	25	250	60	0.128	60.24
6	0.25	0.2125	1.25	30	250	60	0.0336	15.81
Effect of lignin-to-water ratio								
7	0.25	0.2125	1.25	20	250	60	0.114	53.65
8	0.25	0.2125	0.75	20	250	60	0.156	73.41
9	0.25	0.2125	0.5	20	250	60	0.0529	24.89

4.5.1 Temperature

Based on Table 4.1, as the liquefaction temperature increased from 250 to 300 °C, the bio-oil yield increased from 53.65 to 77.41 wt%. The maximum linkage of lignin could not be fully depolymerized at 250 °C, which was also shown in similar research of Feng et al. (2021) . However, the bio-oil yield from EFB derived lignin started to decline when the temperature exceeds a particular critical value. For example, the temperature was further increased to 300 °C, bio-oil yield decreases with a value of 32.4 wt%. The literature claims that when the temperature is too high, bio-oil dehydration increases, the oxygen content decreases, and the bio-oil production also decreases in line with these changes (Jayathilake et al., 2022). Another cause may due to higher reaction temperature was induced the over cracking of lignin in which produced lower bio-oil yield (Feng et al., 2021). As a result, it was discovered that 275°C was the ideal reaction temperature which is lower than other research as they obtained an optimal temperature of 390°C (Chan et al., 2018).

Chemical compounds detected in the bio-oils via GC-MS analysis were summarized in Table 4.2 which based on the total area of the specified peaks in the chromatograms, the composition of the major compounds is indicated as a percentage peak area (%). It was indicated that the formation of phenolics as main GC-MS compounds in all 3 runs. It shows more chemical species were produced at higher temperatures of 300 °C. This may correlate with the over cracking which is an excessive thermal decomposition of lignin which result in more gas and char (Feng et al., 2021).

Figure 4.15 demonstrates a closer look at the FT-IR spectrum from the bio-oil which were a production from run 1,2 and 3. The bio-oils produced within the range of reaction temperature in this experiment have similar trend, indicating the presence of similar types of

functional groups. Identical incidents were also reported (Chan et al., 2018; Wang et al., 2013; Sun et al., 2011). Lignin exhibits multiple fundamental vibrational bands corresponding to various functional groups. The characteristic C-H stretching, commonly present in bio-oils, is indicated by the absorption band ranging from 3000 to 2800 cm^{-1} (Sun et al., 2011). The band observed in 1780–1640 cm^{-1} was indicative of the fundamental stretching vibration of carbonyls (C=O) which indicated the existence of ketones, carboxylic acid, and esters. Furthermore, the absorption peaks observed in the range of 1680 to 1580 cm^{-1} were attributed to the fundamental vibration of the aromatic skeleton. The peak at around 1464 cm^{-1} was assigned to the syringyl ring. Additionally, the bands identified at around 1300–950 cm^{-1} were indicative of C–O vibration attached to the syringyl ring, suggesting the presence of phenolic compounds and esters (Feng et al., 2021). The C–O and C–C stretching was noted at around 1035–1030 cm^{-1} , associated with C–H deformation. The peak at 835–820 cm^{-1} was attributed to para-substituted aromatics. The FT-IR of bio-oils suggested the presence of phenolics, aromatics, carbonyls, and ethers in the bio-oil sample.

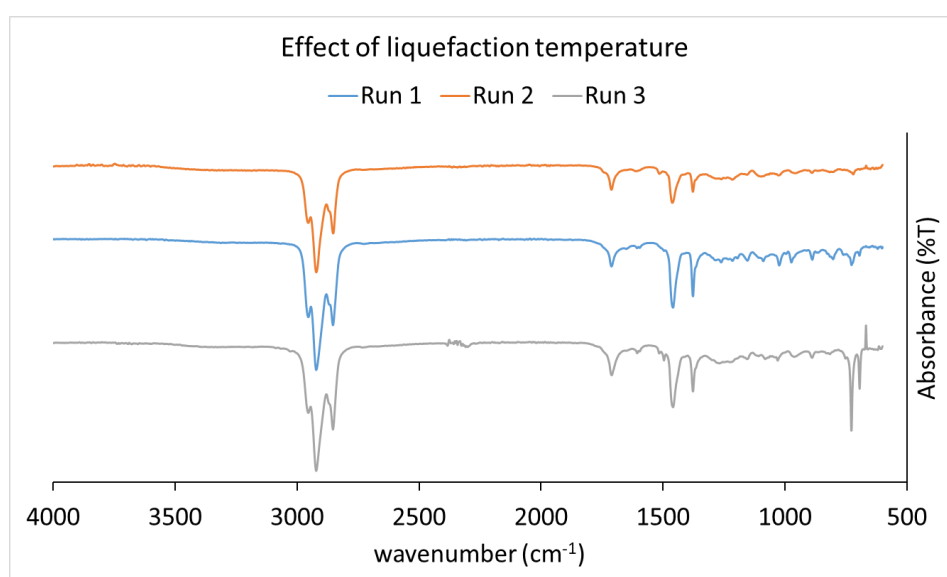


Figure 4.15: FTIR Analysis on Effect of Liquefaction Temperature

Table 4.2: Major Compounds Identified in Bio-oils (Temperature)

Run	Compound	Percentage peak area (%)
1	Phenol	9.27
	9-Eicosene, (E)-	3.86
	Bis(2-ethylhexyl) phthalate	2.67
	Others	84.2
2	Phenol	9.88
	Phenol, 2,6-dimethoxy-	6.75
	Phenol, 4-ethyl-	2.66
	Others	80.71
3	Pentadecanoic acid	4.37
	Phenol	4.22
	Phenol, 4-ethyl-	2.27
	Others	89.14

4.5.2 Pressure

Pressure had less of an impact on the output of bio-oil in comparison with temperature and lignin-to-water ratio. The bio-oil yield increased from 53.65 to 60.24 wt% when the pressure increased from 20 to 25 MPa. The yield of bio-oil decreased (15.81 wt%) with an increase in pressure to 30 MPa. The degree of biomass decomposition is increased by higher pressure because it increases the solvation power and density of the solvent. The local solvent density may rise with further pressure increase, causing a caging effect and inhibiting the cleavage of C=C bonds in biomass (Akhtar & Amin, 2011). Additionally, a rise in pressure could make the gasification reaction dominate at high temperatures (Kruse

et al., 2013). Higher pressure encourages the formation of gases like CO₂ and CH₄ through decarboxylation, reducing bio-oil production. Studies show that increased pressure, such as from 10 to 25 MPa, shifts biomass conversion towards gas products, lowering liquid bio-crude yields (Ramirez et al., 2015).

Figure 4.16 shows the FT-IR spectrums of bio-oils at various pressures. It is displayed that similar compounds are present in Figure 4.15 and Figure 4.16 due to the similarities of the pattern. Thus, the existence of ketones, carboxylic acid, esters, aromatic compounds, and phenolic compounds were also present. The presence of phenols and carboxylic acid was indicated by a characteristic absorption peak in the range of 3600 to 3200 cm⁻¹, attributed to O-H stretching. This observation was consistent with the GC-MS results provided in Table 4.3 and was specifically evident in run 6.

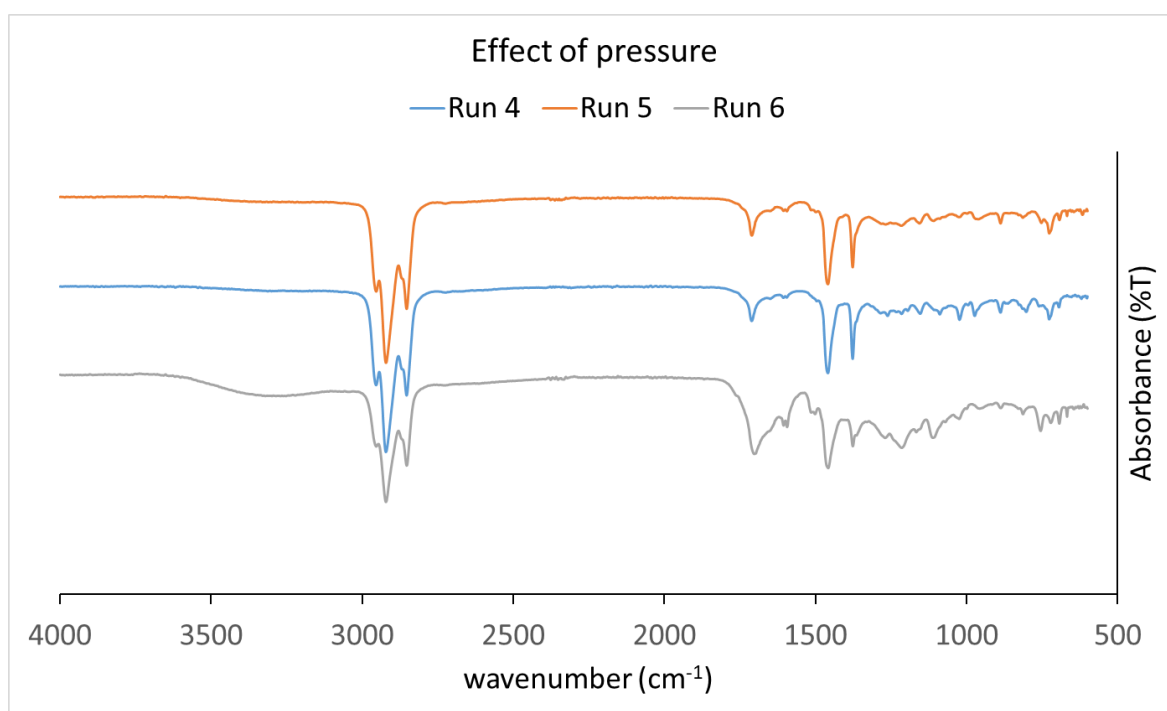


Figure 4.16: FTIR Analysis on Effect of Liquefaction Pressure

Table 4.3: Major Compounds Identified in Bio-oils (Pressure)

Run	Compound	Percentage peak area (%)
4	Phenol	9.27
	9-Eicosene, (E)-	3.86
	Bis(2-ethylhexyl) phthalate	2.67
	Others	84.2
5	Pentadecanoic acid	4.67
	Phenol	3.16
	3-Eicosene, (E)-	2.15
	Others	90.2
6	Phenol	7.69
	Pentadecanoic acid	0.99
	Hexadecanoic acid, methyl ester	0.94
	Others	90.38

4.5.3 Lignin-to-water ratio

The possible impact of water or solvent density on the liquefaction yield of hydrothermal procedures has been studied by numerous researchers (Wang et al., 2021). In general, a high water content is advantageous for the generation of liquids and gases, probably because a denser solvent medium enhances extraction (Sato et al., 2003). The bio-oil output increased from 53.65 to 73.45 wt% when the lignin-to-water ratio increased from 0.2 to 0.33. A further rise in the lignin-to-water ratio to 0.50 led to a sharp decrease in the bio-oil production of 24.89% weight percent. Therefore, it is shown a higher bio-oil

production due to higher lignin-to-water ratio which is also seen in literature (Jayathilake et al., 2022). However, once the ratio reach a critical point, the bio-oil yield decreases, which is also seen in literature (Akhtar & Amin, 2011). Additionally, it discovered that in order to get the highest bio-oil and char yields possible given an increasing lignin-to-water ratio, greater operation temperatures and longer residence times are necessary (Jayathilake et al., 2022).

The GC-MS analysis of bio-oils produced at various lignin-to-water ratios is displayed in Table 4.4 and Fig. 4.17. These substances were consistently found by GC-MS and were verified by FT-IR spectra (Figure 4.13). It is displayed that similar compounds are present in all the process parameters shown in the FT-IR analysis due to the similarities of the pattern. Thus, the existence of ketones, carboxylic acid, esters, aromatic compounds, and phenolic compounds were also present. The presence of phenols and carboxylic acid was revealed by a characteristic absorption peak from 3600 to 3200 cm^{-1} , attributed to O-H stretching. This feature was specifically observed in run 8.

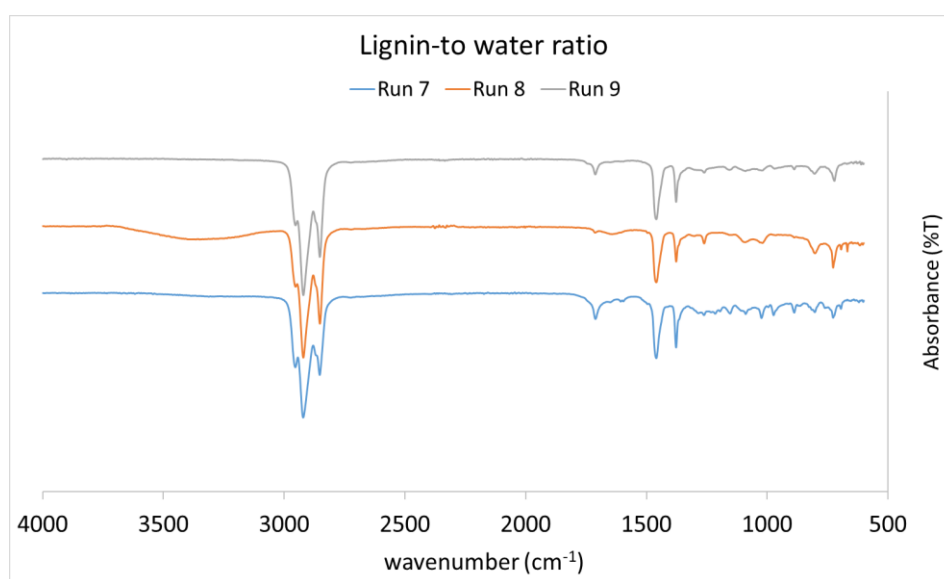


Figure 4.17: FTIR Analysis on Effect of Liquefaction Lignin-to-water Ratio

Table 4.4: Major Compounds Identified in Bio-oils (Lignin-to-water Ratio)

Run	Compound	Percentage peak area (%)
7	Phenol	9.27
	9-Eicosene, (E)-	3.86
	Bis(2-ethylhexyl) phthalate	2.67
	Others	84.20
8	2-Cyclopenten-1-one, 2-methyl-	0.19
	11-Isopropylidene-tricyclo[4.3.1.1(2,5)]undecan-10-ol	0.11
	Retinal	0.07
	Others	99.64
9	Phenol	0.78
	Pentadecanoic acid	0.77
	Hexadecanoic acid, methyl ester	0.64
	Others	97.81

4.6 Kinetic study of HTL of Lignin

The collection of data of the EFB has also been conducted based on the joint collaboration with Kumamoto University, Japan. The analysis of data was conducted in Unimas to determine the kinetic study of SCW-SCCO₂ HTL of EFB derived lignin with respect to time. This section consists of 2 sections, (i) HTL of lignin with respect to time and (ii) equation fitting.

4.6.1 HTL of Lignin with Respect to Time

Table 4.5 summarised the findings of the experiment of HTL of lignin with respect to time. Based on the findings of the data, it established the relationship of the conversion (X), bio-oil yield and time.

Table 4.5: Summary of SCW-SCCO₂ HTL of Lignin with Respect to Time

Run No.	biomass (g)	Pressure (MPa)	Temperature (°C)	Time (min)	Conversion (%)	Bio-oil Yield (%)
Kinetic and reaction mechanism studies						
1	0.2125	20	250	30	81.6	18.4
2	0.2125	20	250	60	46.35	53.65
3	0.2125	20	250	120	38.8	61.2
4	0.2125	20	250	240	29.48	70.52
5	0.2125	20	275	30	85.65	14.35
6	0.2125	20	275	60	22.59	77.41
7	0.2125	20	275	120	36.43	63.57
8	0.2125	20	275	240	17.39	82.61
9	0.2125	20	300	30	88.89	11.11
10	0.2125	20	300	60	67.53	32.47
11	0.2125	20	300	120	63.6	36.4
12	0.2125	20	300	240	55.64	44.36

Figure 4.18 depicts the bio-oil yield of EFB derived lignin via HTL with respect to time at 250, 275, and 300 °C. When reaction time was increased from 30 to 60 min at 250°C,

bio-oil yield increased sharply from 18.4 wt% to 53.65 wt%. It later gradually increases after reaction time increased to 120 min with bio-oil yield of 61.2% and to bio-oil yield of 70.52% when the reaction time increase to 240 min. At 275 °C, a similar trend was shown as the reaction time increased from 30 to 60 min, bio-oil yield increased from 14.4% to 77.4%. When the reaction time increased to 120 min, the bio-oil yield decreased slightly to 63.6% This pattern implies that different secondary reaction processes were used to transform components of the bio-oil into solid and gaseous products (Valdez et al., 2012). While at reaction time of 240 min, the bio-oil yield increased to 82.6% the highest bio-oil yield achieved. At 300 °C, it showed a similar trend but produced the lowest bio-yield in comparison. This is due to the rate of decomposition of biomass increases at higher temperature (Dimitriadis & Bezergianni, 2017).

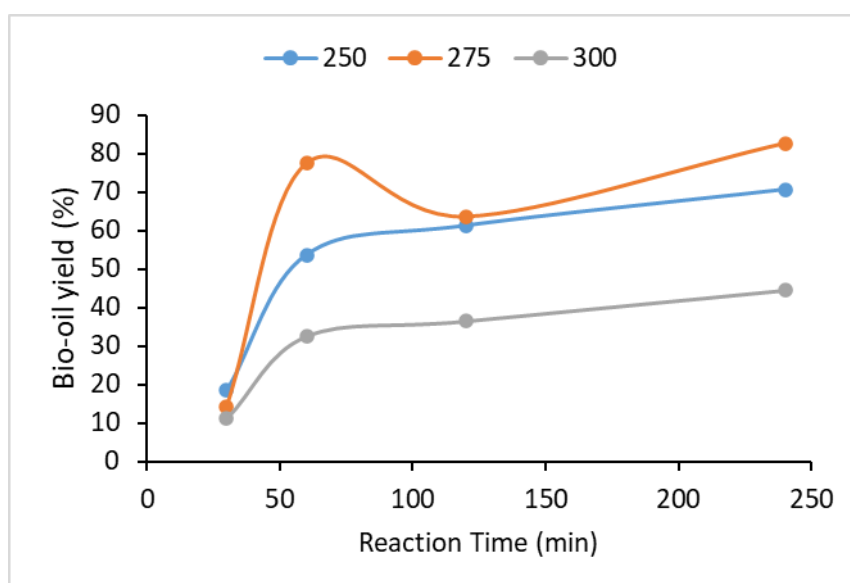


Figure 4.18: Bio-oil Yield with Respect to Reaction Time

Figure 4.19 depicts the relationship of conversion with respect to time. The graph is an inverse of Figure 4.18 which relates to the formula of conversion (Equation 3.2). This data was used for the equation fitting of kinetic modelling. This study shows that temperature

is an important hydrothermal process parameter because it reduces the ideal reaction time for producing the highest yield of bio-oil as the temperature rises (Wang et al., 2013).

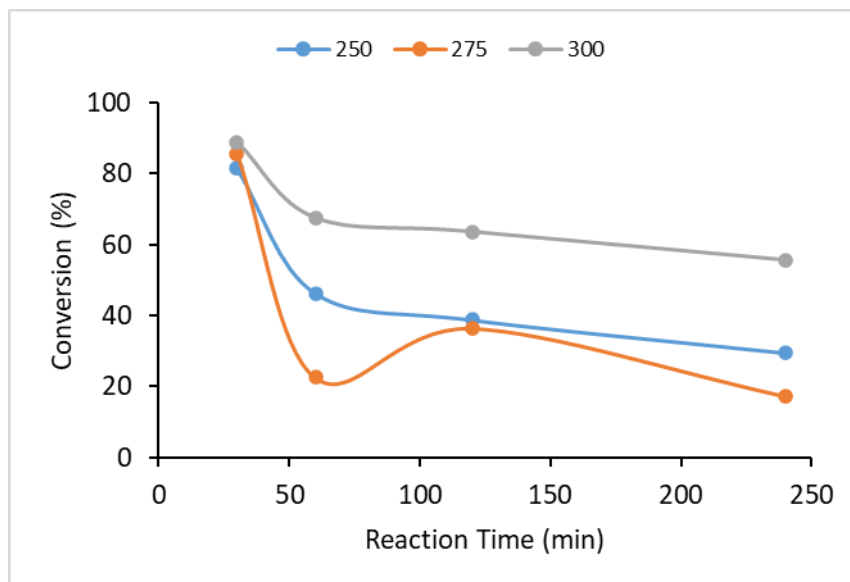


Figure 4.19: Conversion with Respect to Reaction Time

4.6.2 Equation Fitting

The kinetic data, obtained using Equation 3.5, were linearly fitted, yielding the kinetic parameters detailed in Table 4.6 and illustrated in Figure 4.20. According to the results, which showed an excellent agreement (R^2 of 0.87 and higher) with Equation 3.5, the logarithm of conversion rates was directly proportional to that of conversion at various reaction times. As the temperature increased from 250 to 275 °C, the apparent rate constant (k) decreased from 9.59×10^{-4} to $5.99 \times 10^{-4} \text{ s}^{-1}$, then later increase to $1.06 \times 10^{-3} \text{ s}^{-1}$ as the temperature change to 300 °C. The reason for the low apparent rate constant was that these reactions have complicated or multi-step processes that need more intricate molecular interactions and several intermediary stages, usually seen in lump reactions experiments (Forchheim et al., 2014). This pattern was also shown with the high apparent reaction order (n) obtained in this overall kinetic approach (ranged from 3.02 to 5.36). The high reaction order was due to the complex structure of lignin which lead to a variety of scissions during

liquefaction (Abad-Fernández et al., 2020). This was proven in multiple literature that concluded various components are present after liquefaction (Ramirez et al., 2015; Chan et al., 2019; Ciuffi et al., 2021).

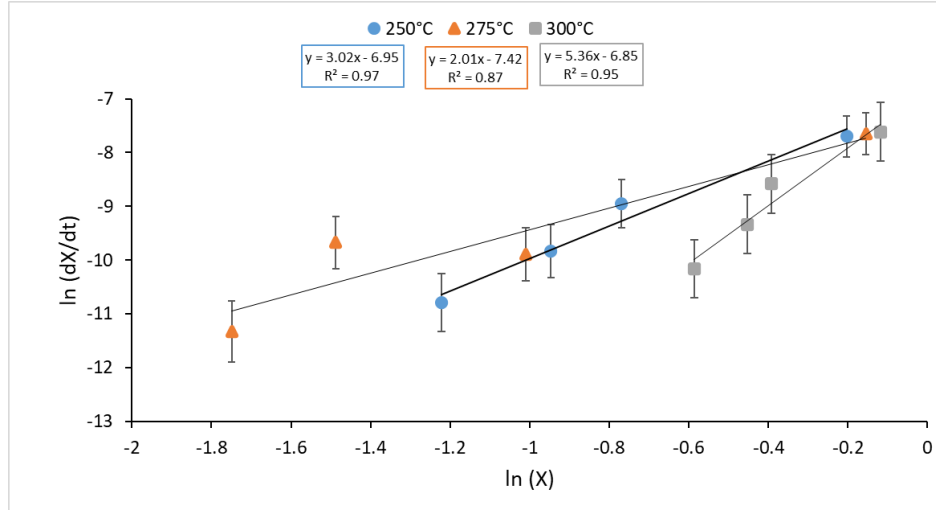


Figure 4.20: Relation Between Liquefaction Reaction Rates and Solid Residue Contents

Table 4.6: Kinetic Parameters Determined from Model Fitting

Temperature (°C)	Linear equation	Rate constant, $k \text{ (s}^{-1}\text{)}$	Reaction order (n)	R^2
250	$y = 3.02x - 6.95$	9.59×10^{-4}	3.02	0.97
275	$y = 2.01x - 7.42$	5.99×10^{-4}	2.01	0.87
300	$y = 5.36x - 6.85$	1.06×10^{-3}	5.36	0.95

Figure 4.21 shows the Arrhenius plot, a temperature-dependant kinetic model of the liquefaction of lignin based on Equation (3.7). The graph shows the relationship between $\ln k$ and $1/T$ which according to the equation, the rate constant for conversion, or k , increases slightly proportion to the rise in reaction temperature. (Yong & Matsumura, 2012). The

apparent activation energy (E) and apparent pre-exponential factor (A) values were 4.2 kJ/mol and $2.13 \times 10^{-3} \text{ s}^{-1}$, respectively. This study's apparent activation energy was equivalent to and closely aligned with values published in the literature. Mishra & Saka (2011) reported the activation energy of lignin to be 12.4 kJ/mol while Chan et al. (2019) work shows it to be 6.70 kJ/mol. Under subcritical and supercritical circumstances, the activation energy of lignin degradation might differ according to the structural type of the lignin (grass, hardwood, or softwood) and the technique used to isolate it from biomass (Yong & Matsumura, 2012). This also proven that this work showed lower activation energy compared to other literature. Several studies have been compiled to show the difference in activation energy in Table 4.7.

Table 4.7: Summary of Activation Energy of Lignin

Biomass	Process	T (°C)	E (kJ/mol)	References
Lignin from EFB	SCW-SCCO ₂ HTL	250– 300	4.2	This research
Japanese Beech	subcritical phenol liquefaction	160– 290	12.4	(Mishra & Saka, 2011)
Palm kernel shell	HTL	330– 360	6.7	(Chan et al., 2019)
Lignin	pyrolysis	260	157.0	(Kristanto et al., 2021)
Organosolv Lignin	depolymerization	225	9.0	(Ročnik Kozmelj et al., 2025)

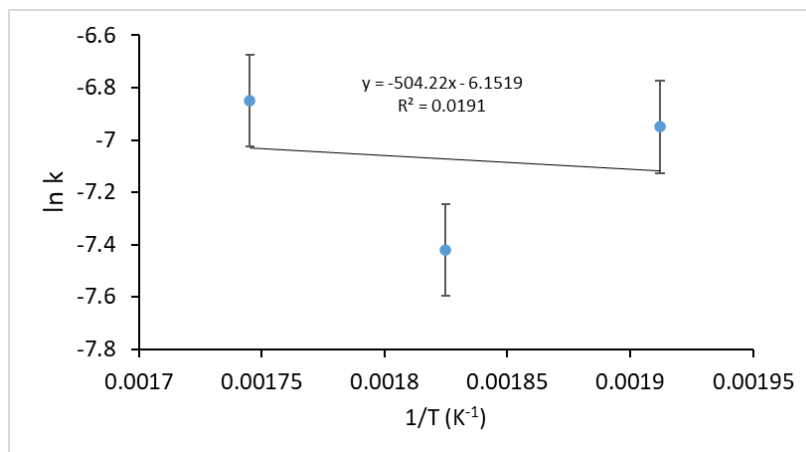


Figure 4.21: Arrhenius Plot of HTL of Lignin

The overall kinetics of bio-oil formation were modeled using the modified Reverchon-Sesti Osseo equation, an empirical kinetic model. Table 4.7 presents the kinetic data obtained in this study, along with the computations of normalized yields Y and Z constant based on Equation 3.12 and 3.10, respectively. The plot of Z constant with respect to reaction time (Figure 4.22) exhibited good linear fits for most kinetic data, with R^2 values above 0.843, whereas data from 275°C showed an R^2 of 0.104.

As shown in Figure 4.23, The Modified Reverchon-Sesti Osseo model demonstrates strong capability in simulating the kinetic behavior of bio-oil yield over time during thermal processing, as it shows good prediction with experimental data at all tested temperatures of 250°C, 275°C, and 300°C. At 250°C, the model accurately reflects both the model and experimental yield, indicating that the simplified kinetic assumptions used in the model perform well under moderate thermal conditions.

At 275°C, the model shows the highest deviation where the model significantly overpredicts the yield during early reaction stages. This was due to the optimum conditions of lignin during HTL which produces the most bio-oil yield. At this stage, macromolecular breakdown occurs efficiently, generating smaller, oil-phase organics (Yan et al., 2018).

At 300°C, as it begins to show a slight overestimation of yield at shorter reaction times, although its long-term predictions remain close to experimental values. This was likely due to the increased influence of secondary reactions at higher temperatures such as repolymerization of intermediates, char formation, or thermal cracking that are not fully incorporated into the model's framework (Senneca & Tucciullo, 2020). These processes can reduce the overall bio-oil yield, especially during rapid heating, leading to deviations between predicted and actual outcomes.

Despite these limitations, the model has successfully captured the general kinetics and yield behavior over time, suggesting that it remains a valuable tool for process optimization. However, further refinement such as incorporating temperature-dependent diffusion, particle swelling, or side reaction pathways would improve its predictive accuracy under more extreme conditions and at shorter reaction durations (Rashid, 2024).

Table 4.8: Normalized Yield Y and Z Constant of Bio-oils at Various Reaction Times.

reaction time (min)	250 °C			275 °C			300 °C		
	Normalized yield (Y)	Z	R ²	Normalized yield (Y)	Z	R ²	Normalized yield (Y)	Z	R ²
30	26.09	-0.3023	0.87	17.37	-0.1908	0.104	34.22	- 0.4188	0.843
60	76.08	-1.4304		93.71	-2.7655		73.20	- 1.3166	
120	86.78	-2.0237		76.95	-1.4676		82.06	- 1.7179	
240	100.00			100.00			100.00		

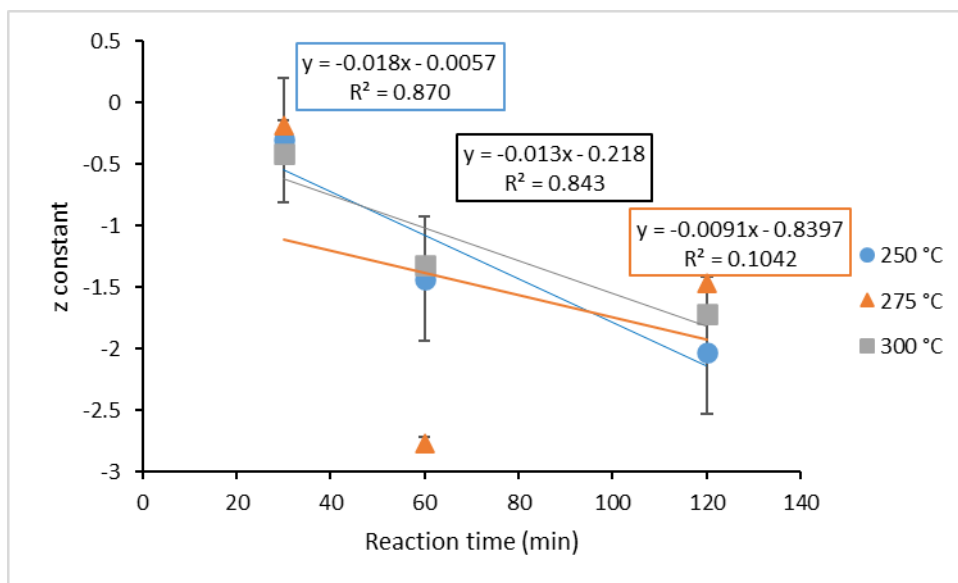


Figure 4.22: Plot of Z Constant Versus Reaction Time

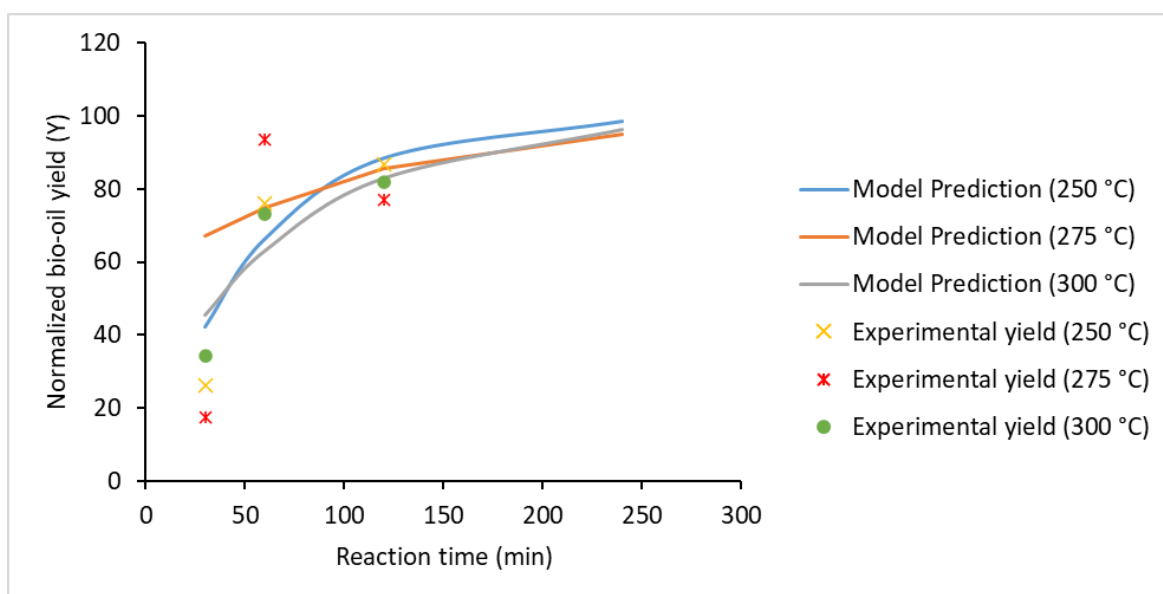


Figure 4.23: Comparison of Experimental Data with Modified Reverchon-Sesti Osseo model

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

The research findings contributed to the expanse of green solvents development (LTTMs), Usage of lignin and efficiency of SCW-SCCO₂ HTL. The conclusions are drawn based on the following objectives as the core of this research project.

- i. To investigate the physicochemical properties of LTTMs and extracted lignin from different parameter.
- ii. To investigate the influence of different process parameters of SCW-SCCO₂ HTL in conversion of lignin into bio-oil.
- iii. To investigate the reaction kinetics of SCW-SCCO₂ HTL in converting lignin while producing a suitable kinetic model.

Based on objective 1, LTTMs were formed from ChCl as the HBA paired with malic acid as the HBD, later incorporated with different levels of water content. Hence, both malic acid and lactic acid are proven to be compatible HBDs with ChCl and further addition of water also demonstrated high compatibility of the LTTM constituents. Delignification of EFB was conducted based on reaction time and shown that the highest amount of lignin obtained is 4 hours using fresh solvent. The delignification of EFB managed to extract 31.98% of lignin from 10g of EFB and is proven to be successful as it is a large amount of lignin to be extracted in comparison to other works. Based on the analysis conducted on lignin, it was shown that it has similar properties of lignin in other studies which proves that the extracted product is lignin.

Based on objective 2, the reaction mechanism was explored using multiple parameters of SCW-SCCO₂ HTL such as temperature, time and lignin-to-water ratio. The optimum for each parameter is 275°C, 25MPa and 1:3 lignin-to-water ratio which result in the bio-oil yield of 77.41% with a conversion of 22.59%. The bio-oils were analyzed for their chemical compositions (by GC-MS and FT-IR). It was found that phenolic compounds were the main constituents of bio-oils derived from lignin for all reaction conditions investigated. Thus, shows that the reaction pathway in this project is EFB to lignin then lignin derivatives and finally to phenolics.

In pursuit of objective 3, the kinetic study of SCW-SCCO₂ HTL, based on the biomass conversion, was analyzed using a kinetic equation adopted from the literature. The kinetic parameters were estimated through the evaluation of the kinetic equation. In this study, the rate constant (k) increased from 9.59×10^{-4} to $1.06 \times 10^{-3} \text{ s}^{-1}$ with a reaction temperature ranging from 250 to 300°C. The relationship between the rate constant (k) and temperature aligned reasonably well with the Arrhenius equation, the temperature-dependent kinetic model. The activation energy (E) and preexponential factor (A) values for the liquefaction process were estimated to be 4.2 kJ/mol and $2.13 \times 10^{-3} \text{ s}^{-1}$, respectively. Furthermore, the experimental bio-oil yields with respect to reaction time obtained R^2 for 250°C (0.87), 275°C (0.104) and 300°C (0.843) were well-fitted while using the modified Reverchon-Sesti Osseo equation, the empirical kinetic model.

5.2 Recommendations

The exploration of the relationship of the bio-crude oil yield and value-added chemical species from the hydrothermal liquefaction process and the usage of the green solvents in extraction on the individual specific chemical compounds could also be the focus

of area of research. Furthermore, the development of theoretical model via simulation models such as computational fluid dynamics (CFD) could be studied to have an in-depth investigation of the complex inherent properties of the biocrude such as viscosity effects and thermodynamic properties. Techno-economic performance of the biorefinery involved the hydrothermal liquefaction can be evaluated via measures of profitability, exergy analysis, and life cycle analysis (LCA) within the whole supply chain network could be conducted. The environmental aspect of the hydrothermal liquefaction process is essential to be evaluated since it is considered as the primary consideration as a prospective technology investment. Hence, it is crucial to evaluate the LCA starting from the beginning process (biomass collection, biomass pre-treatment, and lignin extraction from biomass) to the end process (biofuels and value-added chemicals to end user). This provides optimization information of the supply chain network involved in this conversion process.

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APPENDICES

Appendix A: Journal Publications

1. Yiin, C. L., **bin Odita, E.**, Lock, S. S. M., Cheah, K. W., Chan, Y. H., Wong, M. K., ... & Yusup, S. (2022). A review on potential of green solvents in hydrothermal liquefaction (HTL) of lignin. *Bioresource Technology*, 128075.
2. **bin Odita, E.**, Yiin, C. L., Ngu, J. S. Z., Quitain, A. T., Lock, S. S. M., Chin, B. L. F., & Rahman, M. R. (2023). Sustainable Biomass-to-Energy Transformation: Choline Chloride Based Deep Eutectic Solvent for Lignin Extraction and Liquefaction. *Chemical Engineering Transactions*, 103, 31-36.

Appendix B: Conference

1. Attend the 26th conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction - PRES'23, Thessaloniki, Greece.

Appendix C: Data and calculations

C1: Calculation of lignin content of EFB by using the Klason method

AIL content in untreated EFB = 13.94 wt%

$$\text{ASL content in untreated EFB} = \frac{\text{Absorbance at 205 nm}}{\text{Cell path length} \times \text{Absorptivity}} \times \text{dilution factor}$$

Using the data collected:

Dilution factor = 20

Cell path length = 1 cm

Lignin absorptivity at 205 nm = 110 L g⁻¹ cm⁻¹

Absorbance at 205 nm = 4.37

$$\text{ASL} = \frac{4.37}{1 \text{ cm} \times 110 \text{ L g}^{-1} \text{ cm}^{-1}} \times 20 = 0.795 \text{ g/L}$$

ASL = 7.95 wt% of 10 g EFB

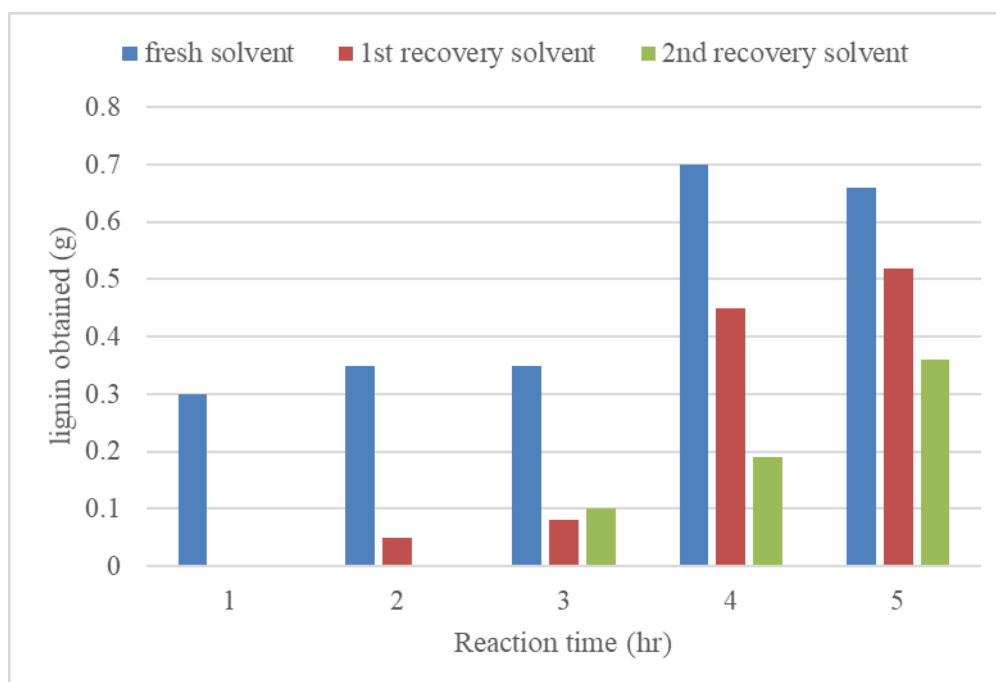
The total lignin content in the untreated EFB is **21.89 wt%**, which means that 21.89% of the total mass of the EFB sample is lignin.

The total amount of lignin in 10 g of EFB is:

$$\frac{21.89}{100} \times 10 \text{ g} = 2.189 \text{ g}$$

So, the **maximum amount of lignin** that can be obtained from 10 g of EFB is **2.18 g**.

C2: Data of delignification of biomass using LTTMs



Time (hr)	fresh solvent (g)	1st recovery solvent (g)	2nd recovery solvent (g)
1	0.3	0	0
2	0.35	0.05	0
3	0.35	0.08	0.1
4	0.7	0.45	0.19
5	0.66	0.52	0.36

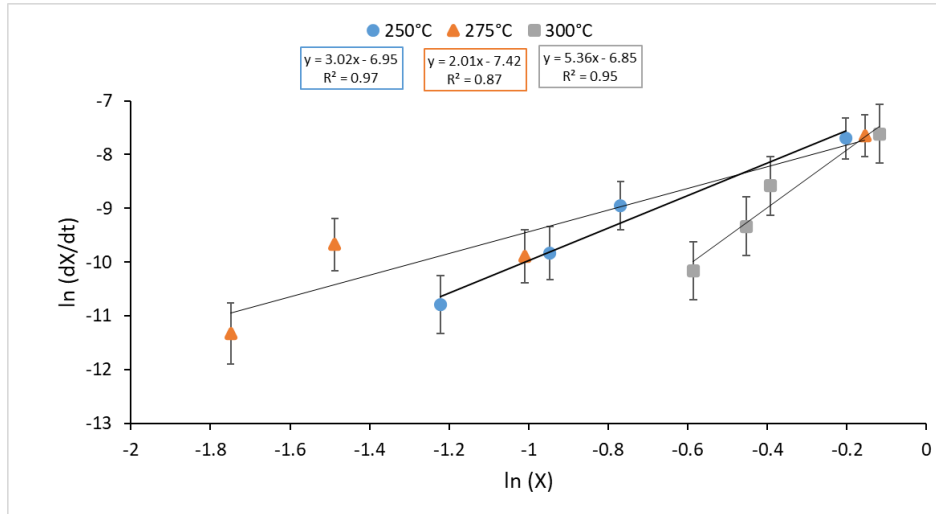
C3: Data and calculation of relation between liquefaction reaction rates and solid residue contents

Summary of SCW-SCCO₂ HTL of Lignin with Respect to Time

Run No.	Lignin (g)	Pressure (MPa)	Temperature (°C)	Time (min)	Conversion (%)	Bio-oil Yield (%)
Kinetic and reaction mechanism studies						
1	0.25	20	250	30	81.6	18.4
2	0.25	20	250	60	46.35	53.65
3	0.25	20	250	120	38.8	61.2
4	0.25	20	250	240	29.48	70.52
5	0.25	20	275	30	85.65	14.35
6	0.25	20	275	60	22.59	77.41
7	0.25	20	275	120	36.43	63.57
8	0.25	20	275	240	17.39	82.61
9	0.25	20	300	30	88.89	11.11
10	0.25	20	300	60	67.53	32.47
11	0.25	20	300	120	63.6	36.4
12	0.25	20	300	240	55.64	44.36

The value of conversion is $X = 100 - Yield$ based on the literature Sasaki & Goto, (2009)

Graph of Relation Between Liquefaction Reaction Rates and Solid Residue Contents



temperature (°C)	time (s)	Conversion (X)	dX/dT	ln (X)	ln(dX/dT)
250	1800	0.816	0.000453333	-0.20334	-7.69888287
250	3600	0.464	0.00012875	-0.76895	-8.95763802
250	7200	0.388	5.38889E-05	-0.94675	-9.82858624
250	14400	0.295	2.04722E-05	-1.22146	-10.7964416
275	1800	0.857	0.000475833	-0.1549	-7.65044291
275	3600	0.226	0.00006275	-1.48766	-9.67635198
275	7200	0.364	5.05972E-05	-1.00978	-9.89161388
275	14400	0.174	1.20764E-05	-1.74927	-11.3242583
300	1800	0.889	0.000493833	-0.11777	-7.61331248
300	3600	0.675	0.000187583	-0.3926	-8.58128737
300	7200	0.636	8.83333E-05	-0.45256	-9.33439302
300	14400	0.556	3.86389E-05	-0.58627	-10.1612513

Calculation of temperature 250°C with time 1800s:

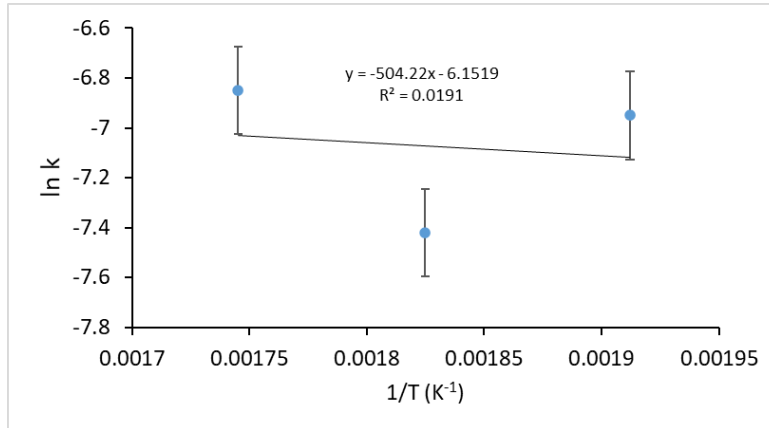
Using given data of temperature (250°C), time (1800s) and conversion (0.816);

$$dX/dT = \frac{0.816}{1800} = 0.000453333$$

$$\ln(X) = \ln(0.816) = -0.20334$$

$$\ln(dX/dT) = \ln(0.000453333) = -7.698882868$$

C4: Data and calculation of Arrhenius plot



Temperature (K)	ln k	1/T	k
523	-6.95	0.001912046	0.000958635
548	-7.42	0.001824818	0.000599149
573	-6.85	0.001745201	0.001059456

Calculation of the Arrhenius plot:

Ln k was determined using data from the graph **Relation Between Liquefaction Reaction Rates and Solid Residue Contents.**

$$1/T = \frac{1}{523} = 0.001912046$$

$$k = e^{\ln k} = e^{-6.95} = 0.000958635$$

Using all the information from the Arrhenius Plot, it can be used to calculate activation energy (E) and the pre-exponential factor (A) using the Arrhenius equation:

$$\ln k = \ln A - \frac{E}{R} \left(\frac{1}{T} \right)$$

$$\frac{E}{R} = 504.22; R = 8.314 \text{ J/mol.k}$$

$$\ln A = -6.15$$

$$E = \frac{E}{R} (R) = (504.22)(8.314) = 4192 \text{ J/mol}$$

$$A = e^{-6.15} = 0.00213 \text{ s}^{-1}$$

C5: Data and calculation of Normalized Yield Y and Z Constant of bio-oils at various reaction times

reaction time (min)	250 °C			275 °C			300 °C		
	Normalized yield (Y)	Z	R ²	Normalized yield (Y)	Z	R ²	Normalized yield (Y)	Z	R ²
30	26.09	-0.3023	0.87	17.37	-0.1908	0.104	34.22	-	0.843
60	76.08	-1.4304		93.71	-2.7655		73.20	-	
120	86.78	-2.0237		76.95	-1.4676		82.06	-	
240	100.00			100.00			100.00		

The following table is calculated using the the modified Reverchon-Sesti Model and Equation 3. 12 (Chan et al., 2019).

$$Z = \ln \left(1 - \frac{Y}{100} \right) \quad \text{equation 3.10}$$

$$Y = \frac{y}{y_{max}} \quad \text{equation 3.12}$$

Additional data:

time (min)	Experimental yield (250 °C)
30	18.4
60	53.65
120	61.2
240	70.52

Calculation of normalized yield Y and Z constant for 250 °C:

To calculate normalized yield (Y), at 250°C, the $y_{\max}$ is 70.52% and $y=18.4$

$$\text{Normalized yield (Y)} = \frac{y}{y_{\max}}$$

$$\text{Normalized yield (Y)} = \frac{18.4}{70.52} = 0.2609; 0.2609 \times 100 = \mathbf{26.09\%}$$

To calculate Z, normalized yield (Y) will be 26.09%

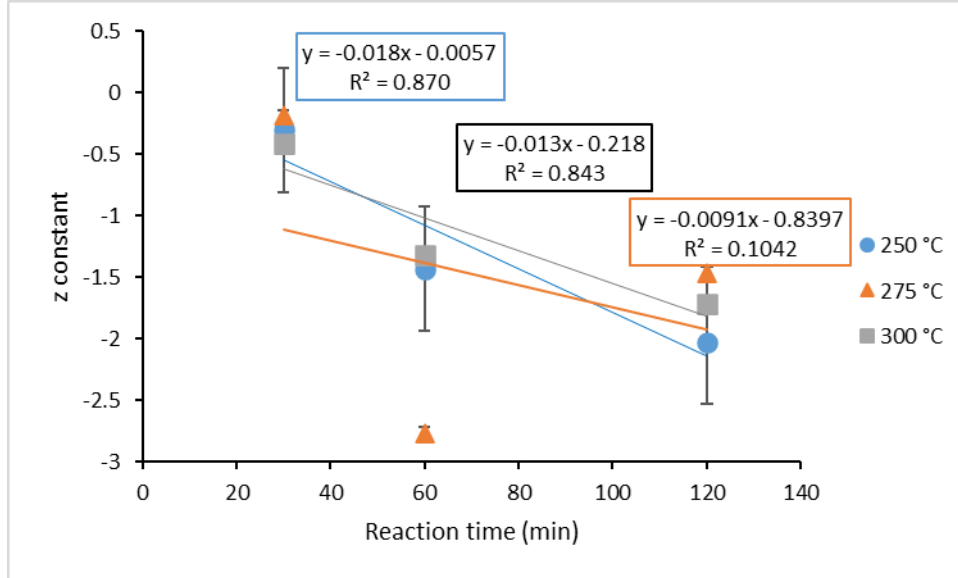
$$Z = \ln \left(1 - \frac{Y}{100} \right)$$

$$Z = \ln \left(1 - \frac{26.09}{100} \right) = \mathbf{-0.3023}$$

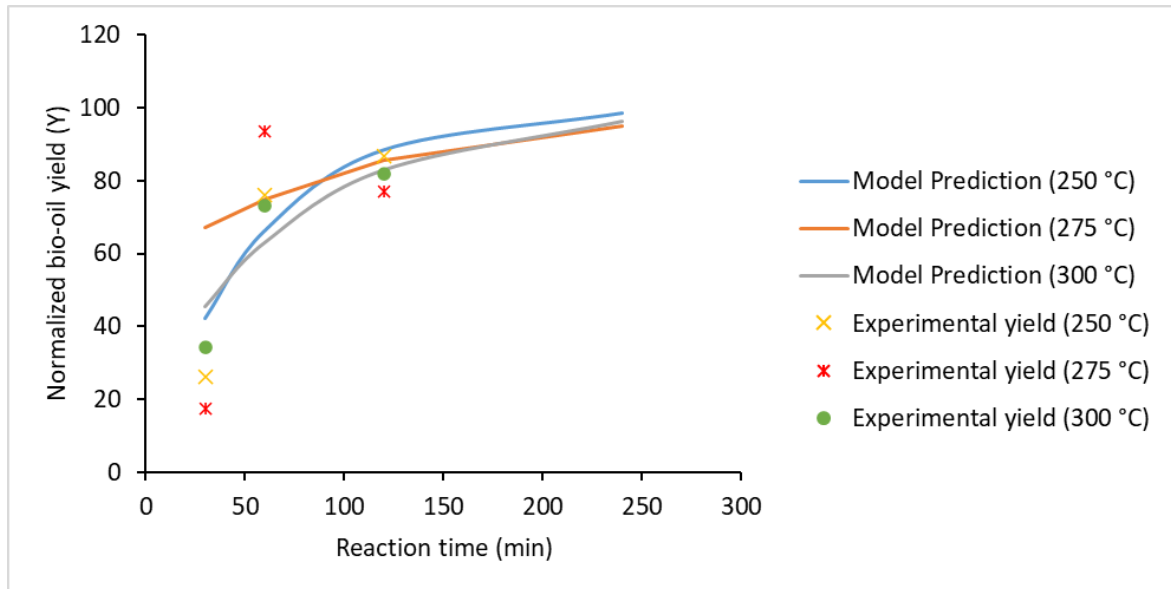
R^2 is determined by using the graph from the data Y and Z from below.

C6: Data and calculation of Experimental Data with Modified Reverchon-Sesti Osseo model

Plot of Z Constant Versus Reaction Time



Comparison of Experimental Data with Modified Reverchon-Sesti Osseo model



The calculation for comparison of experimental Data with Modified Reverchon-Sesti Osseo model will be using the equation 3.11

$$Y = 100(1 - e^{at+b})$$

Calculation of model prediction for 250 °C at reaction time 30min:

Using the data from Plot of Z Constant Versus Reaction Time, **a= -0.018** and **b= -0.0057**

$$\text{Model prediction } Y = 100(1 - e^{at+b})$$

$$\text{Model prediction } Y = 100(1 - e^{(-0.018)(30)+(-0.0057)})$$

$$\text{Model prediction } Y = 42.06$$

This was repeated using different reaction time and temperature which is shown from the table below.

Time (min)	Model Prediction (250 °C)	Model Prediction (275 °C)	Model Prediction (300 °C)
30	42.06	67.13	45.56
60	66.23	74.99	63.14
120	88.53	85.51	83.10
240	98.68	95.14	96.45