CHINHOYI UNIVERSITY OF TECHNOLOGY

SCHOOL OF ENGINEERING SCIENCES AND TECHNOLOGY

DEPARTMENT OF FUELS AND ENERGY

TECHNO-ECONOMIC ANALYSIS AND LIFE-CYCLE ASSESSMENT OF BIO-OIL PRODUCTION FROM MICROWAVE-ASSISTED PYROLYSIS OF PINE SAWDUST

By

Denzel Christopher Makepa

(C21147716S)

A THESIS

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Main Supervisor

Dr. C. H. Chihobo

Chinhoyi University of Technology,

School of Engineering Sciences and Technology

Department of Fuels and Energy

chihobo@gmail.com

Co-Supervisor

Professor D. Musademba

Chinhoyi University of Technology

School of Engineering Sciences and Technology

Department of Fuels and Energy Engineering

dmusademba@gmail.com

Co-Supervisor

Dr. W. R. Ruziwa

Chinhoyi University of Technology

School of Engineering Sciences and Technology

Department of Fuels and Energy Engineering

wruziwa@gmail.com

Declaration

I, Denzel Christopher Makepa, hereby declare that this thesis is entirely original work of mine, with the exception of what is noted in the acknowledgments, references, and comments in the thesis body, and that it has not been submitted in whole or in part for another degree from another university.

The undersigned, hereby certify that they have read and agree to submit this final version of the thesis as the official submission.

………………………………
Mr. Denzel C. Makepa
(Student)
Date: 27 July 2023

………………………………
Dr. C. H. Chihobo
(Main Supervisor)
Date: 27 July 2023

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Dedication

This thesis is dedicated to my future children, with the hope that it will inspire you to pursue your own dreams and passions with the same dedication and determination that I have brought to this research. May it serve as a reminder that hard work, perseverance, and a commitment to lifelong learning are essential to achieving your goals and making a positive impact on the world.

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List of Abbreviations

AAEM	Alkali and alkaline-earth metals
ANOVA	Analysis of variance
APEA	Aspen Process Economic Analyzer
BioFLAME	Biofuels Facility Location Analysis Modelling Endeavor
CCD	Central composite design
CEPCI	Chemical Engineering Plant Cost Index
CFB	Circulating fluidized bed
DCFROR	Discounted cash flow rate of return
DTG	Derivative thermogravimetry
EDXRF	Energy dispersive X-ray fluorescence
FAME	Fatty acid methyl esters
FCI	Fixed capital investment
FE	Fossil energy
FPH	Fast pyrolysis and hydroprocessing
GC	Gas chromatography
GHG	Greenhouse gas
HDPE	High Density Polyethylene
IRR	Internal rate of return
LCA	Life-Cycle Assessment
LCI	Life-cycle inventory
LCIA	Life-cycle impact assessment
LDPE	Low Density Polyethylene
LHV	Lower heating value
MALDI	Matrix-assisted laser desorption/ionization
MAP	Microwave-Assisted Pyrolysis
MFSP	Minimum fuel selling price
MIC	Maximum investment cost
MS	Mass spectrometry

MSP	Minimum selling price
MTPD	Metric tonnes per day
NCG	Non-condensable gas
NMR	Nuclear magnetic resonance
NPV	Net present value
NREL	National Renewable Energy Laboratory
OM	Operating and Maintenance
PAH	Polycyclic aromatic hydrocarbons
PDEC	Percentage of Delivered Equipment Cost
PEC	Purchased equipment cost
RMSE	Root mean square error
RSM	Response surface methodology
SDG	Sustainable development goals
SE	Steam explosion
TAN	Total acid number
TCI	Total capital investment
TDIC	Total direct and indirect cost
TEA	Techno-economic analysis
TGA	Thermogravimetric analysis
TIC	Total installed cost
TIEC	Total installed equipment cost
TPEC	Total purchased equipment cost
TPI	Total project investment
XRD	X-ray diffraction
XRF	X-ray fluorescence

Nomenclature and symbols

%	percent
$	United States Dollar
°C	degree Celsius
μm	micrometer
atm	atmospheres
cm	centimeter
cm^3	cubic centimeter
cSt	centistoke
g	gram
kg	kilogram
kg 1,4-DCB eq.	kilograms of 1,4-dichlorobenzene equivalent
kg CFC-11 eq.	kilograms of chlorofluorocarbon-11 equivalent
kg CO_2 eq.	kilograms of carbon dioxide equivalent
kg Fe eq.	kilograms of iron equivalent
kg N eq.	kilograms of nitrogen equivalent
kg NMVOC eq.	kilograms of non-methane volatile organic compounds equivalent
kg P eq.	kilograms of phosphorus equivalent
kg PM10 eq.	kilograms of particulate matter with a diameter of 10 micrometers or less equivalent
kg SO_2 eq.	kilograms of sulfur dioxide equivalent
kg U235 eq.	kilograms of uranium-235 equivalent
kg oil eq.	kilograms of oil equivalent
km	kilometer
kmol	kilomole
kPa	kilopascal
kWh	kilowatt hour
L	liter
m^2	square meter
m^3	cubic meter

MHz	megahertz
MJ	mega joule
mm	millimeter
ml	milliliter
MM	million
MW	megawatt
rpm	revolutions per minute
s	second
wt.%	weight percent

List of Publications

Journal articles

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2. Makepa, D. C., Chihobo, C. H., Ruziwa, W. R., & Musademba, D. (2023a). A systematic review of the techno-economic assessment and biomass supply chain uncertainties of biofuels production from fast pyrolysis of lignocellulosic biomass. Fuel Communications, 14(1), 100086. https://doi.org/https://doi.org/10.1016/j.jfueco.2023.100086 **(Manuscript details: Published online)**
3. Makepa, D. C., Chihobo, C. H., Ruziwa, W. R., & Musademba, D. (2023b). Microwave-assisted pyrolysis of pine sawdust: Process modelling, performance optimization and economic evaluation for bioenergy recovery. Heliyon, 9(3), e14688. https://doi.org/https://doi.org/10.1016/j.heliyon.2023.e14688 **(Manuscript details: Published online)**
4. Makepa, D. C., Chihobo, C. H., & Musademba, D. (2023). Microwave-assisted pyrolysis of pine sawdust (*Pinus Patula*) with subsequent bio-oil transesterification for biodiesel production, Biofuels, DOI: https://doi.org/10.1080/17597269.2023.2239543 **(Manuscript details: Published online)**
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Abstract

Pyrolysis is a promising method for producing bio-oil from biomass. However, bio-oil must be upgraded before it can be used as fuel in internal combustion engines. While biofuels are often considered renewable and eco-friendly, it is important to understand the complete economic and environmental impacts of biofuel production to make informed decisions about their use. This study aims to evaluate the process's economic viability and the environmental sustainability of converting pine sawdust to crude bio-oil via microwave-assisted pyrolysis. The study used ASTM D 410-84, D3173-5 and ASTM D5373 standards to characterize the feedstock and pyrolysis products, and thermogravimetric analysis to study the thermal degradation behavior of pine sawdust. Gas chromatography-mass spectrometry (GC-MS) and Fourier transform-infra red (FTIR) were used to analyze the compositional properties of the organic phase and fatty acid methyl esters. The study found that the optimal operating conditions for producing the highest amount of bio-oil were achieved at 550℃ and 1 atm, yielding 42.28 wt.% of bio-oil, with phenolics contributing the greatest percentage of organic compounds. Transesterification improved the bio-oil properties by converting organic acids and oxygenated compounds to fatty acid methyl esters with a concentration of 510.05 mg/L. The study also evaluated the economic feasibility of the process, establishing the minimum selling price (MSP) of bio-oil, and predicted MSP for biodiesel. The MSP of bio-oil and biodiesel was established through the use of a discounted cashflow rate of return (DCFROR) analysis. The study found that the process was economically viable, with a MSP of $1.14/L of bio-oil and a predicted MSP for biodiesel of $2.31/L. The minimum selling price of biodiesel was consistent with the prices reported in previous studies, albeit with minor variations primarily attributed to variations in feedstock composition and the complexity of the thermochemical conversion process. The life cycle assessment (LCA) utilized a cradle-to-gate system boundary approach. To evaluate the environmental sustainability of the system, the Ecoinvent v3.7 database in openLCA v2.0 software. They conducted an analysis of 18 environmental impact categories using the ReCiPe 2016 (H) midpoint impact assessment methodology. However, the study found that the process had environmental impacts, including global warming potential, photochemical oxidant formation, and human toxicity, primarily due to the use of methanol in the biofuel synthesis stage. The study suggests that implementing sustainable practices, such as using organic fertilizers, optimizing transportation routes, implementing gas cleaning technologies, and effective waste management practices, could enhance the environmental performance of the biofuel production system.

CHAPTER ONE: INTRODUCTION TO THE STUDY

1.1 Background

Efforts have been consistently made to discover substitute sources of energy that could eventually take the place of conventional fossil fuels like coal, oil, and natural gas. This exploration has stimulated a spirited debate about the most suitable alternatives that could work as a feasible replacement for the existing energy blend (Nunes et al., 2023). The three principal energy sources which are coal, oil, and natural gas were used specifically to create the current global energy mix (Shrestha et al., 2022). More specifically, coal is used primarily in the production of electrical energy (by thermal conversion), oil is used primarily in the production of liquid fuels for transportation, and natural gas, which has only recently come into use, serves the same purpose as coal, which was partially replaced, with the additional function of serving as a fuel for heating, both at the industrial and household levels (Kartal et al., 2022). However, in light of the non-renewable nature of fossil fuels, researchers are seeking for sustainable alternatives to fossil fuels that could eventually replace the current energy mix.

The use of biomass as an alternative renewable energy source has drawn interest on a global scale. The availability of biomass feedstock might, however, be a problem when utilizing biomass as a substitute for other sources of energy (Makepa et al., 2022). Furthermore, food production and other land uses may be in competition with biomass production (Yana et al., 2022). Concerns have also been raised concerning the environmental effects that might result from the harvesting and processing of biomass as well as the sustainability of biomass production.

In Zimbabwe, there is continuous accumulation of waste with low utilization rates. For instance, in the Eastern Highlands, the timber industry is thought to be responsible for between 50 and 80 percent of the biomass waste (Charis et al., 2019). Although it should be feasible to recover 60% of the raw material used in wood products, owing to the use of obsolete equipment, only 40–45% of round wood is recovered, which leads to an increase in waste generation (Charis et al., 2019). The low lumber recovery factor suggests that a lot of wood waste is produced by the timber industry. Commercial sawmills have traditionally used wood chips and offcuts exclusively, in steam boilers used in the process of drying lumber in kilns, leaving huge amounts of sawdust to accumulate over time. Only larger commercial organizations are able to make the enormous capital commitment necessary to use sawdust as boiler fuel for steam (Charis et al., 2019). Waste pine sawdust has been utilized in the pulp, paper, and board manufacturing sectors. However, there is a gap between the supply and demand for sawmill waste. Because of this, communities and plantation owners struggle to keep up with the rate of accumulation. Therefore, the Eastern Highlands are covered in substantial heaps of unused sawdust. In addition to reducing the region's visual attractiveness, these stockpiles also cause a number of environmental issues, such as odor emission and spontaneous combustion. Therefore, there is a requirement for a significant and organized commercial uptake of the waste.

The methods used to dispose of sawdust currently include open-air incineration, dumping at municipal landfills, sawmills, and plantation land (Charis et al., 2019). When waste is burnt in open-air, particulate matter and anthropogenic air pollutants are released, which has an impact on the environment and public health. Additionally, the practice is linked to the release of greenhouse gases that cause global warming (Okedere et al., 2017). During the rainy season, the outdoor stockpiles release a wood residue leachate with significant concentrations of metals and dissolved organic materials. Water bodies that receive the runoff may be at risk from the leachate's poisonous and harmful properties (Liu et al., 1999). In addition to being hazardous, wood leachate can cause the receiving water to have a low pH, be acidic, and lose oxygen. A waste processing system that can successfully reduce the environmental issues and threats to public health connected with present disposal techniques is urgently needed.

Research and development into various thermochemical, biochemical and chemical conversions of biomass into biofuels and value-added materials have been done by several authors (Bharath et al., 2020; Costa et al., 2016; Khelfa et al., 2020; Makepa, Chihobo, et al., 2023b; Manyuchi et al., 2016; Naureen et al., 2015; Sınağ et al., 2011; Wauton & Ogbeide, 2019). Biomass pyrolysis has emerged as a viable option for converting biomass to a composite mixture of organic compounds, biochar fractions, and gas. Pyrolysis is a thermal decomposition process that involves the breakdown of carbonaceous materials by heating them in an inert atmosphere. The process can be classified into three categories based on the heating rate and biomass retention time, namely flash, fast, and slow pyrolysis. The biomass pyrolysis process can convert between 60-75 % of the original biomass waste into bio-oil, which can be utilized in both internal combustion engines and turbines (Kumar et al., 2020). In the context of Canada, bio-oil can be economically transported to biorefineries located within a radius of 250 km from the bio-resources for processing to obtain value-added products (Pootakham & Kumar, 2010).

An alternative to conventional heating commonly used during fast pyrolysis is the use of microwave radiation. The process is commonly known as Microwave-Assisted Pyrolysis (MAP). This process has been proven to be fast and energy-efficient. Furthermore, current research reported that MAP technology is easy to use and control. MAP produces high-quality liquid products that can be utilized as feedstock in the manufacture of biochemicals and biofuels sustainably, and the energy balances for the process are favourable (Chen, 2015; Kpalo et al., 2020; Sambe et al., 2021; Sansaniwal et al., 2017). Uniform heating in MAP permits the direct utilization of large-sized particles as feedstock (Mutsengerere et al., 2019). Microwave-absorbing agents such as silicon carbide, activated carbon, and biochar are normally added to facilitate heating in MAP processes because not all materials can absorb microwaves.

Despite having characteristics that are comparable to those of petroleum-based diesel, bio-oil cannot be utilized directly as a fuel due to its instability, high acidity and other unfavourable characteristics (Sánchez-Borrego et al., 2021). As a result, bio-oil has to be improved to increase its quality and suitability for use as fuel. Several procedures are employed in the upgrading bio-oil to enhance its physical and chemical characteristics, such as lowering its acidity, enhancing its stability, and raising its energy density (Kumar et al., 2020). Esterification, hydrotreating, hydrodeoxygenation, and fractionation are a few examples of these procedures.

There are various reasons why bio-oil has to be upgraded. First, because bio-oil is highly acidic, it can cause corrosion in storage tanks and engines, which can result in expensive maintenance expenditures (Lahijani et al., 2022). Second, bio-oil's potential as a fuel source is constrained by its low energy density. Increasing the energy density of bio-oil can make it more cost-effective and efficient for use in engines and other applications (Hu & Gholizadeh, 2020). Finally, improving bio-oil can make it more compatible with the fuel distribution and infrastructure already in place. Bio-oil that meets the industry standards can be blended with conventional diesel fuel derived from petroleum by taking advantage of the existing pipes and other distribution infrastructure (van Dyk et al., 2019). Therefore, it is essential to upgrade bio-oil to convert it into a fuel that can be used.

While large-scale commercialization of advanced biofuel production technologies utilizing bio-oil remains elusive, there is potential for biomass-derived products to replace fossil-fuel-based alternatives, provided they can be produced sustainably and cost-effectively. One approach to assessing the economic feasibility of biomass conversion pathways is through techno-economic analysis (TEA) (Makepa et al., 2023a). The Life-Cycle Assessment (LCA) method is a systematic approach for assessing the potential environmental effects of a product system over the course of its entire life-cycle chain. Especially for first generation and second-generation biofuels, LCA has been widely used to evaluate the environmental impact of biomass-derived fuels (El Joumri et al., 2022).

Despite the increasing interest in the production of bio-oil from MAP of pine sawdust, there is a lack of research that comprehensively evaluates the techno-economic feasibility and environmental impact of this process. Previous studies have focused on the optimization of the pyrolysis process and the characterization of the resulting bio-oil, but there is a need for a more holistic analysis that takes into account the entire life-cycle of the process, including the economic viability and environmental sustainability. Therefore, a research gap exists in the comprehensive evaluation of the techno-economic feasibility and environmental impact of bio-oil production from MAP of pine sawdust.

Therefore, the focus of the study is to assess and evaluate the technical and economic aspects of MAP of sawdust as an option for the production of biofuels and value-added chemicals. Furthermore, a LCA is carried out to evaluate the potential environmental impact of the process. Addressing this research gap is important as it can provide valuable information for policymakers, investors, and other stakeholders who are interested in promoting the development and adoption of sustainable and renewable energy sources. It can also help to inform the development of new technologies and approaches to bio-oil production, with the potential to reduce greenhouse gas emissions and mitigate the impact of climate change. Furthermore, this information is essential in the adoption and subsequent commercialization of biorefineries in Zimbabwe.

1.2 Problem statement

The production of bio-oil from MAP of lignocellulosic biomass has been proposed as a potential alternative to traditional fossil fuels. However, the use of pine sawdust as a feedstock for the production of biofuels and value-added bio-based products has not been well explored, and there is a lack of comprehensive research on the techno-economic feasibility and environmental impact of this process. Additionally, the commercial exploitation of the abundant pine sawdust and other biomass materials in Zimbabwe for energy production requires adequate and robust TEA. Therefore, there is a need to conduct a TEA and LCA of bio-oil production from MAP of pine sawdust to evaluate the economic viability and environmental sustainability of this process.

1.3 Aim

The overall aim of this project is to determine whether or not the production of bio-oil via the MAP of pine sawdust is economically and environmentally feasible.

1.4 Objectives

1. To design and conduct a microwave-assisted pyrolysis experiment to produce bio-oil.
2. To characterize the bio-oil and evaluate the feasibility of its conversion into biodiesel through a base-catalyzed transesterification process.
3. To develop process simulations in Aspen Plus® for the microwave-assisted pyrolysis of pine sawdust.
4. To conduct a technoeconomic analysis of biorefinery scenarios for microwave-assisted pyrolysis based on process simulations and experimental data.
5. To evaluate the potential environmental impact of the microwave-assisted pyrolysis of pine sawdust.

1.5 Hypothesis

The production of bio-oil from microwave-assisted pyrolysis of pine sawdust is expected to demonstrate favorable techno-economic feasibility and environmental sustainability, making it a viable alternative to traditional fossil fuels. This hypothesis assumes that the production process of bio-oil from pine sawdust using microwave-assisted pyrolysis will yield positive results in terms of economic viability and environmental impact. The hypothesis anticipates that the techno-economic analysis, along with the life-cycle assessment, will reveal promising outcomes, supporting the potential of this process as a sustainable and economically feasible solution for biofuel production.

1.6 Practical relevance and significance of the study

In 2015, the United Nations adopted the 17 sustainable development goals (SDGs) aimed at steering member countries towards sustainable (economically viable, socially responsible and environmentally conscious) development (United Nations, 2015). The production of bio-oil from renewable sources such as pine sawdust can contribute to SDG 7 (Affordable and Clean Energy) by providing a sustainable alternative to traditional fossil fuels. Bio-oil can be used as a feedstock for energy production, which can reduce the dependence on fossil fuels and help reduce greenhouse gas emissions. The study can contribute to SDG 9 (Industry, Innovation and Infrastructure) by developing new and innovative technologies for the production of biofuels. The use of MAP in this study is a new and promising technology for producing bio-oil from biomass. This study can also contribute to SDG 12 (Responsible Consumption and Production) by promoting sustainable production and consumption patterns. By analyzing the life-cycle of bio-oil production from MAP of pine sawdust, the study can identify potential environmental impacts and help develop more sustainable production techniques. The research can also contribute to SDG 13 (Climate Action) by offering a potential solution to reduce greenhouse gas emissions and mitigate climate change. The use of bio-oil as a feedstock for energy production can reduce carbon emissions and promote a more sustainable energy mix.

The production of biofuels through MAP of pine sawdust supports the National Biofuels Policy in Zimbabwe which was developed in 2013 to promote the production and use of biofuels (ZERA, 2019). One of the key objectives of the policy is to encourage the production of biofuels from sustainable biomass feedstock. The policy stipulates that biofuels production should not compete with food production, and that the use of non-food feedstock such as waste biomass and non-edible oils should be prioritized (ZERA, 2019). In addition to promoting the production and use of biofuels, the policy also encourages the establishment of research and development centres to support the development of new technologies. However, this study is of practical relevance in supporting the uptake of biofuels in Zimbabwe.

Advanced biofuels can minimize the emissions of greenhouse gases compared to petroleum-based fuels. Incorporated into the soil, biochar can amend the soil to improve productivity, conserve water, retain nutrients and sequester carbon for hundreds of years (Lehmann et al., 2006; Yanai et al., 2007; Yu et al., 2009; Beesley et al., 2010; Major et al., 2010; Karhu et al., 2011; Zhang et al., 2013). Thus, a carbon negative economy can be envisioned, in which fuel production reduces carbon dioxide into the atmosphere while providing energy products to society. Furthermore, using biofuels in Zimbabwe reduces over reliance on fossil fuels saving the much-needed foreign currency.

The study demonstrates the potential of using non-food biomass feedstock such as pine sawdust for biofuels production. This is important as the use of food crops for biofuels production has been criticized for contributing to food insecurity and driving up food prices. The use of non-food biomass feedstock can help avoid these negative consequences while still promoting the development of a sustainable biofuels industry.

In addition, the study provides insights into the feasibility of producing bio-oil from pine sawdust using MAP. The technical and economic aspects of the process, as well as the LCA, which is important for assessing the environmental impact of biofuels production were analyzed. By identifying potential environmental impacts such as greenhouse gas emissions and global warming potential, the study can help policymakers and industry stakeholders develop more sustainable production methods.

1.7 Research novelty and contribution to knowledge

The production of bio-oil from MAP of pine sawdust is a relatively new research area that has gained significant attention in recent years. The use of MAP for the production of bio-oil is a relatively new technique that offers several advantages over traditional pyrolysis methods. Microwave heating can significantly reduce the retention time, increase the yield of bio-oil, and improve the quality of the bio-oil produced. Pine sawdust is a low-cost and abundant biomass resource that is readily available in many regions of the world. The use of pine sawdust as a feedstock for bio-oil production can help to reduce the dependence on fossil fuels and contribute to sustainable development. The use of pine sawdust as a feedstock for biofuel production does not compete with food crops, which is a major concern with some other feedstock materials. Furthermore, the use of pine sawdust as a feedstock for biofuel production does not require significant land-use change or deforestation and promotes sustainability by utilizing a waste material that would otherwise be discarded. This helps to reduce waste and promote the development of a circular economy.

The chemical composition and properties of bio-oil produced from different biomass feedstock materials and pyrolysis conditions can vary significantly. Therefore, the characterization of the bio-oil produced from pine sawdust can provide valuable information on its potential applications of bio-oil as a renewable energy source and the optimization of the pyrolysis process.

TEA is a technique used to evaluate the economic feasibility of a process or technology, while LCA assesses the environmental impact of a process or technology throughout its entire life-cycle. The integration of these two techniques can provide a comprehensive assessment of the economic and environmental sustainability of bio-oil production from MAP of pine sawdust. The application of these techniques to bio-oil production from MAP of pine sawdust is also a novel aspect of this research. While the production of bio-oil from pyrolysis has been studied extensively, the application of TEA and LCA to this process is relatively new. The evaluation of the economic feasibility and environmental impact of bio-oil production from MAP of pine sawdust can provide valuable information for the optimization of the process and the development of sustainable bioenergy systems.

The identification of key factors that affect the economic and environmental sustainability of bio-oil production from MAP of pine sawdust is another contribution to the field of study. The identification of these key factors can help to guide the development of strategies to optimize the process and improve its economic and environmental performance.

The findings of this study have the potential to inform future research and development in the field of bio-oil production, as well as guide policy decisions related to the adoption of renewable energy technologies.

1.8 Overview of the research methodology

The research study aimed to achieve specific objectives outlined in section 1.4. Firstly, the suitability of pine sawdust as a feedstock for bio-oil production was evaluated. Subsequently, the economic viability and environmental sustainability of pine sawdust were assessed. The adopted methods for achieving these objectives are summarized in sections 1.8.1 to 1.8.4, while detailed discussions can be found in Chapters 4 to 7 to avoid redundancy and repetition.

1.8.1 Experimental design

Representative samples of pine sawdust were obtained from selected sawmills in the Eastern Highlands in Zimbabwe. The pine sawdust samples were characterized to analyse their physical and chemical properties. Controlled pyrolysis experiments were conducted through microwave-assisted pyrolysis to convert pine sawdust into bio-oil. The bio-oil was converted to biodiesel through a base-catalysed transesterification reaction. The bio-oil and biodiesel samples were characterised to determine their physical properties and chemical composition. The water content, ash content, viscosity, total acid number (TAN) and flash point of the bio-oil and biodiesel were evaluated. GC-MS and FTIR analysis was performed to determine the chemical composition of the bio-oil and biodiesel samples.

1.8.2 Simulation study

The research design employed Aspen Plus® V11 software for the modelling and simulation of the pyrolysis process applied to pine sawdust. Aspen Plus® offers a range of built-in tools that facilitate the calculation of energy and mass balances, reaction kinetics, chemical equilibrium, and process optimization. The software's extensive databases, physical properties, and thermodynamic models enable the modelling of complex and comprehensive systems. It is capable of handling conventional and non-conventional solids, liquids, and gaseous compounds, making it well-suited for simulating chemical processes (Shoaib Ahmed Khan et al., 2022).

Aspen Plus® distinguishes between two types of components: conventional and non-conventional. Conventional components have well-defined molecular structures and can be found in various Aspen Plus® databanks. On the other hand, non-conventional components are represented based on proximate and ultimate analysis, as they lack a molecular formula (Ward et al., 2014).

The parameters for biomass fast pyrolysis were optimized using Response Surface Methodology based on Central Composite Design. A second-order model was fitted using CCD, which is a standard RSM design. CCD is particularly useful for fitting a quadratic surface and reduces the number of tests required to maximize the efficacy of parameters while studying their interactions. The primary objective of optimizing the process was to develop a regression model that evaluates system performance by taking into account the interactions among key parameters. Design-Expert® Software was utilized to create a design matrix using simulated data from Aspen Plus®.

1.8.3 Techno-economic analysis

The Aspen Process Economic Analyzer (APEA) was used to estimate equipment costs and sizes based on the process simulations developed in Aspen Plus. The pyrolysis and transesterification reactor costs were calculated using a scaling equation that relates equipment cost to size. Costs were updated to 2022 values using the CEPCI index. Operating costs considered included biomass, utilities like electricity and cooling water, as well as process materials such as methanol, catalysts and activated carbon. Assumptions for the discounted cash flow analysis included a 40% income tax rate, 5% revenue and cost escalation, 10% required rate of return, and a 20-year plant lifetime.

Total project investment was estimated using factors developed by Peters et al. (2003) to determine total installed cost (TIC). This included direct costs like installed equipment, instrumentation, piping and buildings. Indirect costs such as engineering, construction and fees were also included. Contingency and location factors were applied to the fixed capital investment (FCI) to obtain TIC. Working capital was added to determine total capital investment (TCI).

Sensitivity analysis examined how the minimum fuel selling price was affected by varying key parameters like FCI, yield, costs and escalation rates by ±25% while holding other values constant. Uncertainty in parameters was addressed through a Monte Carlo analysis using triangular distributions and 5000 trials to assess performance under uncertainty.

1.8.4 Lifecycle Assessment (LCA)

A LCA was conducted to evaluate the potential environmental impacts and advantages of producing biodiesel from MAP of pine sawdust. The LCA follows the ISO 14040 framework and assesses the full life cycle from raw material extraction and processing through to end-of-life disposal. The system boundaries include four subsystems - pine biomass production, pre-processing of the biomass, pyrolysis of the biomass into bio-oil, and synthesis of the bio-oil into biodiesel. Pine cultivation and timber production data is obtained from Zimbabwean forestry sources. The pyrolysis and biodiesel production stages are modelled using Aspen Plus process simulation software.

The functional unit is defined as 1 kg of biodiesel produced. Impact categories to be assessed using the ReCiPe 2016 methodology include 18 midpoint indicators. OpenLCA software is used to conduct the LCA and inventory analysis. Life cycle inventory data is collected for each stage. For biomass production, this includes fertilizer and diesel inputs as well as emissions from fertilizer application. Yields of timber, sawdust and wood waste are also accounted for.

Pre-processing involves grinding pine sawdust to smaller particles below 10% moisture content to enhance pyrolysis. Energy requirements for these stages are obtained from literature. The MAP plant is designed to pyrolyze 2000 tonnes per day of sawdust at 500 °C, resulting in a 65% bio-oil yield. Transesterification uses a 3:1 methanol to bio-oil ratio with 1% KOH catalyst at 30-60°C to produce biodiesel and glycerol. The inventory analysis quantifies materials, energy and emissions from each stage. The impact assessment then evaluates the 18 environmental impact categories based on the LCI to identify advantages and disadvantages of the MAP process.

1.9 Overview of the study

The thesis is composed of eight chapters. In the first chapter, the background of the research, the context of the research problem, aims and objectives, practical relevance and significance of the study, research novelty and contribution to knowledge is introduced. Chapter 2 and 3 maps out the research landscape.

Chapter 2 presents an account of the literature review conducted for this study. The topics covered include the pyrolysis mechanism of lignocellulosic biomass, the properties and applications of pyrolysis products, the analytical techniques that are employed when analyzing pyrolysis products, the in-situ characterization of pyrolysis products, factors affecting the pyrolysis process, the co-pyrolysis and catalytic pyrolysis of lignocellulosic biomass, pyrolysis reactor designs and the LCA of biomass pyrolysis. The solar-assisted and MAP of biomass has been reviewed as recently developed pyrolysis mechanisms.

Chapter 3 presents an overview of the various types of methodologies or techniques used in the TEA of biomass pyrolysis processes, and highlight the uncertainties that need to be taken into account in the evaluation model. The findings of this chapter helped develop a methodology for the TEA of MAP of pine sawdust (objective 4).

Chapter 4 presents the thermochemical conversion of pine sawdust to crude bio-oil via the MAP (MAP) technique with subsequent bio-oil transesterification for biodiesel production. A MAP experiment was designed and conducted, the bio-oil was upgraded to biodiesel via transesterification fulfilling objectives 1 and 2.

In Chapter 5, an Aspen Plus model for the conversion of pine sawdust to bio-oil via MAP has been developed. The process conditions for the thermochemical conversion of pine sawdust to bio-oil through pyrolysis were optimized in order pin point the optimal operating conditions for maximum bio-oil yields (objective 3). An economic evaluation of this process was carried out in this chapter.

Chapter 6 presents an economic evaluation of MAP of pine sawdust with subsequent bio-oil transesterification for biodiesel production. A model was developed in Aspen Plus based on the experimental data obtained in Chapter 4 (objectives 1 and 2). The findings of this chapter help fulfil objective 4.

Chapter 7 presents the LCA of MAP of pine sawdust. The potential environmental impacts of this process were evaluated in this chapter based on experimental data obtained in Chapter 4 (objectives 1 and 2) and simulation data obtained in Chapter 5 (Objective 3) and Chapter 6 (Objective 4).

Chapter 8 presents an integration of the research findings. A comprehensive discussion of the research findings, conclusions and recommendations for future research are provided in this chapter.

CHAPTER TWO: LITERATURE REVIEW

2.1 Chapter overview

The chapter provides a thorough assessment of current developments in biomass pyrolysis research, including both basic research and technological applications. Recent advances in pyrolysis products characterization methods, particularly on the online characterization of biomass pyrolytic intermediates and spectroscopic and microscopic imaging methods for biochar and bio-oil are discussed. Then, relevant optimization and regulation approaches for the biomass pyrolysis process are discussed in light of the demands made to enhance the physicochemical features of the relevant pyrolysis products. Previous studies have shown that co-pyrolyzing biomass with another feedstock can improve the physicochemical characteristics of the pyrolysis products and efficiently realize waste recycling. As a result, this study includes a thorough assessment of current developments in biomass co-pyrolysis using four different feedstocks (coal, plastics, tyres, and sludge). Recent activities of catalytic biomass pyrolysis, or catalytic co-pyrolysis, are also described as an essential part of general biomass pyrolysis. Reactor design aspects and economic evaluation of pyrolysis technologies have been reviewed. Additionally, two cutting-edge heating techniques (microwave heating and solar heating) for biomass pyrolysis are discussed, and their advantages and disadvantages are contrasted with those of the traditional heating approach. A life-cycle assessment methodology to quantify the environmental impacts of biomass pyrolysis has been reviewed in this chapter. This chapter is concluded with some predictions for the development of biomass pyrolysis in the future.

This chapter is based on a review paper published in the journal Biofuels.

Makepa, D. C., Chihobo, C. H., & Musademba, D. (2022). Advances in sustainable biofuel production from fast pyrolysis of lignocellulosic biomass, Biofuels, 14:5, 529-550, DOI: https://doi.org/10.1080/17597269.2022.2151459

2.2 Pyrolysis mechanism

The complexity of biomass pyrolysis results from the diversity in reaction mechanisms and rates that occur during the degradation of the various components of the biomass, which is also partially dependent on the thermal processing settings and reactor designs. Prior research has established interactions between the main components of woody biomass, such as cellulose, hemicelluloses, and lignin, during pyrolysis (Wang et al., 2014), which makes the prediction of biomass pyrolysis characteristics simply based on the thermal behaviour of the three individual components very difficult. For instance, the interaction between lignin and hemicellulose encourages the development of phenols generated from lignin while inhibiting the production of hydrocarbons (Wang et al., 2011). While cellulose-hemicellulose contact has a lesser impact on the synthesis and dispersion of pyrolysis products, lignin and cellulose interact extensively during pyrolysis since lignin prevents the polymerization of levoglucosan from cellulose and hence reduces biochar formation (Hosoya et al., 2007).

Dehydration, depolymerization, isomerization, aromatization, decarboxylation, and charring are only a few of the numerous parallel and series reactions that occur during biomass pyrolysis (Collard et al., 2012). It is generally accepted that the pyrolysis of biomass consists of three main stages: (i) initial evaporation of free moisture, (ii) primary decomposition followed by (iii) secondary reactions (oil cracking and depolymerization) (White et al., 2011). These stages coexist, and thermal analysis can be used to observe how they transition between one another. Through the use of computer-aided thermal analysis at various heating rates, the apparent specific heat of biomass during pyrolysis and the associated temperatures of reactions throughout various pyrolysis stages have been thoroughly researched in the past (Hossain et al., 2011; Mulligan et al., 2010).

The main decomposition of biomass, which results in solid char at temperatures between 200 and 400°C, often causes the most decomposition of biomass. The solid matrix continues to experience secondary reactions as the temperature continues to rise (Fisher et al., 2002).

The primary biomass constituents' individual degrading routes have each been studied. After cellulose, which largely decomposes between 325 and 400°C with levoglucosan as the main pyrolysis product, hemicellulose, which is typically represented by xylan, decomposes mostly between 250 and 350°C (Stefanidis et al., 2014). Lignin is the most stable component which decomposes at a higher temperature range of 300–550°C (Lange, 2007).

Among the three major biomass constituents of cellulose, hemicelluloses, and lignin, the decomposition of cellulose has been most widely analyzed and best comprehended (Van de Velden et al., 2010). The widely accepted Waterloo mechanism, presented in Figure 2.1, shows the cellulose pyrolysis reaction route in a simplified form. The key competitive processes that predominate at various temperature ranges are dehydrogenation, depolymerization, and fragmentation.

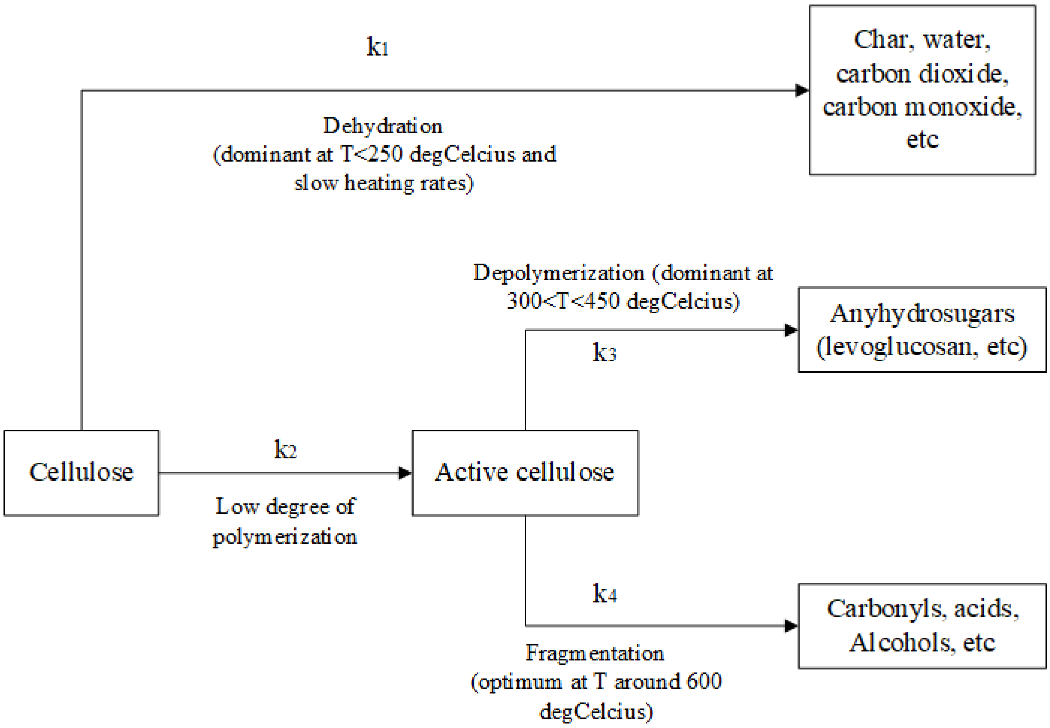


Figure 2.1: Waterloo mechanism of primary decomposition of cellulose (García et al., 2001)

2.3 Properties and applications of pyrolysis products

2.3.1 Bio-oil

Fast or flash pyrolysis is the method of choice to maximize bio-oil yields when producing bio-oil as the main product of interest. The key elements of fast pyrolysis typically include moderate pyrolysis temperatures (450–650 °C), biomass particle sizes of less than 2mm, extremely high heating rates (103–105 °C/s), extremely short vapour residence times (2 s), and rapid quenching of pyrolytic vapours to suppress secondary reactions (Bridgwater, 2012). Primary char must be removed quickly because it catalyzes the formation of secondary char, gas, and water from primary organic vapours, which reduces the yield of bio-oil. Based on the dry biomass feed weight, the fast pyrolysis process typically generates bio-oil, gas, and char yields of 60–70 wt.%, 13–25 wt.%, and 12–15 wt.% respectively (Isahak et al., 2012). With typical feed particle sizes of not more than 2 mm and higher temperatures of about 800–1000 °C, flash pyrolysis produces bio-oil yields that are typically 75 wt.% and gas and char yields that are 12–13 wt.% (Jahirul et al., 2012). Typically, slow pyrolysis takes place at low temperatures with a prolonged residence time and slow heating rate. Due to the primary product cracking, which may have a negative impact on the yield and quality of the bio-oil, this method of pyrolysis can yield more char when the operating conditions are controlled than fast and flash pyrolysis (Pourkarimi et al., 2019).

Bio-oil, also known as "*pyrolysis oil, pyrolysis liquid, pyrolysis tar, bio-crude, wood liquid, wood oil or wood distillate"* (Kan et al., 2016), is a dark brown, freely flowing organic liquid mixture that typically contains a significant amount of water (15–35 wt.% on average) and a large number of organic compounds, including acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, alkenes, nitrogen compounds, and various oxygenates, as well as solid particles (Rezaei et al., 2014). The initial moisture content of the feedstock and water generation during pyrolysis in relation to the reaction parameters determine the ultimate water content of the bio-oils. Due to the presence of pyrolytic lignin with molecular weights as high as 5000 amu or even more, it is exceedingly difficult to accomplish chemically accurate identification of some individual components in the bio-oils (Weldekidan et al., 2018).

The normal range of the bio-oils' higher heating value (HHV) is between 15 and 20 MJ/kg, which is only 40–50% of the HHV of conventional petroleum fuels (42–45 MJ/kg) (Demirbas, 2004). This is a result of the significant oxygen content, which ranges from 30-35 wt.% on a dry basis weight.

The low pH value of 2–3.7 caused by the presence of carboxylic acids is one of the negative properties of pyrolysis bio-oils in addition to their high oxygen content. As a result, bio-oils have the potential to be destructive to common structures, have high instability during storage due to ongoing chemical reactions that result in larger molecules (primarily polymerization, etherification, and esterification) (Weldekidan et al., 2018), and retain solids to the extent of 0.01–1.0 wt.% of their weight. Concerning moisture content (15–30 wt.% vs. 0.1 wt.%), specific gravity (1.2 vs. 0.94), elemental makeup, and a few additional fuel indices, such as pour point (-33 °C vs. -18 °C), extensive comparisons between bio-oil and heavy fuel oil were offered (Parvez et al., 2019).

Bio-oils have undergone considerable testing as potential fuels for gas turbines, diesel engines, boilers, furnaces, and combustors (Czernik & Bridgwater, 2004). Long-term operation is not possible due to the poor quality of the bio-oils, which include weak volatility, high viscosity, high corrosiveness, and coking. Bio-oils were successfully burnt in a diesel test engine with limited operation time (Bridgwater, 2012). It is well acknowledged that bio-oils need to be upgraded further before they may be used in engines through hydrogenation (Dimitriadis et al., 2021), hydrodeoxygenation (Qu et al., 2021), catalytic pyrolysis (Wang et al., 2022), catalytic cracking (Qiu, Yang, et al., 2022), steam reforming (Xiong et al., 2022), molecular distillation (Chen et al., 2017), use of supercritical fluids (Omar et al., 2021), esterification (Prasertpong et al., 2020), or emulsification (Leng et al., 2018). Additionally, bio-oils can be utilized as a feedstock for the manufacturing of chemicals, including phenols for resin manufacture, additives in the fertilizing and pharmaceutical sectors, flavouring agents (like glycolaldehyde) in the food industry, and other specialized chemicals (Balat, 2011; Czernik & Bridgwater, 2004).

2.3.2 Biochar

The main solid product, known as biochar or charcoal, is composed primarily of unconverted organic solids, carbonaceous wastes, and a mineral fraction that results from the partial or total breakdown of biomass components (Demirbas, 2004). The kind of feedstock and pyrolysis working conditions affect the chars' physical, chemical, and mechanical characteristics. Slow pyrolysis at pyrolysis temperatures between 300 and 800 °C favours the production of biochar by reducing the yields of bio-oil (typical product yields: bio-oil 30wt%, biochar 35 wt.%, and gas 35 wt.%) (Demirbas, 2004). The elemental composition (carbon content varying from 53 to 96 %), HHVs (20–36 MJ/kg), and yields (30–90 wt.%) of biochar from the pyrolysis of various biomass feedstock, as well as pyrolysis at varied heating rates and temperatures, were summarized by Demirbas (2004). Char is a desirable coal alternative in several fuel applications due to their high HHV.

The microscopic surface structure of biochar produced during pyrolysis gives them the ability to filter and adsorb organic and inorganic contaminants (Ahmad et al., 2014; Mohan et al., 2014), especially after the chars are physically or chemically activated. The ideal biochar qualities for filtration (surface area of 1400 m^2/g and micropore volume of 0.7 cm^3/g) were produced from coconut shells using a fluidized bed reactor at reaction temperatures of 850 °C and 1.5h under steam. Olive seed waste was pyrolyzed in a fixed-bed heated under N_2 at 800 °C for 1h to form biochar, which was then activated with KOH to produce biochar with similar qualities (surface area of 1690 m^2/g and micropore volume of 0.7 cm^3/g) (Skodras et al., 2007). Manyà (2012) has provided more information regarding the properties of several activated biochars, including BET surface area, micropore volume, and the ratio of micropore volume to total pore volume, as well as the activation conditions (reaction atmosphere, temperature, and retention time).

Biochar contains a range of plant nutrients, making them valuable as soil amendments (Hossain et al., 2011) and they can also contribute to carbon sequestration to mitigate atmospheric carbon (Lee et al., 2013). The type of biomass and the pyrolysis conditions have a significant impact on the concentration of the various nutritional components. Due to the loss of biomass bulk at higher temperatures during pyrolysis, the concentrations of nutritional components are increased in the biochar. The concentrations of nitrogen might vary based on the type of biomass and the chemistry of the nitrogen in the feedstock because it is more volatile than the other nutrients.

2.3.3 Non-condensable gases (NCGs)

CO_2, CO, hydrogen (H_2), low carbon number hydrocarbons like methane (CH_4), ethane (C_2H_6), and ethylene (C_2H_4), as well as trace amounts of other gases like propane (C_3H_8), ammonia (NH_3), nitrogen oxides (NO_x), sulphur oxides (SO_x), and low carbon number alcohols, can all be released during the pyrolysis of biomass. Depending on their actual composition, the usual low heating values (LHVs) of the syngas range from 10 to 20 MJ/Nm^3. As the primary products of biomass pyrolysis, CO_2 and CO mainly originate from the decomposition and reforming of carbonyl (C=O) and carboxyl (COO) groups (Qu et al., 2011; Strezov et al., 2008). Light hydrocarbons (primarily CH_4) are primarily attributed to the decomposition of weakly bonded methoxyl ($-O-CH_3$) and methylene ($-CH_2-$) groups as well as the secondary decomposition of the oxygenated compounds, while H_2 results from secondary decomposition and reforming of the aromatic C=C and C–H groups at high temperatures (Uddin et al., 2014).

Biomass pyrolysis can result in the production of hydrogen-rich gas or synthetic gas. Wet biomass could give up to 40% higher H_2 yield and content in the gas, compared to dried biomass (Guoxin et al., 2009). Temperature and catalysts can further enhance the hydrogen production from biomass (Valin et al., 2009). Catalysts which can promote H_2 production and adjust the gas composition for downstream applications (e.g., Fischer–Tropsch synthesis) include $ZnCl_2$, dolomite, K_2CO_3, Na_2CO_3, Ni/Al, Ni/Fe, CaO, Fe_2O_3, Cr_2O_3 and Rh/CeO_2 (Qinglan et al., 2010; Xu, Ye, et al., 2011). Before the syngas can be used in practice, it must undergo several treatments to decrease or remove the undesirable constituents, which may include dust/aerosols, tars, steam, and evaporated heavy metals, HCN, H_2S and NH_3.

The syngas has multiple potential applications, such as direct use for the production of heat or electricity (e.g., gas combustion in spark ignition and compression ignition engines (Hossain & Davies, 2013)), either directly or co-fired with coal, production of individual gas components, including CH_4, H_2 or other volatiles, or in production of liquid biofuels through synthesis. In some situations, the hot pyrolytic gas can be recycled into the pyrolysis reactor as a carrier gas or utilized to pre-heat the inert sweeping gas.

2.4 Analysis of pyrolysis products

The bio-oil, char, and gaseous by-products of pyrolysis have been chemically and physically characterized using a variety of analysis techniques. The characteristics of these products and the relevant analysis techniques are summarized in Table 2.1.

Table 2.1: Biomass and pyrolysis products analysis techniques

Pyrolysis Products	**Properties**	**Analysis Methods**	**Reference**
Bio-oil	Water content	Water content ASTM E203 or ASTM D-1744 by Karl-Fischer titration	(Kanaujia et al., 2014)
	Carbon residue	ASTM E203 by destructive distillation method	(Kanaujia et al., 2014)
	Qualitative and quantitative identification of bio-oil compounds	Gas chromatography-mass spectrometry (GC–MS), high-performance liquid chromatography (HPLC)	(Kanaujia et al., 2014)
	Molecular weight distributions	Gel permeation spectroscopy (GPC), Matrix-assisted laser desorption/ionization (MALDI) mass spectroscopy	(Hossain et al., 2009)
	Gross calorific value (GCV)	ASTM D4809	(Kanaujia et al., 2014)
	HHV	Theoretical calculation	(Li & Suzuki, 2009)
	Elemental composition (C, H, N and O by difference)	ASTM D5373	(Kanaujia et al., 2014)
	Sulphur content	ASTM D4294 by Energy dispersive X-ray fluorescence (EDXRF) spectrometry, or ASTM D4239 by Infrared measurement of SOx after combustion of bio-oils	(Kanaujia et al., 2014)
	Functional groups	Infrared techniques including near-IR (NIR) and Fourier transform infrared (FTIR) spectroscopy	(Kanaujia et al., 2013)
	Types of hydrogens or carbons in specific structures	Nuclear magnetic resonance (NMR) spectroscopy	(Rogovska et al., 2014)
	Acid number	ASTM D664 by potentiometric titration method, or ASTM D974 by colour-indicator titration	(Kanaujia et al., 2014)
	Density at 15 °C (kg/m^3)	ASTM D4052 by digital density meter	(Kanaujia et al., 2014)
	Kinematic viscosity(mm^2/s)	ASTMD445–03	(Kanaujia et al., 2014)
	Flash point, pour point and boiling range (°C)	ASTM D93, D97, and D2887, respectively	(Kanaujia et al., 2014)
	Water insolubles	FTIR, ^{13}C NMR, and column chromatography	(Kanaujia et al., 2013)

Biomass/ Char	Proximate analysis (moisture, ash, volatile matter, and fixed carbon contents)	ASTM D1762-84,2007	(Rogovska et al., 2014)
	Ultimate analysis (elemental analysis of CHN, and O by difference)	ASTM D3176-89,2002	(Rogovska et al., 2014)
	Metal content	X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES)	(Liao et al., 2007)
	Elemental surface distribution	Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX)	(Chia et al., 2012)
	Functional groups	FTIR	(Xu et al., 2017)
	Aromaticity	^{13}C NMR	(Jiang et al., 2019)
	Mass/heat change during heating in different atmospheres (N_2, O_2, air, etc.)	Thermogravimetric analysis with differential scanning calorimetry (TGA/DSC)	(Chintala et al., 2017)
	Crystalline phases, and their qualitative and semi-quantitative data	X-ray diffraction (XRD)	(Chattopadhyay et al., 2016)
	Brunauer–Emmet–Teller (BET) surface area, porous structure	Nitrogen gas sorption	(Shaaban et al., 2014)
	Surface morphology	SEM	(Jiang et al., 2019)
	Particle size distribution	Laser sizing equipment	(Grierson et al., 2009)
	Electrical conductivity (EC)	Conductivity meter	(Uras et al., 2012)
	Particle size distribution	Microscopy, particle counter laser sizing equipment	(Grierson et al., 2009)
	Surface acidity and alkalinity	Boehm titration	(Shaaban et al., 2014)
	Organic carbon	DPI in-house method 236	(Grierson et al., 2011)
	Cation exchange capacity	Ion chromatography (IC)	(Sınağ et al., 2011)
Gas	Gases species and concentrations	Gas chromatography (GC); mass spectrometry (MS); non-dispersive infrared (NDIR) analysis	(Ismail et al., 2020)
	Functional groups	FTIR	(Wang et al., 2011)
	Lower heating value (LHV)	Calculation from gas composition: $LHV(MJ/m^3)=(107.98*H_2 + 126.36*CO + 358.18*CH_4 +$	(Bosong et al., 2012)

		59.036*C_2H_4 + 63.772xC_2H_6)/1000, where gas species represent the respective volumetric fractions	
	H_2S content	Lead sulphur precipitate through a reaction between H_2S and lead nitrate	(Karayildirim et al., 2006)
	Tar content and composition	Cold trapping; solid-phase adsorption (SPA)	(Myrén et al., 2002)
	Size distribution of particles	Scanning mobility particle sizer (SMPS)	(Gustafsson et al., 2011)

2.5 In-situ characterization of biomass pyrolysis

2.5.1 Pyrolysis–Gas Chromatography and Mass Spectrometry (Py-GC/MS)

Py-GC/MS is employed to identify the chemical composition and structure of the pyrolysis vapours that emerge during the pyrolysis of biomass. During the pyrolysis process, the biomass sample is heated at elevated temperatures, in an inert environment, and the pyrolysis volatiles that emerge are transferred to the GC column, where they are chemically identified by mass spectrometry. Flame ionization or a thermal conductivity detector then quantifies the pyrolysis volatiles. A typical schematic of a Py-GC/MS system is illustrated in Figure 2.2. In a study by Ye et al. (2017), this technique was employed to analyze the products of biomass fast pyrolysis. In their study, the pyrolysis volatiles were first observed at 400 °C, and high yields were observed at temperatures as high as 600-700 °C. The pyrolysis volatiles constituted mainly levoglucosan, anhydro-sugar derivatives, furans, phenols, aromatic hydrocarbons and light linear carbonyls. The pyrolysis volatiles increased as the temperature and feedstock residence time increased. Mullen and Boateng (2015) employed the same technique to quantify the aromatic hydrocarbons produced from catalytic fast pyrolysis of biomass. Fe-Modified HZSM-5 zeolites were employed as catalysts and the results showed that around 18% of selected aromatic hydrocarbons, including benzene, toluene, and ethylbenzene, can be obtained. The aromatic yield of switchgrass was 17% and cellobiose 25%. With this information and technique, a possible pyrolysis mechanism can be developed depending on the required product characteristics. The only drawback with this technique is that Py-GC/MS can only allow non-continuous analysis, therefore, it cannot give evolution characteristics over a wide range of temperatures. However, TG-based techniques (TG-MS, TG- FTIR, and TG- FTIR-MS) counter all these problems.

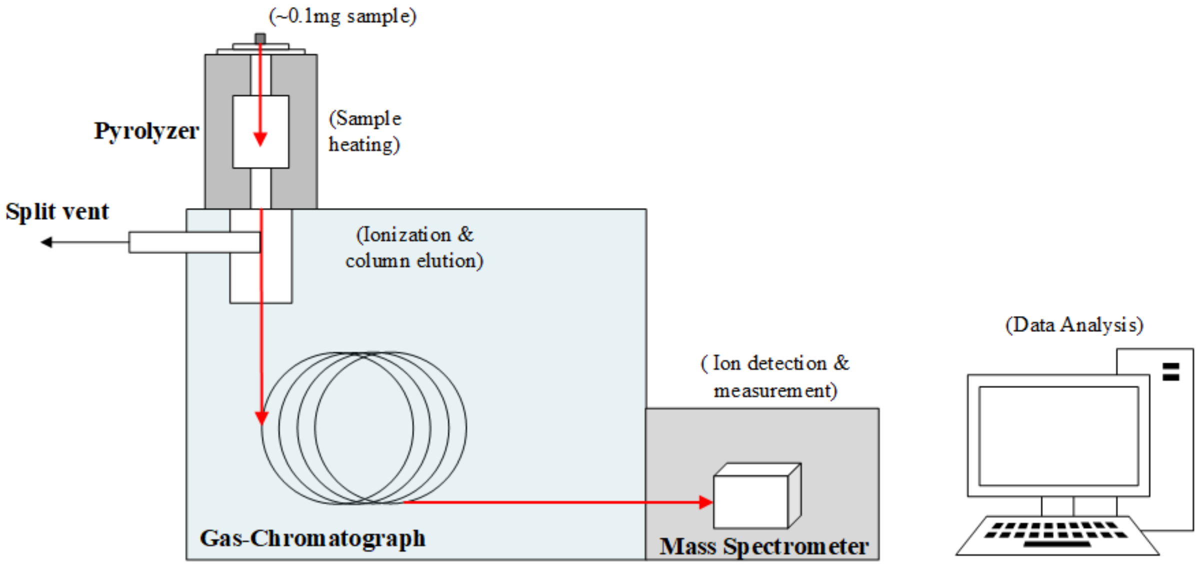


Figure 2.2: A typical schematic of a Py-GC/MS system (Chen et al., 2020)

2.5.2 TG-based techniques

2.5.2.1 Thermogravimetric and mass spectrometric (TG-MS)

TG-MS can identify the pyrolysis volatiles that evolve during the biomass pyrolysis process. A research study by Sanchez-Silva et al. (2012) employed this technique for thermochemical degradation characteristics of lignocellulosic biomass. It was found that biomass pyrolysis takes place in four distinct stages: (i) moisture evaporation, (ii) hemicellulose degradation, (iii) cellulose and lignin degradation and (iv) carbonization of lignin. At temperatures between 200°C and 450°C, light hydrocarbons, CO_2 and H_2O were produced, and at temperatures above 700°C, secondary reactions known as char self-gasification took place, liberating H_2 as a product. A research study by Magdziarz and Werle (2014) discovered that biomass devolatilization takes place at 200-540°C, and pyrolysis volatiles constituted H_2, CO_2, CO, and CH_4.

2.5.2.2 Thermogravimetric Fourier transform infrared spectroscopy (TG- FTIR)

TG- FTIR technique can detect numerous volatile compounds in the gaseous mixture of the pyrolysis products and offers real-time and non-destructive measurements. The FTIR spectrometer can in-situ detect the functional groups of the pyrolysis volatiles that evolve from the TG. A research study by Gao et al. (2013) employed this technique to assess the pyrolysis characteristics of pine sawdust. They discovered that the second stage of the pyrolysis process produced most of the pyrolysis volatiles and CO, CO_2, CH_4, H_2O, phenolic compounds, and paraffin gas were detected as the main constituents. Chen et al. (2015) observed similar results in the pyrolysis of bamboo over a temperature range of 300-700 °C. The results of their study have shown at elevated temperatures, pyrolysis vapour yields increased and biochar yields decreased. According to their study, the gaseous products (CH_4, CO, H_2O, alkane, and aldehydes compounds) were liberated at 240-400 °C. CH_4 was formed as a result of the high binding energy of methylene groups and the weakly bound methoxy groups ($-OCH_3-$). The production of CO resulted from the breakdown of ether groups, which were generated from ether compounds found in pyrolysis vapours and/or lignin. H_2O was primarily liberated at temperatures between 100 and 500 °C mostly from the crystallization of water and moisture bound in the biomass. H_2O is also produced at temperatures exceeding 500°C due to secondary reactions of oxygen functional groups created during pyrolysis process. The amount of CO_2 released grew as the temperature increased and peaked at 360 °C. It subsequently reduced between 360 and 400 °C and then spiked again when the temperature was raised to 700 °C. The primary reaction in the pyrolysis process, known as solid-phase polymerization, occurs as the temperature rises and releases low amounts of CO_2.

2.5.2.3 Thermogravimetric Fourier transform infrared mass spectroscopy (TG- FTIR-MS)

Even though TG- FTIR is a useful tool for analyzing the pyrolysis behaviours and the evolution of pyrolysis vapours from biomass, there is frequently overlap between the spectrum bands of several groups. As a result, it was challenging to reliably determine complicated molecular structures that are present in the pyrolysis vapours. The MS technique is used as an efficient supplement for TG- FTIR to solve this limitation, and it has become more widely used in the pyrolysis of biomass feedstocks (Figure 2.3) (Wang et al., 2019). The fundamental mechanisms of the pyrolysis of sewage sludge were first studied by Tian et al. (2014) using the TG- FTIR-MS online approach, particularly the migration and modification of N-containing constituents. The TG results revealed that there were primarily two processes involved in the degradation of sludge. The initial weight loss (15 wt.%), which took place between 150–350 °C, was attributable to the breakdown of biodegradable materials. The subsequent weight loss (25 wt.%) was caused by the breakdown of dead bacterial biomass between 350 and 550 °C. By using TG- FTIR-MS, it was possible to pinpoint the precursors of NO_x and N_2O, N-containing substances, and short-chain hydrocarbons that were produced during the pyrolysis of sludge. The mechanisms of nitrogen migrations and alterations in the biomass feedstock during the pyrolysis process can be established based on the TG- FTIR-MS study of the intermediates. Qian et al. (2014) also employed the TG- FTIR-MS technique to investigate the production of P-containing substances during the co-pyrolysis of biomass and plastic. Results showed that butyl propionate, 2-butoxyethanol, and 1, 2-dibutoxyethaneare were the primary chemicals produced at temperatures between 220 and 390 °C, which were caused by the cleavage of the side chain of Tris(2-Butoxyethyl) Phosphate. P-containing substances, such as dimethyl hydrogen phosphate and diethyl hydrogen phosphate, were found to exist between 370 and 620 °C. These substances could be a result of breaking down of Tris(2-Butoxyethyl) Phosphate that has vaporized at low temperatures. Recent research by Nan et al. (2019) used TG- FTIR-MS to examine how the minerals in cow dung interacted with biomass carbon and pyrolysis. Small molecules (such acetic acid and butane) as well as middle- and large-molecular compounds (such as furfural, furan, and pyrazole, D-glucopyranoside, cortisol and cholestane) made up the majority of the gaseous by-products of the pyrolysis of cow manure. According to the findings, less oxygen containing material was liberated from the original cow manure than from the demineralized cow manure. According to this finding, the pyrolysis process was affected by minerals, which led to a greater release of aromatized compounds.

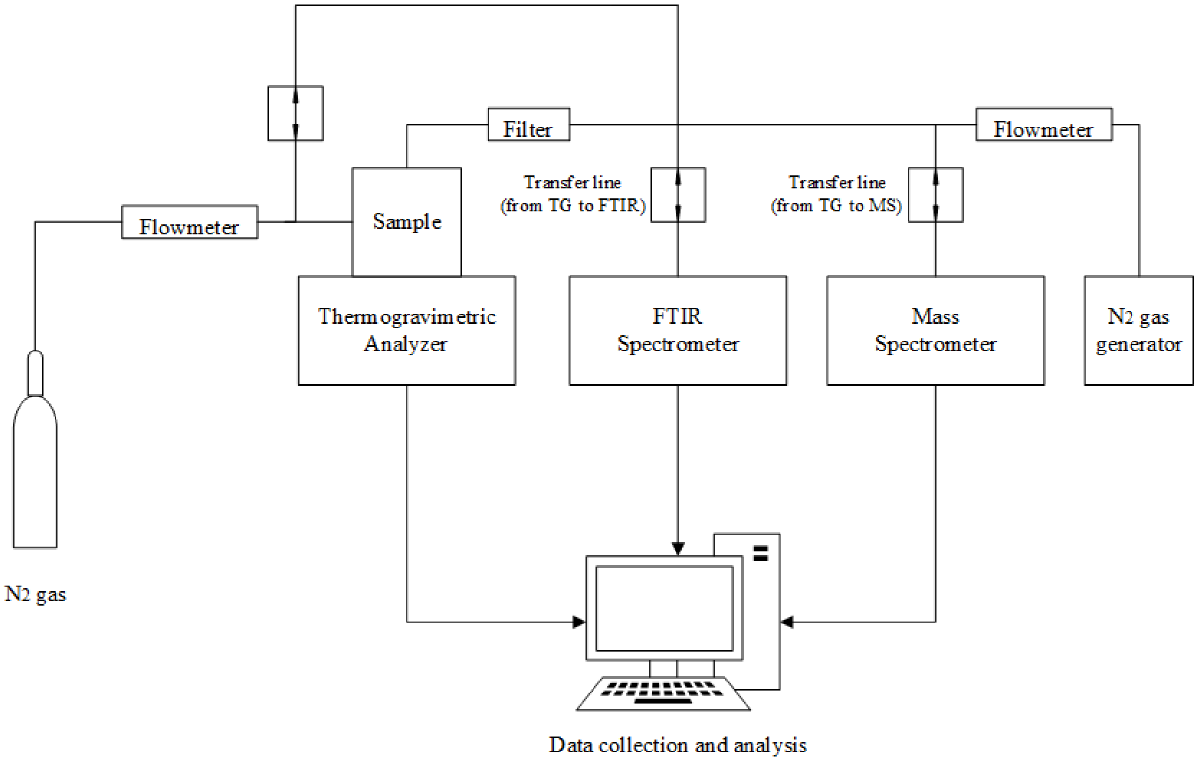


Figure 2.3: Illustration of the principle of the TG- FTIR-MS (Xu et al., 2017)

2.5.3 Photoionization Mass Spectrometry (PI-MS)

The molecules of analytes can only be detected at the ionized level by mass spectra, not at a molecular scale. The "hard" ionization approach known as electron impact ionization is the most frequently utilized in mass spectra. It may be challenging to interpret the mass spectra because the ionization fragments from the collision of electrons may overlap. “Soft” ionization methods, such as chemical, electrospray, photon ionization (PI), and matrix-assisted laser desorption/ionizations (Lunsford et al., 2011), can produce fragment-free ions, which can avoid misleading the mass spectra. The advancement of optical technology, particularly the vacuum UV (VUV) light sources, has caused the PI, one of those ionization techniques, to gain more attention (Hanley & Zimmermann, 2009). The synchrotron VUV PI-MS technique was first employed by Weng et al. (2013) to examine the pyrolysis behaviour of poplar biomass. When compared to mass spectra obtained using the electron ionization method, the recorded mass spectra displayed less fragmentation and greater sensitivity. Coniferyl, p-coumaryl, and sinapyl alcohol made up the majority of the pyrolysis products produced by poplar, and with higher temperatures, all of these compounds' spectrum intensities decreased. Zhou et al. (2019) recently integrated the TG with PI-MS to explore the co-pyrolysis behaviour of kraft lignin and lignite and the synergistic influence on the yield and quality of gaseous products. According to PI-MS findings, the synergetic impact can promote the production of aromatics like phenol, cresol, and syringol. At low temperatures, the guaiacol product yield was increased; while, at high temperatures, it was inhibited. The PI-MS can identify solitary radicals in addition to stable products during pyrolysis, which is useful for understanding the theory behind biomass pyrolysis. Jarvis et al. (2011) pyrolyzed $C_6H_5C_2H_4OC_6H_5$, a model compound in lignin, and examined the radicals that were produced. The existence of the radicals of cyclopentadienyl, phenoxy, phenyl, and benzyl demonstrated the homolysis of $C_6H_5C_2H_4$-OC_6H_5 and $C_6H_5CH_2$-$CH_2OC_6H_5$. As a result, PI-MS generated consolidated data for developing the biomass pyrolysis mechanism.

2.5.4 In-situ solid characterization

X-ray diffraction (XRD) and FTIR are the in-situ technologies that are most frequently utilized to characterize solid products of pyrolysis. Zickler et al. (2007) used synchrotron radiation to conduct in-situ XRD research to examine the kinetics of thermal degradation of crystalline cellulose. They discovered that when the temperature was raised, the Scherrer size in the equatorial 0 0 2 direction dropped. The outcomes showed that the fibril diameter reduction and breaking during the thermal treatment procedure are the key contributors to the thermal degradation of crystalline cellulose. However, because the wood cellulose barely deteriorated below 300 °C and the reaction kinetics moved too quickly to allow for in-situ measurements beyond 360 °C, the temperature in the study was solely restricted to the range between 300-360 °C. In-situ FTIR was utilized by Uchimiya et al. (2013) to examine how biochar's surface functionality changed over time as it underwent pyrolysis. The pyrolysis parameters included a heating rate of 10 °C per minute, a pyrolysis temperature of 500 °C, and an hour of residence time. According to the findings, the majority of the spectral transition took place prior to the temperature peak. The most noticeable modifications were between 325 and 500 °C, and once 500 °C had been achieved for 20 minutes, no more changes were seen. Aliphatic functional groups' O–H and C–H stretching bands diminished over time and vanished after 70 minutes. When the temperature was increased to 500 °C, the carboxyl vibrational band was visible. It reached its peak strength after the temperature was held at 500 °C for 15 minutes, and then it vanished after 40 minutes. We can achieve the desired characteristics of biochar and improve the understanding of biomass pyrolysis by analyzing the biochar in-situ during the pyrolysis process.

2.6 Parameters influencing biomass pyrolysis

2.6.1 Biomass type

Lignocellulosic biomass is composed of cellulose (25–50 wt.%), hemicellulose (15–40 wt.%), lignin (10–40 wt.%), extractives (0–15 wt.%), and generally a small fraction of inorganic mineral matter (Stefanidis et al., 2014). The process of pyrolysis and the products produced depend on the kind of biomass in several different ways. First, depending on the kind of biomass feedstock used, the climate where it originated, and the time of harvesting, different organic and inorganic components relative mass ratios exist. Each constituent's pyrolysis has its specific reaction routes, and thermochemical properties, and results in a variety of products (Stefanidis et al., 2014). The output of bio-oil is enhanced by the presence of cellulose and hemicelluloses, whereas lignin produces a higher percentage of solid char (Akhtar & Saidina Amin, 2012). The molecular mass and viscosity of the bio-oils may increase with higher lignin content, while their water content may drop. The non-structural components of lignocellulosic biomass known as extractives, including saturated fats, simple sugars, waxes, and sterols, can be extracted using solvents such as water, ethanol, acetone, benzene, and toluene (Fahmi et al., 2008). Wang et al. (2011) found that the extractives may boost the bio-oil yield and decrease the production of char and gas when utilizing maize stalks and wheat straw during the pyrolysis process.

Additionally, the bio-oils from the enhanced extracted samples exhibited more oxygen and fewer alkane contents than the initial samples. In a different investigation, it was established that the extractives reduced the activation energy and yields of CO_2, CO, and aldehydes while increasing acid formation during the pyrolysis of pine Guo et al. (2010). The structural arrangement of the components varies from biomass to biomass, changing the interactions between components as a result. The effectiveness of pyrolysis is significantly changed by this. Additionally, due to its catalytic action during biomass pyrolysis, the mineral matter composition in the various biomass types might potentially be variables that affect the distribution and characteristics of products (Fahmi et al., 2008).

2.6.2 Biomass pretreatment

It is usually essential to pre-treat the biomass feedstock before pyrolysis. To improve pyrolysis efficiency, the lignocellulosic structure of the biomass is altered or even destroyed during the pretreatment. There are five main categories in which biomass pretreatment technologies can be categorized: 1) physical (such as milling/grinding and extrusion); 2) thermal (such as torrefaction, steam explosion/liquid hot water pretreatment, and ultrasound/microwave irradiation); 3) chemical (such as treatment with acids, bases, and ionic liquids); 4) biological (such as fungal, microbial consortium, and enzymatic); and 5) above combined pre-treatments (Zheng et al., 2014).

2.6.2.1 Physical pretreatment

The process of milling or grinding biomass feedstock into tiny particles can simplify the biomass input into reactors and improve pyrolysis performance. Because biomass is often a poor heat conductor, the biomass pyrolysis process will be influenced by the temperature differential across the particle (Shuping et al., 2010). Smaller particles often facilitate heat and mass transfer to create constant temperature within particles during pyrolysis, which increases the production of bio-oil by limiting char formation and secondary vapour cracking. This boosts the production of bio-oil by reducing biochar formation and subsequent vapour cracking. However, particle size reduction can be quite costly and significantly increase the overall cost of the process.

Biomass is extruded at greater pressures to create biomass pellets, which often resemble compact cylinders and have a higher volumetric energy density while having a lower moisture content (Erlich et al., 2006). Bigger particle sizes improved biochar and syngas output as well as biochar density (Xue et al. 2013), but they lowered bio-oil output. Erlich et al. (2006) also documented instances of similar circumstances.

2.6.2.2 Thermal pretreatment

Prior to pyrolysis, biomass is dried, which improves the process' energy efficiency and raises the quality of the bio-oil output. According to Isaksson et al. (2013), several industrial dryers may be used to dry biomass. These dryers are created to recycle the fugitive heat emitted during the heated pyrolysis process and extract the moisture in the biomass. The water content of the biomass is eliminated and the oxygen content is slightly decreased when the thermal pretreatment is carried out at temperatures between 200 and 300 °C, a procedure known as torrefaction (Uslu et al., 2008). Torrefied biomass provides several advantages versus untreated biomass. It has a greater energy density, better grindability, reduced hygroscopicity when kept outdoors, reduces the chance of biological deterioration and self-ignition, and enhances reactor feeding (Kasparbauer, 2009). Some disintegration reactions start to occur during torrefaction, producing CO_2, CO, acetic acid, and levoglucosan (Boateng & Mullen, 2013). According to Boateng and Mullen (2013), torrefied biomass generates bio-oils with lower acidity and better energy density as compared to untreated biomass. Other studies validated the results, which showed a higher quality and lesser output of bio-oils from the pyrolysis of torrefied biomass (Zheng et al., 2013). It was discovered that torrefaction increases the H_2 and CH_4 concentrations of generated syngas while decreasing their CO_2 level (Ren et al., 2013).

To "break up" the biomass structure, steam explosion (SE) involves exposing biomass to saturated steam for a brief period at a pressure of 1.5 to 5 MPa and a temperature of 150 to 260 °C in a sealed vessel (Chen & Liu, 2015). SE changes the physical characteristics of lignocellulose and breaks down carbohydrate connections, altering the behaviour of biomass pyrolysis and the qualities of the final product. By using thermogravimetric analysis at 10 °C/min to evaluate the pyrolysis of willow chips following SE pretreatment at 205 °C, Biswas et al. (2011) found that the cellulose crystallinity was higher than in the untreated material. Hemicellulose breakdown became more active and migrated to a lower temperature region during this process, although cellulose and lignin experienced an increase in thermal stability. Loblolly pine chips were pre-treated by SE (1.3 MPa and 173–193°C) (Wang et al., 2011). The raw materials and the pre-treated components were subsequently pyrolyzed separately in a customized auger reactor. The findings revealed that the chips after SE pretreatment had greater cellulose and lignin contents and reduced hemicellulose contents when compared to the untreated feedstock. A bio-oil with a variation of viscosities (from 6.5-3.9 cSt at 40 °C), acid values (from 90.1-64.2), and water contents (from 20.8-29.3 %) was also obtained by the SE pretreatment. Similar to this, hot liquid water is occasionally used to partly dissolve the hemicellulose in biomass feedstock, which helps to lower the amount of acetic acid present and stabilize bio-oils (Carpenter et al., 2014).

For the pretreatment of biomass, unconventional thermal methods including ultrasound and microwave irradiation are used. The primary purpose of ultrasonography is to increase the generation of biogas, primarily methane, from the anaerobic digestion of sludge (Bundhoo et al., 2013). Furthermore, there have been several studies conducted on lignocellulosic biomass. Yachmenev et al. (2009) used ultrasonic treatment to effectively speed up the enzymatic hydrolysis of cellulose in maize stover and sugarcane bagasse to produce sugars because the cavitation effects might improve the mobility of enzyme molecules and the opening up of the substrate's surface. To extract hemicellulose from wheat straw, Sun and Tomkinson (2002) utilized a KOH solution and ultrasonic irradiation. They discovered that the ultrasound assistance generated hemicellulose with more linearity and less acidity than those obtained from traditional KOH extraction. The impact of ultrasonic pretreatment on biomass pyrolysis has to be studied further. Nowadays, lignocellulosic biomass is frequently heated via microwave irradiation, which can cause "hotspots" in the biomass (Bundhoo et al., 2013; Hoseinzadeh Hesas et al., 2013). Although biomass pyrolysis with microwave assistance has received much research (Motasemi & Afzal, 2013), research on the pretreatment of biomass with microwave radiation is lacking (Wang et al., 2008). Due to the inhibition of secondary reactions during pyrolysis following biomass drying in a microwave oven, microwave drying at 600W and six min were proposed to increase the bio-oil and char yields with a performance exhibiting better yields than traditional electric oven drying (Wang et al., 2008).

2.6.2.3 Chemical pretreatment

The process of biomass pyrolysis is thought to be affected by the presence of inorganic minerals, particularly alkaline-earth (Mg, Ca, etc.) metal salts and alkali (K, Na, etc.). For instance, during the first pyrolysis of cellulose, potassium in the biomass mineral matter catalytically promotes the synthesis of lower molecular weight molecules and inhibits the creation of levoglucosan (Eom et al., 2012). As catalysts, the cations cause the biomass monomers to fragment rather than depolymerize, which favours char production and reduces bio-oil yields (Collard et al., 2012). The build-up of salts on the inside walls of the reactor and pipeline also leads to corrosion and engineering challenges (Deng et al., 2013). Ash in bio-oils influences their later uses and speeds up the ageing process, in addition to other effects.

The aforementioned flaws can be eliminated by decreasing the ash concentration with water or acid cleaning. Water washing is used to wash away dirt and minerals from the surface of the biomass particles during harvesting, transportation, and storage. However, the structural minerals will still be present in the biomass matrix. Acid washing using HNO_3 and HF can further lower the ash concentration (Carrier et al., 2012). Blasi et al. (2000) investigated how water washing affected the pyrolysis properties of straw and discovered that while char production is lowered, bio-oil yields are increased. To increase the generation of levoglucosan and levoglucosenone in the bio-oils, phosphoric acid was used to pre-treat the cellulose feedstock. In certain instances, concentrated acids (such as H_2SO_4) were used to hydrolyze and solubilize carbohydrates in biomass to extract lignin (Carrier et al., 2011), while alkaline solutions (such as NaOH) were used to eliminate lignin, hemicellulose, and/or cellulose (Zheng et al., 2014).

Ionic liquids are a class of recently discovered chemicals that, at temperatures below 100 °C, may assume the form of or transform into liquids. They mostly consist of organic cations and inorganic/organic anions (Hallett & Welton, 2011). They are seen as environmentally friendly solvents because of their distinctive physical and chemical properties, which include low vapour pressure, high chemical stability, and non-flammability. Ionic liquids are used in several industrial processes, including catalysis, chemical synthesis, and the production of engineering fluids. They are also used in the breakdown and dissolving of cellulose, hemicellulose, and lignin (Brandt et al., 2013). Ionic liquids have been used to pre-treat lignocellulosic biomass for the production of sugars from enhanced enzymatic hydrolysis of oil palm fronds (Tan & Lee, 2012), renewable chemicals of vanillin, syringyl and allyl guaiacol from eucalyptus, switchgrass and pine respectively (Varanasi et al., 2013), levulinic acid from cellulose (Muranaka et al., 2014), and biogas from improved anaerobic digestion of water hyacinth, rice straw, mango leaves and spruce (Gao et al., 2013). Following their pretreatment with ionic liquids, biomass materials' thermal behaviour can also be altered. Zhang et al. (2014) discovered that the Avicel and switchgrass samples had greater heat resistance following the pretreatment with 1-butyl-3-methylimidazoliumacetate as a result of the cellulose's alteration in crystal structure and the removal of minerals, respectively.

2.6.2.4 Biological pretreatment

When compared to physical and chemical pretreatment techniques, biological techniques are slower but use less energy and have a better impact on the environment (Yu et al., 2013). It has been demonstrated that pyrolysis performance is enhanced by fungal pretreatment of lignocellulose. White-rot fungus has been selected to pre-treat the natural lignocellulose as it could selectively decompose the refractory lignin component during pyrolysis (Nigam & Singh, 2011). Yang et al. (2010) bio-pre-treated maize stover with three different white-rot fungus species (Pleurotus ostreatus BP2, Echinodontium taxodii 2538, and Irpex lacteus CD2) before studying the corn stover's thermal properties as it was being pyrolyzed in a TGA instrument. As a result of reducing the sulphur content of the feedstock by 30–45%, the results indicated that this bio-pretreatment may successfully lower the pyrolysis temperature by 1–35 °C and reduce the emission of harmful SO_x. Yu et al. (2013) explored the rapid pyrolysis of maize stover pre-treated by I. lacteus CD2 white-rot fungus in the presence of Zeolite Socony Mobil-5 (ZSM-5) and found that yields of important aromatics products were improved by 10% and coke deposition on catalysts was reduced by 20%.

Pre-treating lignocellulosic biomass with a microbial consortium has often been employed to increase the production of biogas. It uses specific bacteria drawn from the environment that primarily break down the cellulose and hemicellulose components (Zheng et al., 2014). The procedure can raise the methane output by 25% to almost 100% and lasts up to many days (Zheng et al., 2014). It has been suggested that using enzymes to hydrolyze lignin before it is pyrolyzed will increase the number of aromatic phenols and hydrocarbons that are produced (Lou & Wu, 2011). The chars that were created also seem to have vesicles and to be quite porous.

2.6.3 Effects of reaction conditions

2.6.3.1 Reaction atmosphere

Usually, N_2 gas is used to provide an inert environment needed for biomass pyrolysis. To change the pyrolysis process conditions, other gases might be utilized. For instance, steam can partially gasify the biomass and slightly oxidize it. The steam is employed as the carrier gas and may also participate in the processes in a recently developed pyrolysis procedure known as steam pyrolysis. For biomass pyrolysis, steam has several benefits. Primarily, it can upgrade the yield of organic oxygenated products by preventing to some extent the secondary cracking reactions in the gas phase (Pütün et al., 2008). The effects of N_2, CO_2, CO, CH_4, and H_2 atmospheres on biomass pyrolysis in a fluidized bed reactor were examined by (Zhang et al., 2011). The highest bio-oil yields were discovered to be in the CH_4 environment (58.7%), whereas the lowest yields were in the CO atmosphere (49.6%). When CO and CO_2 were used as the sweeping gases, it resulted in the detection of bigger monofunctional phenols and lower methoxy-containing compounds in the bio-oils. When compared to other atmospheres, the HHV of bio-oils under H_2 could reach a maximum of 24.4MJ/kg, and more oxygen in biomass was transformed into H_2O. The char obtained in the CO_2-containing atmosphere had increased surface area and different chemical atmosphere.

2.6.3.2 Temperature

Pyrolysis temperature significantly influences the distribution and properties of products. The bio-oil yields typically reach their peak concentrations between 400 and 550°C and then start to fall as the heating process continues. At temperatures higher than 600°C, the bio-oils and char products are converted into gas due to the dominant secondary cracking reactions (Li et al., 2007). The polar, aliphatic and aromatic fractions in the bio-oils enhance with increased temperatures from 300–500 °C to 600–800 °C (Ateş & Işıkdağ, 2008). Generally, temperatures exceeding 700 °C increase the carbon content of the bio-oils in the form of polycyclic aromatic hydrocarbons (PAHs), such as aspyrene and phenanthrene, due to the decarboxylation and dehydration reactions (Akhtar & Saidina Amin, 2012). Uddin et al. (2014) have studied how the pyrolysis temperature affects the yields and composition of gases (CO, CO_2, CH_4, H_2, etc). Previous research has also looked at the physicochemical properties of biochar produced by biomass rapid pyrolysis at various temperatures, including its surface area, electrical conductivity, the concentration of inorganic components, carbon content, aromatic structure, and HHV (Burhenne et al., 2013; Park & Jang, 2012).

2.6.3.3 Heating rate

The primary factor that distinguishes between flash, fast, and slow pyrolysis of biomass is the heating rate. Fast heating rates encourage the biomass to break down rapidly, producing more gases and less char in the process. Fast heating rates also increase bio-oil production because mass and heat transfer constraints are reduced and secondary reactions have less time to complete (Akhtar & Saidina Amin, 2012). Prior research has revealed how heating rate affects product yields and attributes (Niu et al., 2013; Trinh et al., 2013). Salehi et al. (2009) found that increasing the heating rate from 500°C/min to 700 °C/min results in increased bio-oil yields from wood shavings by 8%. However, when the heating rate was increased further from 700 to 1000 °C/min, no discernible change in the bio-oil yields was found because mass and heat transfer constraints had been overcome. Similar to this, pyrolysis of cotton seed cake showed a rapid increase in liquid yield when heating rate was increased from 5 °C/min (26 wt.%) to 300 °C/min (35wt.%), but there was no discernible change in liquid yield when heating rate was increased further from 300 °C/min to 700 °C/min (Ozbay et al., 2006).

2.6.3.4 Vapour residence time

Shorter residence times favour the synthesis of bio-oil because organic vapours are removed from reactors quickly and reduce secondary reactions. Scott et al. (1999) found that for the pyrolysis of raw sorghum bagasse at 525 °C, changing the residence time from 0.2 to 0.9s led to a drop-in the bio-oil yields from 75% to 57% and an increase in the char and gas yields. Similarly, by extending the vapour residence time from 0.7s to 1.7s during the pyrolysis of sweetgum hardwood at 700 °C, the bio-oil output decreased from 22 wt.% to 15 wt.%.

Although the impact of vapour residence time on product distribution has been extensively investigated, further research is necessary to understand the impact of the relationship between vapour residence time and pyrolysis temperature on product yields as well as product quality (Uddin et al., 2014).

2.7 Co-pyrolysis of biomass

As an effective alternative method to improve the quality of pyrolysis products, the co-pyrolysis of biomass has attracted more and more interest (Alvarez et al., 2019). In contrast to the conventional biomass fast pyrolysis, co-pyrolysis concurrently adds various raw materials as fuel, such as plastics, coal, sludge, etc. (Ismail et al., 2020). The recent research on the co-pyrolysis of biomass with various raw materials is discussed in sections to follow.

The unique feature of co-pyrolysis is that the synergistic effect among the chemical reactions between different feedstocks plays an important role in co-pyrolysis (Hassan et al., 2020). Nevertheless, the synergistic effect varies dramatically with the added raw materials of co-pyrolysis.

2.7.1 Co-pyrolysis behaviour of biomass with coal

Because of its advantages like high energy density and low price, coal is a good material for biomass co-pyrolysis. Zhu et al., (2020) analyzed the composition of liquid bio-oil from the fast co-pyrolysis of cedar sawdust with low-rank coal. Their results showed that there were more generations of single-ring and two-ring aromatic compounds and less formation of three-ring and four-ring aromatic compounds. They ascribed this to the hydrogen supply by the pyrolysis of cedar sawdust, thereby restraining the secondary polymerization of volatile in fast co-pyrolysis. Alkali and alkaline-earth metals in biomass have an impact on the co-pyrolysis process in addition to their function as hydrogen donors. Li et al. (2019) studied the co-pyrolysis of Xilinhot lignite and rice husk, and they revealed that the secondary cracking of volatiles from both feedstocks was promoted by alkali and alkaline-earth metals in biomass.

However, the interactions of biomass and coal, especially the synergistic effect, still need to be explored. Ferrara et al. (2014) evaluated the co-pyrolysis process of the mixtures of biomass and coal and argued that the synergistic effect was negligible, which was consistent with the study of Montiano et al. (2016). In contrast, the synergistic effect was captured and emphasized in many other studies (Zhao et al., 2020; Zhu et al., 2020). Zhao et al. (2020) carried out a thermogravimetric analysis of cellulose and lignite blends, where a strong synergistic effect between the feedstocks was observed between 300 and 400 °C and the decomposition of lignite was accelerated by the increasing content of cellulose during co-pyrolysis. Qiu et al. (2019) identified the existence of a synergistic effect, by the apparent activation energy, and the lower frequency factor of the poplar and fat coal blends, compared with the pyrolysis of pure polar compounds. According to Xiye Chen et al. (2019), the occurrence of the interactions, including the positive and the negative (the inhibitory effect) synergistic effects, is dependent on the operating parameters of the co-pyrolysis process of biomass with coal, such as the type of coal feedstock and the blend ratio.

Besides, some previous studies have shown that co-pyrolysis with biomass can reduce or prevent the emission of harmful substances in coal. Guo et al. (2018) studied the co-pyrolysis of biomass with several different low-rank coals with high sulphur contents. They found that, during co-pyrolysis with biomass under a CO_2 atmosphere, large amounts of sulphur elements in coals were transferred to thiophenes contained in the char, rather than along with gas emissions.

2.7.2 Co-pyrolysis behaviour of biomass and plastics

To efficiently extract energy from used plastics, Garcia & Robertson (2017) suggested that the pyrolysis of plastics would be a potential chemical recycling process. In addition, the low oxygen concentration and high carbon and hydrogen content of plastics make co-pyrolysis of waste plastics and biomass potentially valuable for upgrading bio-oil.

Many related studies have focused on the co-pyrolysis behaviour of biomass and plastics wastes, several of which have indicated the significance of the synergistic effect (Chattopadhyay et al., 2016; Hassan et al., 2020). Nguyen et al. (2019) examined the characteristics and yields of bio-oil produced from the co-pyrolysis of waste polystyrene foam and pure pine sawdust. The results revealed that co-pyrolysis of pine sawdust and used polystyrene foam provided a greater yield of bio-oil and enhanced the HHV of the produced bio-oil from 17.81 MJ/kg to 39.65 MJ/kg. Yuan et al. (2018) discovered that when cellulose and high density polyethene (HDPE) was pyrolyzed together, the production of compounds containing oxygen was inhibited while the development of alkane and alkene groups was supported. It has been noted that the synergistic effect may cause the quality of the bio-oil to improve. The interaction between various free radicals generated by the biomass and plastics, respectively, is primarily responsible for the synergistic effect (Chattopadhyay et al., 2016). The pyrolysis behaviours of sugarcane bagasse, HDPE, and their blends in a fixed-bed reactor were examined by Hassan et al. (2020). According to their hypothesis, the generation of co-pyrolysis products was significantly influenced by the hydroxyl radical produced from sugar cane bagasse at various mixed feedstock ratios.

2.7.3 Co-pyrolysis behaviour of biomass and tyres

Similar to waste plastics, waste tyre is another high hydrogen and carbon-containing waste-derived fuel; the major components of waste tyres are rubber compounds including natural or synthetic rubber, and carbon blacks, making it practical to utilize waste tyres in pyrolysis (Czajczyńska et al., 2017). Waste tyres can be introduced into biomass co-pyrolysis as raw materials to enhance the quality and yield of bio-oil. Slightly different from waste plastics, the components in waste tyres are relatively complex, which might result in some differences in the co-pyrolysis bio-oil.

Positive effects on the quality of final products have been shown by introducing waste tyres into co-pyrolysis with biomass. According to Ahmed et al. (2018), when sugarcane bagasse and tyres were co-pyrolyzed, the bio-oil yields increased as the ratio of tyres increased. Furthermore, the HHV of bio-oil produced by co-pyrolysis of sugarcane bagasse and tyres could reach as high as 41 MJ/kg. In the co-pyrolysis of biomass with waste tyres, Wang et al. (2018) demonstrated that the production of PAHs was reduced while the formation of olefin components was increased. Alvarez et al. (2019) assert that the co-pyrolysis bio-oil includes less moisture and oxygen than the bio-oil produced by the pyrolysis of pure pinewood sawdust due to the synergistic effect of pinewood sawdust and waste tyres. Shah et al. (2019) reported that, at the optimal blend ratio (3:2), the yield of liquid products from the co-pyrolysis of cotton stalk and waste tyres could increase by 10%, compared with that from cotton stalk pyrolysis. Additionally, the outcomes demonstrated that the synergetic effect during co-pyrolysis led to the formation of additional alkanes, demonstrating that the bio-oil from co-pyrolysis was more suitable for use in vehicles (Shah et al., 2019). Besides, additives in tyres have a certain influence on the properties of the co-pyrolysis products. Shah et al. (2019) also observed that the co-pyrolysis bio-oil had a relatively high sulphur content, leading to the requirement for desulfurization of such bio-oil.

2.7.4 Co-pyrolysis behaviour of biomass and sludge

The sludge used as raw material for biomass co-pyrolysis mainly includes sewage sludge and oily sludge. The former is mainly generated as the by-products of numerous municipal sewage plants, while the latter is a form of a complex waste emulsion that accumulates during particular stages of the petroleum industry (Hu et al., 2017; Lin et al., 2017). These two different types of sludge both contain several various organic chemicals that are acceptable as raw materials for co-pyrolysis, while they also contained some harmful compositions, such as heavy metals, etc (Hu et al., 2017; Huang et al., 2017). Various researchers examined the properties of the co-pyrolysis products made from biomass and sewage sludge. Wang et al. (2016) discovered that when sewage sludge and wheat straw were co-pyrolyzed, the reaction rate increased, producing more bio-oil and less biochar. Lin et al. (2017) proposed that the compounds that have more than seven C atoms yielded more in the co-pyrolysis bio-oil of bagasse and sewage sludge. Chen et al. (2020) reported that the yields of hydrocarbons and phenols were enhanced, while the yields of acids and nitrogenous chemicals production decreased in the co-pyrolysis of sewage sludge and coffee grounds. These researchers found that the synergetic effect significantly affected the co-pyrolysis of biomass and sewage sludge, changing the properties of the co-pyrolysis products. According to Xu et al. (2017), interactions changed as temperature ranges varied during the co-pyrolysis of hazelnut shell and sewage sludge. Particularly, at lower temperatures (260–400 °C), the interactions were reduced, whereas at higher temperatures (450–900 °C), they were accelerated. The characteristics of biochar products for uses like soil amendments have been a major focus of other research on the co-pyrolysis of sewage sludge and biomass (Wang et al., 2019; Xu et al., 2017; Yin et al., 2019). Wang et al. (2019) found the biochar from biomass co-pyrolysis with sewage sludge to be more profitable, featuring a larger specific surface area, better pore size distribution, and lower risk of heavy metals. Yin et al. (2019) studied the adsorption capacity of biochar from sewage sludge and walnut shell co-pyrolysis and found that the adsorption of NH_4^+ was improved by the mixture of feedstocks. Compared with sewage sludge, studies on biomass co-pyrolysis with oily sludge are relatively limited. However, because of its high concentration of various petroleum hydrocarbons (PHCs), high content of hydrogen and low content of oxygen is found in the oily sludge (Hu et al., 2017); as a result, co-pyrolysis of biomass and oily sludge can increase the yield and quality of the liquid products while also lowering harmful pollution, notably heavy metal contamination. Hu et al. (2017) compared the bio-oils produced from pure sawdust pyrolysis and co-pyrolysis of sawdust with oily sludge, respectively. Higher H/C ratio and higher HHV were found in the bio-oil from co-pyrolysis, which were increased by 0.5 and 5 MJ/kg, respectively. Meanwhile, the bio-oil yield was also increased by 4% due to the synergetic effect. Lin et al. (2018) studied the properties of liquid products from co-pyrolysis of rice husk and oily sludge, and they suggested that more saturates and aromatics were generated while less oxygenated compounds were formed because of the synergetic effect.

2.8 Catalytic co-pyrolysis

A favourable synergy between biomass and plastics is present during catalytic pyrolysis of biomass and plastics, which increases hydrocarbon production while lowering biochar yield (Wan Mahari et al., 2018). Two feedstocks interact with each other during pyrolysis to produce the synergistic effect. Yuan et al. (2018) utilized hydrogen transfer to identify the synergetic breakdown between polymer and cellulose. Oxygen compounds derived from cellulose increase the cracking of HDPE, and hydrogen from HDPE can promote the breakdown of cellulose. However, the product distribution during the non-catalytic co-pyrolysis of cellulose and low-density polyethene (LDPE) was comparable to that of individual pyrolysis. This indicates that pyrolysis without a catalyst results in the absence of interaction between two pyrolysis intermediates (Li et al., 2013). As a result, to create mutual contact between two feedstocks, catalysts are required. A higher synergetic effect can be produced by utilizing acid/base catalysts through several processes, some of which are covered in the following sections.

2.8.1 Acid catalysts

Dehydration, decarbonylation, cracking, and aromatization processes are favoured by acid catalysts such as zeolites (Charoenwiangnuea et al., 2016). Strong acid sites in zeolites have a major role in promoting the aromatization process, which produces high-value monocyclic aromatic hydrocarbons including benzene, toluene, ethylbenzene, and xylene, which are among the most significant petrochemicals (Zhang et al., 2016). Due to its distinct microporous structure and relatively high Bronsted acidity, zeolite ZSM-5 is regarded as the best acid catalyst for the synthesis of monocyclic aromatic hydrocarbons (Carlson et al., 2011).

2.8.2 Base catalysts

In the residual ash of biomass, alkali and alkaline-earth metals (AAEMs) including Ca, K, Mg, and Na are typically present. These metals can be deposited on the acid sites of the catalyst easily, which immediately deactivates the acid catalyst (Kalogiannis et al., 2018). On the other hand, catalysts with base sites, as opposed to acid sites, withstand deactivation by AAEMs much better. With acid sites, the base active sites display several reaction pathways, such as carbon coupling (C-C) reactions. Carbon coupling processes transform low molecular weight substances like organic acids, ketones, and aldehydes into gasoline and diesel range products. Base catalysts that produce CO_2 during the ketonization of acids, such as MgO (Fan et al., 2017) and CaO (Chen, Li, et al., 2019), facilitate the deoxygenation of pyrolysis products. With regard to preserving carbon, the deoxygenation pathway is more effective than the acid catalyst pathway since the latter encourages the creation of CO (Aho et al., 2010). Base catalysts also reduce H_2O generation to preserve the hydrogen level in the bio-oil, hence improving the energy and quality of the bio-oil (Aho et al., 2010; Kalogiannis et al., 2018).

However, a key mechanism of base catalyst-assisted catalytic pyrolysis has not yet been explored. A few processes of individual components, biomass, and plastic over base catalysts were studied in earlier investigations. Processes for biomass pyrolysis over base catalyst correspond to the ketonization of acids with simultaneous generation of CO_2 and aldol condensation of aldehydes and smaller ketones (Stefanidis et al., 2016). Alkali metal oxides can deoxygenate bulky oxygenates, linear aldehydes, and carboxylic acids during the catalytic pyrolysis of lignocellulosic biomass. Ketonenization, fragmentation, and aldol condensation processes are used to create light hydrocarbon compounds and oxygenates with low molecular weight when alkali metal oxides deoxygenate a substance (Wang et al., 2019).

2.9 Pyrolysis reactor designs

In the process of pyrolysis, the reactor design and the heating system plays an important role. Several reactors have been developed during the last two decades to accomplish this aim, depending on the heating technique used. Figure 2.4 illustrates the various heating techniques that are employed in pyrolysis reactors.

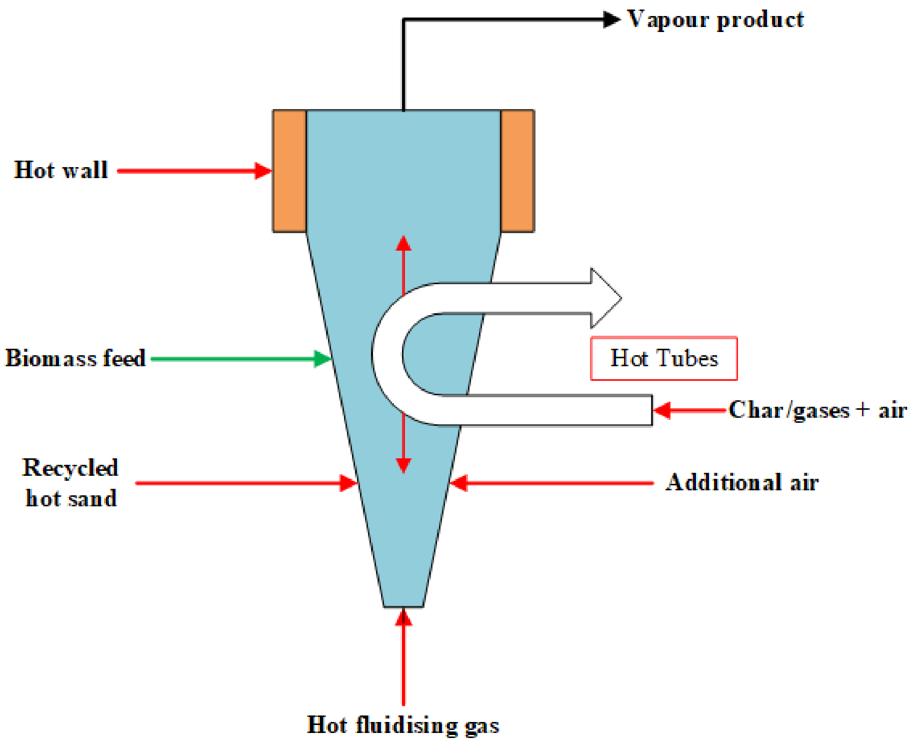


Figure 2.4: Various heating techniques are used in pyrolysis reactors (Bridgwater & Peacocke, 2000)

2.9.1 Bubbling fluidized beds

The performance of bubbling fluidized bed pyrolyzers is associated with a high liquid production from biomass of approximately 70–75 wt.% on a dry basis. For high biomass heating rates, the feedstock particle sizes must be less than 2-3 mm (Bridgwater, 2012). The heating rate of the particles is typically the limiting stage in fluidized bed reactors. The retention time of char and pyrolysis vapours is governed by the flow rate of the fluidizing gas. Char typically has a longer residence duration than vapours. Upon completion of the pyrolysis process, the char that is generated needs to be removed from the bio-oil since it works well as a catalyst for vapour cracking. An ejection and entrainment system is often constructed for this purpose, accompanied by segregation in cyclones (Bridgwater, 2012). Figure 2.5 illustrates a typical schematic of a bubbling fluidized bed reactor.

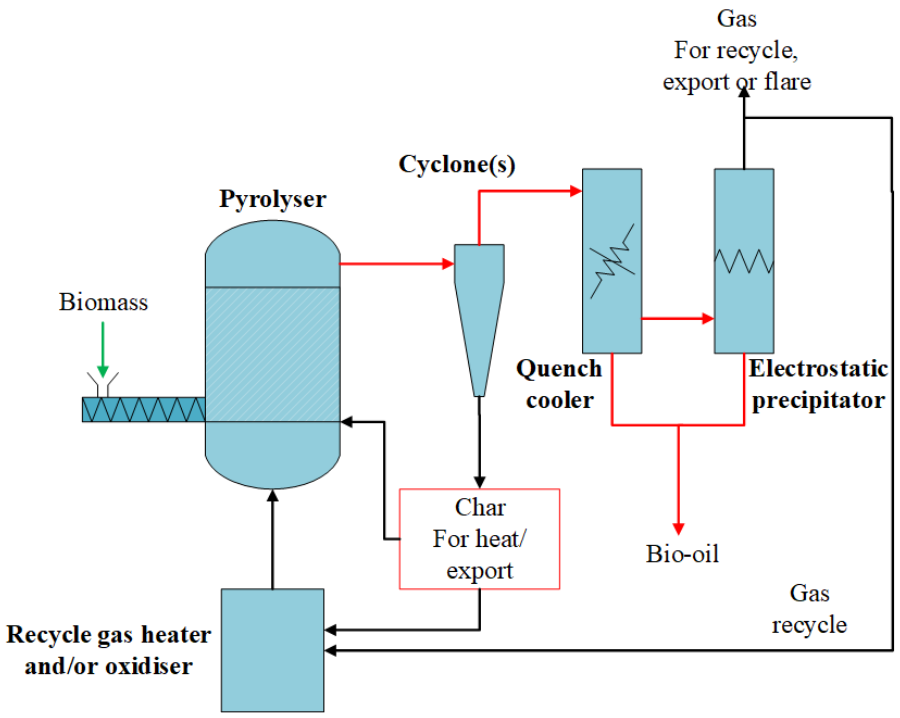


Figure 2.5: A typical schematic of a bubbling fluidized bed reactor (Bridgwater & Peacocke, 2000)

2.9.2 Circulating fluidized beds and transported beds

The operating principle of a circulating fluidized bed (CFB) and transporting bed reactor is similar to that of a bubbling bed reactor, with the exception that the residence period for char is nearly identical to that of vapours and gas. Additionally, the recovered bio-oil may have a larger char content than the fluidized bed reactor due to this. Despite having more complicated hydrodynamics, CFB has the advantage of being suited for very high throughputs. It is commonly employed in the oil and petrochemical industries at extremely high throughputs as a result of this property. The heat is provided by the recirculation of hot sand from a secondary char combustor (Bridgwater, 2012; Hu & Gholizadeh, 2019). Figure 2.6 illustrates a typical schematic of a CFB reactor.

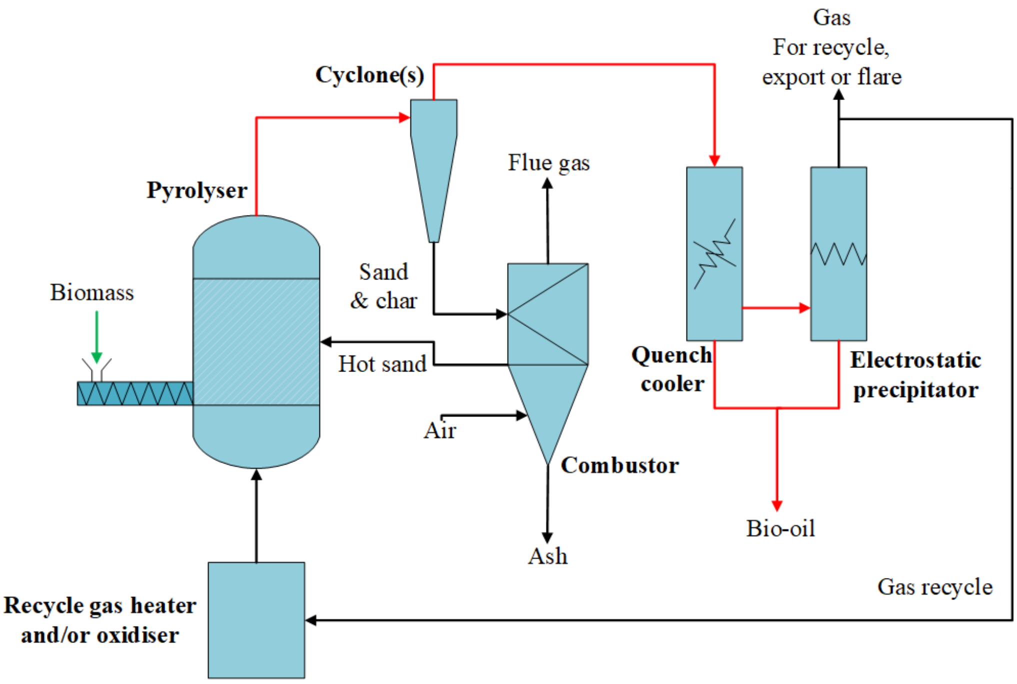


Figure 2.6: A typical schematic of a CFB reactor (Bridgwater & Peacocke, 2000)

2.9.3 Rotating cone

The University of Twente developed a rotating cone reactor for the flash pyrolysis of biomass (Bridgwater, 2012). Since vigorous mixing of hot inert particles and biomass is the most efficient method of transferring heat to the biomass, this method is the foundation of the spinning cone reactor's design. In contrast, the heat transmission of a fluidized bed requires an excessive amount of unproductive inert carrier gas. The development of a rotating cone reactor eliminated the need for inert gases and simplified the design of the reactor's components and supporting machinery, such as the oil condenser and gas cleaning systems. The rotating cone reactor's first design from 1989 relied only on the ablative principle; no inert sand was employed. Later, the rotating cone reactor with a transportable bed of sand was established. Upon completion of the pyrolysis process, the sand and char are then moved to a different fluidized bed where the char is burned (Bridgwater, 2012; Hu & Gholizadeh, 2019). Figure 2.7 shows an illustration of the spinning cone reactor.

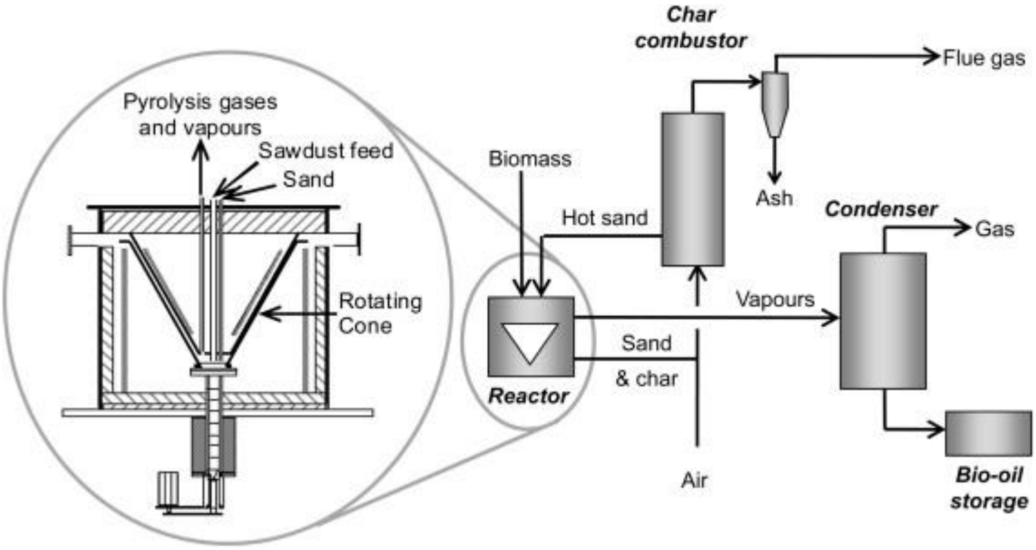


Figure 2.7: An illustration of the spinning cone reactor (Bridgwater, 2012) Copyright 2012, Elsevier

2.9.4 Ablative pyrolysis

With smaller equipment, lower costs, and better controllability, ablative reactors are utilized to produce bio-oil at high yields. When biomass moves across a hot surface, heat is transferred as a result (Figure 2.8). The rate of heat transmission through the biomass particle serves as the reaction's limiting factor in an ablative reactor. Temperature, relative feedstock velocity on the heat transfer surface, and pressure all influence how fast a reaction happens. The main characteristics of pyrolysis inside an ablative reactor are strong particle pressure on a heated reactor wall, relatively high movement between the particle and the reactor wall, and a hot reactor wall temperature. Additionally, inert gas is not necessary (Bridgwater, 2012; X. Hu & Gholizadeh, 2019).

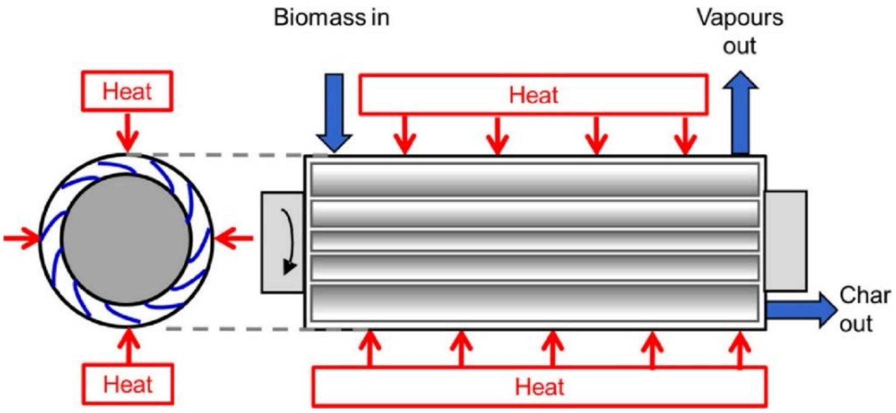


Figure 2.8: A typical schematic of an ablative pyrolysis reactor (Bridgwater & Peacocke, 2000)

2.9.5 Auger reactor

This kind of reactor consists of a hot, tubular, inert tube through which augers feed biomass. Figure 2.9 illustrates an auger reactor design. The feedstock temperature is raised to the pyrolysis temperature by the temperature within the tube. The volatiles are assumed to liquefy in a condenser. Both bio-oil and char outputs for the auger reactor's end products are comparable to those of the fluidized bed reactor (Garcia-Nunez et al., 2017; Yu et al., 2016). Auger reactors can be categorized into four different types: single screw laboratory-scale reactors (1 kg/h), single screw laboratory-scale reactors with a large capacity or pilot-scale (1-15 kg/h), single screw industrial-scale reactors (>15 kg/h), and twin-screw reactors (Hu & Gholizadeh, 2019).

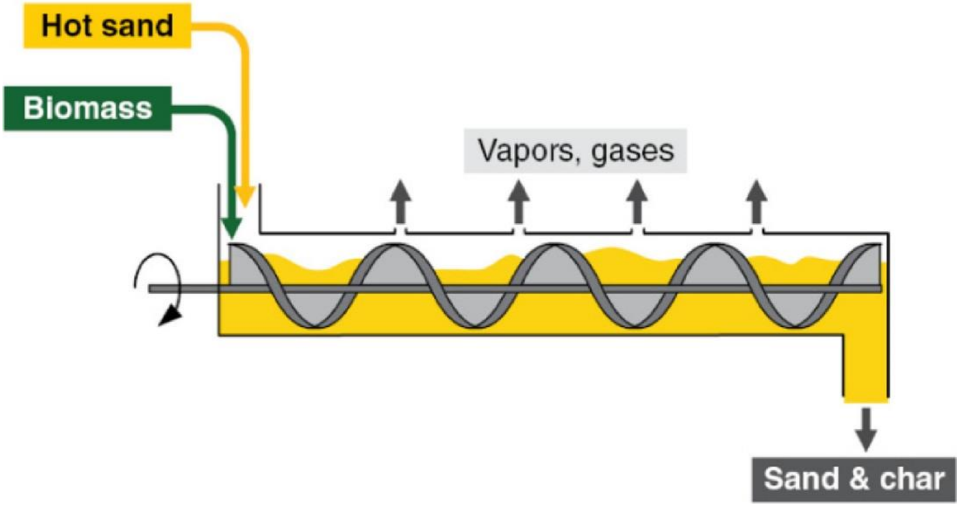


Figure 2.9: An illustration of an auger reactor (Bridgwater & Peacocke, 2000)

2.9.6 Fixed-bed reactor

Fixed-bed reactors are more appropriate in lab-scale investigations because of their simplicity and simpler control mechanism. However, its deployment in large scales requires more research, particularly the homogenous heat energy distribution inside the reactor. Xiong et al. (2018) employed a fixed-bed reactor to pyrolyze rice husk biomass. Their investigation used temperature variations between 300 and 800 °C to track the production of coke. Also modified was the heating rate. According to their findings, the coke produced at low temperatures and a slow heating rate was impervious and had a smooth surface. However, it became porous when the heating rate or pyrolysis temperature was increased. This was due to the fact that greater temperatures or faster heating rates produced more free radicals, which encouraged the condensation process of big molecules, particularly aromatics.

2.10 Recently developed pyrolysis methods

A wide range of biomass pyrolysis-related technologies has recently emerged. Due to their unique benefits over more traditional electrical heating-assisted biomass pyrolysis, microwave- and solar-assisted pyrolysis have received the most attention (Chintala, 2018; Mutsengerere et al., 2019). Hence, they were summarized with particular emphasis on the combination of existing related biomass pyrolysis technologies (such as co-pyrolysis, catalytic pyrolysis, etc.) with these new heating methods.

2.10.1 Microwave-assisted pyrolysis (MAP)

The microwave heating method is the critical technology for biomass MAP systems. Different from the electrical or the combustion heating method of pyrolysis by-products, microwave heating does not use an external temperature field to heat biomass but converts microwave energy into heat energy through the agitation of molecules in the electromagnetic field and the generated heat will diffuse from the inside of the materials to their outside, as shown in Figure 2.10 (Bhattacharya & Basak, 2016).

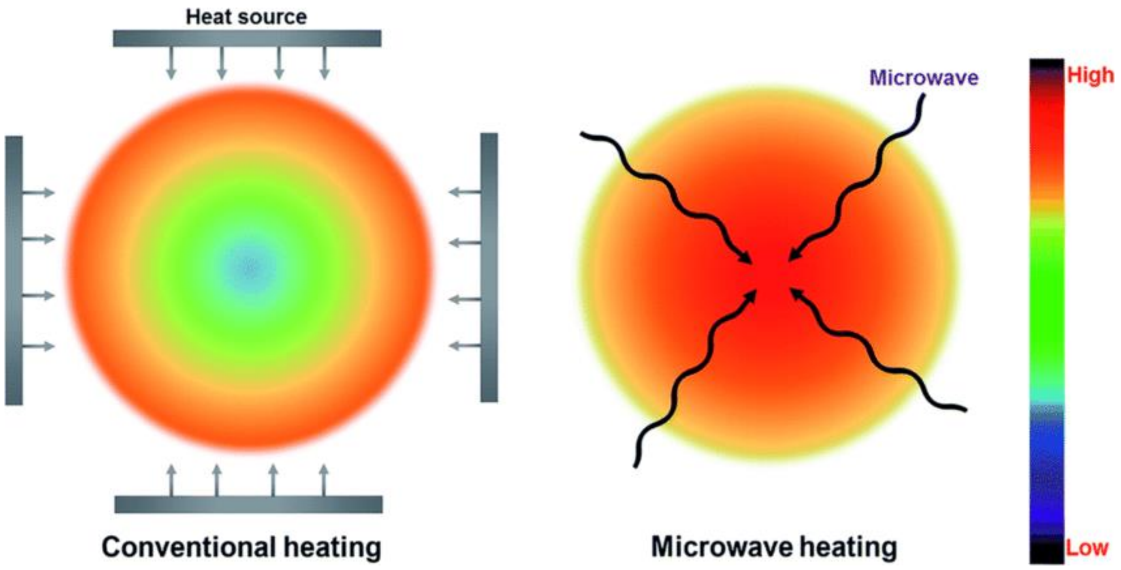


Figure 2.10: Comparison of microwave heating and conventional heating methods (Bhattacharya & Basak, 2016). Copyright 2016, Elsevier

Besides, a very important feature of microwave heating is that the microwave absorption rate of different materials might vary, leading to selective heating (Bu et al., 2016; Gadkari et al., 2017). Biomass can only partially absorb or reflect microwaves; therefore, microwave absorbents such as SiC, activated carbon, graphite, CaO, $CaCO_3$, NiO, Ni_2O_3, TiO, Fe_2O_3 and charcoal are always added to improve the microwave heating efficiency (Zhang et al., 2020).

Because of its special energy conversion mechanism, microwave heating has the following advantages: a high heating rate, uniform heating, instantaneous regulation, low energy dissipation, selective heating, and high energy conversion efficiency (Bu et al., 2016; Mutsengerere et al., 2019; Zhang et al., 2020). Huang et al. (2016) noted that microwave heating was superior to conventional heating, in terms of heating rate, efficiency, and biomass weightlessness.

The MAP of various feedstocks has already been conducted (Abas et al., 2018; Borges et al., 2014; Gautam et al., 2019; Kostas et al., 2020; Parvez et al., 2019; Wang et al., 2016). Gautam et al. (2019) reported that a type of bio-oil with lower oxygen content and more aromatic hydrocarbons content than that from conventional fast pyrolysis was obtained from MAP of macroalgae. Borges et al. (2014) investigated the bio-oil yields obtained from the MAP of wood sawdust and corn stover, respectively. Their results showed that the maximum bio-oil yields of these two raw materials were higher than those from conventional fast pyrolysis. Wang et al. (2016) found that the temperature could affect the content of hydrocarbons in the MAP of soap stock and the optimal temperature for the formation of aromatics was 550°C. However, product quality improvement is not prominent. According to Kostas et al. (2020), olive pomace MAP generated bio-oil with a greater acetic acid concentration. Abas et al. (2018) found a greater amount of water and different organic acids in the bio-oil generated via MAP of oil palm fibre. Although several strategies for commercializing MAP have been put forth, the majority of associated initiatives are now still in the laboratory research stage (Beneroso et al., 2017; Ge et al., 2021). To produce more favourable products, current biomass MAP methods still require optimization and modification. Microwave-assisted co-pyrolysis and catalytic pyrolysis might be a potential approach to upgrade the target products and give full play to the advantages of MAP (An et al., 2017; Mohamed et al., 2019).

A range of co-pyrolysis raw materials, including biomass and lignite, biomass and plastics, biomass and soap stock, etc., have been used in microwave-assisted co-pyrolysis experiments (An et al., 2017; Jiang et al., 2019; Suriapparao et al., 2018). An et al. (2017) found that microwave-assisted co-pyrolysis of biomass and lignite can produce more liquid oil and pyrolytic gas, because of the synergetic effect of biomass and lignite. Suriapparao et al. (2018) revealed that the bio-oil from microwave-assisted co-pyrolysis of numerous types of biomasses with polypropylene and polystyrene had a reduced water content and improved HHV, about 38-42 MJ/kg. Due to internal interactions, various raw materials have varying effects on the product quality of microwave-assisted co-pyrolysis. Li et al. (2019) investigated the composition of the by-products of oil sands and sawdust co-pyrolysis with microwave assistance. Their results showed that the yields of both liquid bio-oil and gas products were changed due to the synergetic effect, and the content of aromatic hydrocarbons in liquid bio-oil was improved, because of the microwave radiation.

Microwave-assisted catalytic pyrolysis not only has the advantages of microwave heating and can also promote the directional conversion of biomass. Wang et al., (2019) noted that the modified HZSM-5 could promote the formation of bio-oil and increase the selectivity of phenols during the microwave-assisted catalytic pyrolysis process of cellulose. According to Zhu et al. (2018), the microwave-assisted catalytic pyrolysis of Douglas fir pellets in the presence of biochar as a catalyst resulted in a hydrocarbon content of bio-oil of 52.77%. However, Mohamed et al. (2019) reported that coke deposition on the catalyst surface might affect the microwave heating rate, which could result in changes in product distribution. The performance of the catalyst and the prevention of coke deposition is still critical in microwave-assisted catalytic pyrolysis.

2.10.2 Solar-assisted pyrolysis

Solar-assisted pyrolysis is a relatively new research direction in the field of biomass pyrolysis. Compared with conventional biomass pyrolysis, solar-assisted pyrolysis directly converts solar energy to the thermal energy required for pyrolysis, achieving the clean utilization of the primary energy. Additionally, a unique method of solar pyrolysis has been developed for the disposal and improvement of biomass polluted with heavy metals (Zeng et al., 2019, 2020). As shown in Figure 2.11, the most notable feature of the solar-assisted pyrolysis system is the solar concentrator (Zeng et al., 2017). Some particular solar concentrators, such as Fresnel lenses and parabolic troughs, are used in solar-assisted pyrolysis systems to gather and concentrate solar energy (Chintala, 2018; Weldekidan, Strezov, & Town, 2018). The biomass pyrolysis process is then aided by the concentrated solar radiation being converted to heat in the pyrolysis reactors. Li et al. (2016) indicated that solar heating could meet the temperature requirements for biomass pyrolysis and have a wide adjustment range of heating temperature (up to 2000 °C) and heating rate (5‒450 °C/s). Higher temperatures and faster heating rates will lead to the formation of more gaseous products. However, the adjustment range of solar heating mainly relies on the types of solar concentrators (Chintala et al., 2017). Hence, a specific solar heating technique should be selected reasonably, according to the requirements of the pyrolysis reactions.

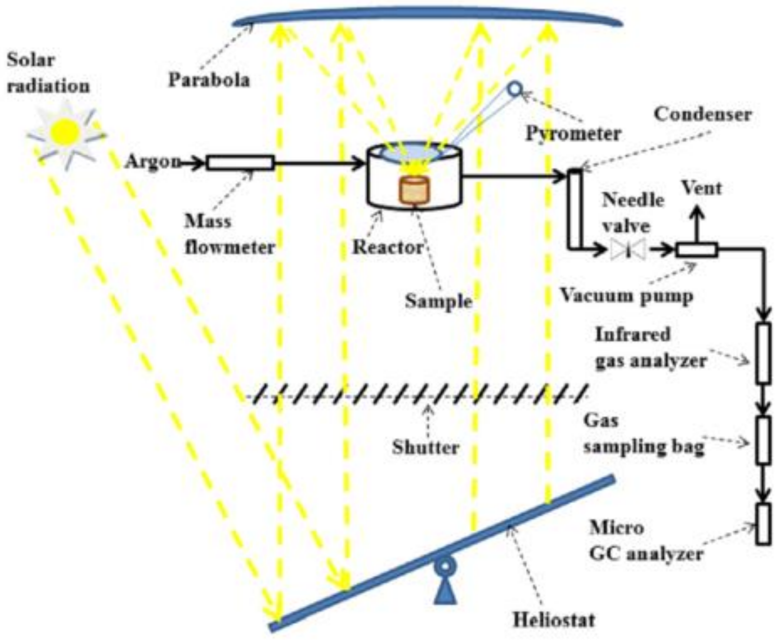


Figure 2.11: Solar-assisted pyrolysis experimental setup (Zeng et al., 2019). Copyright 2019, Elsevier

Pyrolysis with solar assistance can store solar energy as chemical energy in the pyrolysis by-products. Recently, there have been some reports of biofuel production from solar-assisted pyrolysis (Chintala et al., 2017; Li et al., 2016; Rony et al., 2019; Weldekidan et al., 2018; Zeng et al., 2017). Rony et al. (2019) reported that the bio-oil of corn stover obtained via solar-assisted pyrolysis had high contents of phenols (~44%) and furans (~13%), which indicated that solar-assisted pyrolysis of biomass had the potential to generate fuels and chemicals.

Chintala et al. (2017) evaluated the properties of bio-oil formed from the solar-assisted pyrolysis of non-edible Jatropha seeds and found that the bio-oil was rich in ester compounds, and it had the potential to be used as engine fuel. Besides, they also indicated that reducing the heat loss during the solar-assisted pyrolysis process could effectively improve the yield of the bio-oil. Bashir et al. (2017) studied the solar-assisted pyrolysis of biomass via CFD simulation and found that the bio-oil yield could reach 51.5% under the simulated operating conditions. Zeng et al. (2017) found that the temperature of solar heating can have a significant impact on the yields of pyrolysis products, and due to its high oxygen content, bio-oil produced from solar-assisted pyrolysis of beech wood still has to be improved in terms of its heating value. As a consequence, it is significant to regulate and control solar-assisted pyrolysis to enhance the quality of solar pyrolysis products.

Catalysts were used in the solar-assisted catalytic pyrolysis method to enhance the selective conversion of target products due to their effective performance in conventional catalytic pyrolysis. Weldekidan et al. (2019) reported that the CaO catalyst significantly lowered the number of fatty acids in the bio-oil produced from chicken litter (decreased to 8% in the in-situ catalytic process and 3% in the ex-situ catalytic process).

Barbosa et al. (2020) identified that more microalgae bio-oil was formed in the solar-assisted pyrolysis and more hydrocarbons were detected in the bio-oil, because of the catalysis of hydrotalcite. Hijazi et al. (2018) found that the TiO_2 catalyst could increase the tendency of hydrocarbon chain cleavage during the solar-assisted catalytic pyrolysis of rubber tyres. However, research on the solar-assisted catalytic pyrolysis field is relatively scarce. The selection of excellent catalysts and the optimization of related operating parameters for the solar-assisted catalytic pyrolysis still needs to be studied further.

2.11 Life-cycle assessment (LCA)

LCA, a tool for quantifying the eco-profiles of goods and services, processes inputs, outputs, emissions, and databases that are readily available. The four steps of the LCA analysis of biomass pyrolysis are goal and scope definition, life-cycle inventory (LCI), life-cycle impact assessment (LCIA), and interpretation of the results (Nah et al., 2017).

2.11.1 Goal and scope definition

The LCA study starts with defining the goals and scope. The definition of the intended application, the justification for the research, the target audience, and other details should be made explicit in this step, in accordance with ISO 14040 and 14044 (Foteinis et al., 2020). The current rules and standards, however, are primarily concerned with the definition of the word "step," but they lack any pertinent advice (Specification, 2008). This section provides guidance for making important methodological decisions (such as system boundary, functional unit, and allocation) during the performance objective and scope step based on the described LCA standards, guidelines, and research.

2.11.1.1 System boundary

System boundary definition is crucial to the LCA analysis. According to Ubando et al. (2019), biomass conversion is typically separated into multiple phases, as depicted in Figure 2.12. The input and output of each phase in the boundaries of the generalized system are explained in detail in Figure 2.12. Plant development, biomass collection, handling, and transportation from local or farm storage to the transit warehouse and final biorefinery are all steps that make up

Stage 1 (Wong et al., 2016). Normally, stage 2 includes pyrolysis, bio-oil conversion (if necessary, conversion of bio-oil to intermediate or final product), biomass preparation (shredding, grinding, drying, and acid washing), and bio-oil (Dhyani & Bhaskar, 2018). The biomass pretreatment will adjust accordingly depending on the pyrolysis requirements. The energy demand for each LCA analysis system is different due to the parameter differences in temperature, pressure, heating rate, and other aspects (Fahmy et al., 2020). The raw experiment or model software, such as Aspen Plus, can be used to retrieve the mass data and energy flows for the central reaction zone (Adeniyi et al., 2021). The recycling and destruction steps are included in LCA system boundary stage 3. Few studies, meanwhile, have included all three stages in the system boundary and conducted a thorough analysis from cradle to grave. One of the gaps in the existing LCA literature is this phase.

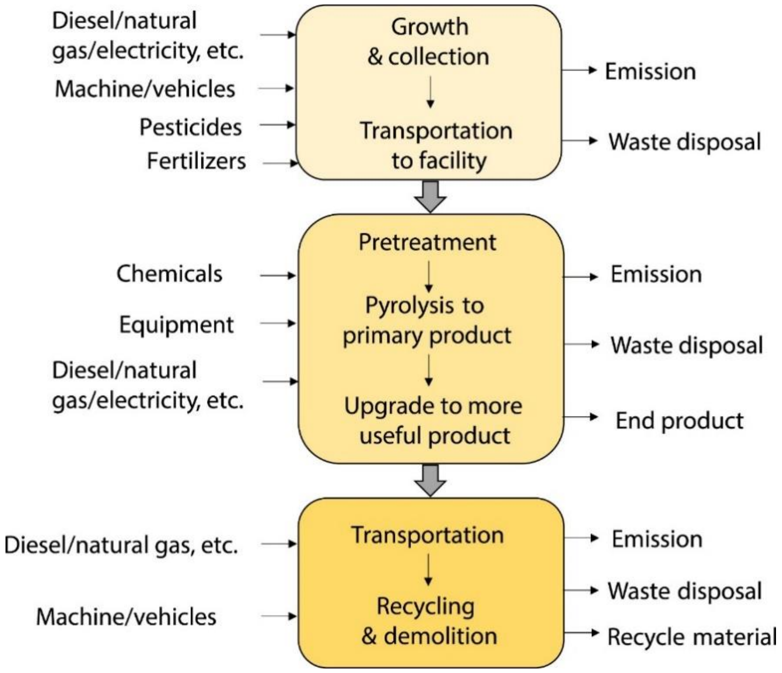


Figure 2.12: Generalized system boundary for an LCA analysis

2.11.1.2 Functional unit

The selection of an appropriate functional unit is a crucial component of the aim and scope specification. A necessary component of the LCA results in comparing many alternative scenarios or goods is the functional unit, which serves as the standardized basis for the calculation and the reference (Han et al., 2013). The end product and system scope specification are used to guide the selection of functional units. Typical functional units are typically separated into energy-based (1 MJ/1 kWh/1 MW end products, for example) and mass-based (1 kg/1 ton feedstock/product) functional units (Han et al., 2013). The use of the same functional unit might offer a practical foundation when the various scenarios and projects are compared. In biomass conversion systems, the functional units of area and distance are less usually utilized, but they may be chosen if the product's purpose can be clearly demonstrated. For instance, Zhang et al.'s (2013) functional unit for the biofuel production system is 1 km, which is the distance covered by a light-duty passenger car running on fuel produced through fast pyrolysis.

2.11.1.3 Allocation

The decision of how to divide the environmental cost of a certain manufacturing system between products and co-products is a difficult problem in LCA. In order to address the issue of environmental allocation in LCA, four approaches to handle co-product surplus have been proposed in the literature (Schrijvers et al., 2016). The first approach is called no allocation, and it entails that the product bears the entire manufacturing system's environmental burden. Economic allocation, the second approach, assumes that the distribution of environmental impacts should be based on the worth of each commodity. In LCA studies, it is one of the most popular allocation techniques (Nguyen & Hermansen, 2012). However, implementing partitioning based on end-user price rather than the immediate value after manufacturing is a common mistake made by LCA practitioners (Ardente & Cellura, 2012). The biophysical allocation technique is the third. The foundation of this strategy is physicochemical characteristics, such as the mass and energy content of the co-products and outputs. Some studies believe that energy allocation is more accurate. Additionally, because the market value is primarily determined by its energy content, the energy-based allocation might also reflect economic considerations (Luo et al., 2009). Compared to economic allocation, which changes with potential price variations, mass allocation has a higher level of stability over time. With regard to co-product allocation, the attributional approach divides the environmental impact of the product using allocation variables based on mass, energy, or economic value. The final way to assess the co-product's environmental impact is system growth. The environmental burden can be determined by deducting the averted emissions from the overall emissions less the co-product displacement. Expanding the system is an appropriate strategy to handle the co-products when employing the consequential approach.

2.11.2 Life-cycle inventory (LCI)

LCI entails the production of products, outputs, and inventory inputs. The physical amounts of inputs (or energy/material consumption), direct emissions (N_2O, CO, CO_2, CH_4, NOx, NH_3, etc.), and wastes at each stage are computed for assessing LCI of the bioenergy production systems by pyrolysis (Eggleston et al., 2006). In addition, non-duplicated data gathering is necessary for LCI analysis, which is a crucial step in the overall LCA analysis.

The gathering of data immediately affects the analysis of the entire LCA model, for which accurate, and realistic data are essential. A significant obstacle to creating a LCI for LCA is the absence of unit process data. Primary and secondary sources of data can be distinguished; the majority of data is accessible through private and public databases. However, some sources, like laboratory testing, surveys, and literature reviews, are still used in the creation of databases (Hellweg & Milà i Canals, 2014), which requires substantial labor and financial investment. Additionally, these databases are insufficient for some growing businesses or speciality materials. Machine learning techniques have been applied to tackle data issues in LCA studies in order to fill in the gaps. Wernet et al. (2008), Song et al. (2017), and Zhu et al. (2020) used artificial neural network to estimate the life-cycle impacts of chemicals based on molecular structure information. Lee et al. (2020) and Romeiko et al. (2020) estimated the environmental impacts by using boosted regression tree. Zhao et al. (2021) created a more adaptable machine learning model (decision tree) to obtain the required data. Data collecting might be a barrier, but machine learning techniques have shown promise in LCA studies.

2.11.3 Life-cycle impact assessment

Environmental categories in the LCIA can be split into midpoint indicators and end-point indicators (Muench & Guenther, 2013). In general, midpoint categories are used to indicate the environmental effects of the life-cycle, such as the potential for global warming (GWP), acidification (AP), ecotoxicity (EP), eutrophication, water depletion, fossil energy, and so on. The outcomes of end-point categories can be found by integrating midpoint categories. The majority of research include human health, ecosystem quality, and resource depletion as end-point categories. However, the majority of researchers continue to utilize midpoint indicators to display the findings because they think that midpoint categories make it simple to discuss environmental consequences. The most typical impact utilized in LCA study is GWP.

In comparison to the corresponding number for CO_2, the GWP expresses the cumulative radiative forcing value induced by the emission of a unit mass of a specific greenhouse gas over a specified time horizon. The following is the mathematical representation of GWP (Levasseur et al., 2010):

$$GWP\frac{TH}{i} = \frac{\int_0^{TH} a_i[C_i(t)dt]}{\int_0^{TH} a_r[C_r(t)dt]} \tag{2.1}$$

“TH” is the chosen time horizon; “a” is the instantaneous radiative forcing per unit mass increase in the atmosphere; “C(t)” is the time-dependent atmospheric load of the released gas; “i” is the released gas; “r” is the reference gas, carbon dioxide.

When fuels like coal, coke, products made from crude oil, natural gas, peat, wood, and other biomass fuels are burnt, direct greenhouse gas emissions, such as CO_2, CH_4, and N_2O, are produced (Soimakallio et al., 2011). Production method and fuel composition/quality have a significant impact on greenhouse gas emissions. In an LCA analysis, the greenhouse gas emission can be determined in "kg CO_2 equivalent" by multiplying the LCI results for each greenhouse gas by their respective GWP. Particularly for short-lived greenhouse gases, the GWP value depends on the time horizon used (Table 2.2). In LCA study, GWP is often computed over a 100-year time horizon (Brown & Caldeira, 2017). However, according to other research, the time scale for greenhouse gas emissions should be 20 years, which is consistent with the infrastructure's life duration (Cusenza et al., 2021).

Table 2.2: GWP values for CO_2, CH_4 and N_2O for the time horizons of 20, 100 and 500 years (Yu et al., 2022)

	20 years	**100 years**	**500 years**
CO_2	1	1	1
CH_4	72	25	7.6
N_2O	289	298	153

2.11.4 Interpretation

Identification of key concerns, completeness, sensitivity, and consistency checks are used to build the interpretation of the results. In the same system, any stage change will have an impact on the LCA results. Sensitivity analysis is frequently employed to make the LCA analysis more reasonable and practical (Zhou et al., 2018). According to the ISO standard, sensitivity analysis should concentrate on the most important concerns in order to assess the impact of variations in assumptions, procedures, and data. Under a specific set of assumptions, sensitivity analysis determines how different values of an independent variable impact a dependent variable (Wang et al., 2021). Parameter value, allocation rule, system boundary, model or process choice are all examples of independent variables in LCA. Dependent variables might be the rankings of alternatives in comparison research or the values of output parameter (continuous). Table 2.3 displays various sensitivity analysis types with various combinations of input and outcome variables (Björklund, 2002).

Table 2.3: Tools available in sensitivity analysis in LCA (Yu et al., 2022)

Input variable	Output variable	
	Parameter value	Priority
Parameter value	Tornado diagrams One-way sensitivity analysis	Ratio sensitivity analysis Critical error analysis
Allocation rule	Scenario analysis Factorial design + multivariate analysis	Scenario analysis
Boundary	Scenario analysis Factorial design + multivariate analysis	Scenario analysis
Model	Scenario analysis Factorial design + multivariate analysis	Scenario analysis
Process	Scenario analysis Factorial design + multivariate analysis	Scenario analysis

In order to evaluate the validity of LCA-based judgments and to direct future research toward lowering uncertainty, knowledge of the sensitivity of the model findings is useful. Additionally, when performing a sensitivity analysis, it's necessary to stand back and gather data on a few key areas. However, re-evaluation and re-analysis will be required if certain conclusions and outcomes from the sensitivity analysis are critical to the study. As a result, sensitivity analysis is crucial to the LCA model's data collection and boundary determination processes.

2.12 Conclusion and future directions

In recent years, a lot of research has been done to better understand the process of biomass pyrolysis by investigating the pyrolysis characteristics of cellulose, hemicellulose, and lignin. The pyrolysis behaviour of biomass is greatly influenced by a variety of additional components, such as inorganic chemicals, whose composition is quite complex. Furthermore, the complex interactions between the components of the biomass make the pyrolysis mechanism particularly difficult. Future studies on the mechanism of biomass pyrolysis should be integrated with the actual production process and genuine biomass samples to better understand the process of biomass pyrolysis. This work should be based on advanced measuring techniques and modelling methodologies. Further consideration should be given to the relationships between the pyrolysis behaviour of biomass components and the heat and mass transport in the pyrolysis process. Additionally important is the development of more accurate CFD models and the optimization of associated algorithms for biomass pyrolysis.

Although biomass co-pyrolysis demonstrated some promising results in terms of oxygen removal and oil quality improvement, the liquid oil produced is still insufficient and cannot be used as a direct alternative for petroleum oil. Additionally, the synergistic effects between biomass and feedstock with a high hydrogen content are yet unknown; therefore, biomass pyrolysis still requires attention to how to improve the synergistic effects and produce higher quality products. The development of catalysts is essential for the advancement of catalytic fast pyrolysis technology and is an efficient way to generate liquid oil that is higher grade and aromatics enriched. Because of their strong aromatic selectivity, ZSM-5 catalysts have received a lot of attention. High coke and low liquid output, however, are two significant issues that are impeding the advancement of biomass catalyst fast pyrolysis. Therefore, it is important to continue designing new catalysts that are affordable, highly efficient, durable, and well-suited for biomass. To fully exploit the benefits of each approach, it is also worthwhile to consider applying co-pyrolysis and catalytic pyrolysis together.

Microwave pyrolysis and solar pyrolysis have drawn a lot of attention due to their distinctive heating properties when compared to traditional biomass pyrolysis by electrical heating. However, the resulting bio-oil is still of low quality. As a result, some research has been done to further improve the quality of products, such as the integration of current relevant biomass pyrolysis technologies (such as co-pyrolysis, catalytic pyrolysis, etc.) with these new heating methods. Despite this, there has not been much research done in this area, therefore more work needs to be done in the future to optimize pertinent operational parameters, catalyst compositions, and pyrolysis reactors to produce cheaper higher quality liquid oil. An in-depth study of the mechanism is also necessary to comprehend the process completely.

CHAPTER THREE: SYSTEMATIC LITERATURE REVIEW

3.1 Chapter overview

Biomass plays an essential role in enhancing global energy security and decreasing carbon emissions as a promising renewable energy option. Comprehensive techno-economic assessments have been carried out to spark industry stakeholders' interest and increase their investment in biomass-based enterprises. To provide a more accurate and reliable feasibility estimate, the evaluation must also take into account a variety of uncertainties in the biomass conversion industry. This chapter aims to present an overview of the various types of methodologies or techniques used in the techno-economic assessment of the viability of biomass conversion processes, and highlight the uncertainties that need to be taken into account in the evaluation model. A systematic literature review is used where four electronic databases viz., Scopus, Web of Science, Dimensions, and PubMed were used to identify the most recent original research articles in peer-reviewed journals. A total of 346 studies, covering the period 2012-2022 were screened for relevance to the study. Seventy-eight records (n=78) which include only original research articles met the inclusion criteria. The review identified several financial factors and uncertainties that affect the economic performance of fast pyrolysis systems. Furthermore, upgrading the bio-oil to transportation fuels and value-added biochemicals can significantly improve the economic performance of fast pyrolysis plants as opposed to selling raw bio-oil.

This chapter is based on a systematic review paper published in the journal Fuel Communications.

Makepa, D. C., Chihobo, C. H., Ruziwa, W. R., & Musademba, D. (2023a). A systematic review of the techno-economic assessment and biomass supply chain uncertainties of biofuels production from fast pyrolysis of lignocellulosic biomass. Fuel Communications, 14(1), 100086. https://doi.org/https://doi.org/10.1016/j.jfueco.2023.100086

3.2 Introduction

Due to the advent of industrialization and the astronomical rise in the number of automobile vehicles over the past two decades, fossil fuels are being exhausted (Ramalingam et al., 2022). To counter the increase in energy demand, efforts are being made around the world to find alternative sources of energy. Biomass resources are extensive and widely dispersed around the world. Biomass plays an essential role in enhancing global energy security and decreasing carbon emissions as a promising renewable energy option. Fast pyrolysis is a potential cellulosic biofuel production process that thermochemically decomposes lignocellulosic biomass into gases, solids, and liquids. Owing to their renewable nature and eco-friendliness, as well as their simplicity of handling and storage, biofuels have shown to be a superior substitute (Ramalingam et al., 2022). Fast pyrolysis is characterized by a rapid heating rate, a moderate temperature, and a short resident duration of a few seconds (Mutsengerere et al., 2019). Biofuels' commercial viability is dependent on lowering production costs, increasing product output, and having access to a plentiful and sustainable source of biomass (Sorunmu et al., 2020).

Commercially produced first-generation biofuels rely on food crops like corn, sugarcane, and soyabeans, which threaten food and feed markets (Manochio et al., 2017). This constraint has sparked interest in producing second-generation biofuels made from non-consumable biomass resources such as crop, animal, and forest wastes that are sustainable (Sims et al., 2008).

Biochemical pretreatment, enzymatic hydrolysis, fermentation, and thermochemical (torrefaction, pyrolysis, and gasification) techniques are used to convert lignocellulose (biomass) into biofuels. To date, TEA has been utilized to estimate the economic performance of second-generation biofuels that are not yet commercial (Brown, 2015; Brown & Brown, 2013; Crawford et al., 2016; Dutta et al., 2016; Thilakaratne et al., 2014; Zhang, Brown, et al., 2013). Such analyses aid in determining the possibilities for scale-up and the expected costs if a commercial investment is made (Thomassen et al., 2019). Findings from biomass thermochemical conversion TEAs (Brown, 2015) and combined with LCA (Patel et al., 2016) have previously been reviewed in the literature. Nevertheless, more studies have occurred in recent years, focusing on the conversion and upgrading of bio-oils produced by fast pyrolysis of biomass.

Fast pyrolysis is a thermochemical process that can convert biomass into value-added fuels and chemicals (Mutsengerere et al., 2019). Bio-oil, biochar, and vapour are the process's main products, with bio-oil regarded as the most valuable. Bio-oil is a complex mixture of chemical substances, predominantly oxygenates, generated through high-temperature decomposition/recombination reactions in the absence of oxygen (Liu et al., 2014). The oxygenated chemicals in bio-oil are acidic and unstable, making them incompatible with the existing refining infrastructure. As a result, deoxygenation, a method of upgrading the bio-oil, is required. Bio-oil is upgraded to improve its physical and chemical characteristics to meet current fuel standards (Mutsengerere et al., 2019). Depending on the deoxygenation technique, the upgrading of bio-oil can be done in the presence or absence of a catalyst. Fast pyrolysis, on the other hand, can be done with or without a catalyst.

The economic effectiveness of fast pyrolysis systems is highly dependent on the location of the biorefinery. Feedstock varieties, availability, and cost, as well as capital and operational costs, tax levels, soil composition and properties, biochar varieties and markets, crop classifications and asset prices, and biomass and biofuel logistics, differ greatly by area. We need to better understand the regional variations in economic implications of bio-oil applications to appraise recent breakthroughs in fast pyrolysis of lignocellulosic biomass aimed at producing carbon-negative energy. The market value of bio-oil varies depending on its end-use (Li et al., 2019).

The goal of this review is to provide a collection of biomass energy techno-economic analyses that include lignocellulosic biomass valorization to energy using fast pyrolysis. The main purpose of this paper is to deliver an overview of the economic implications and biomass supply chain uncertainties of fast pyrolysis systems. The variability of reported results due to methodology choices is a noticeable element of biomass energy techno-economic analyses. The fast pyrolysis technology used, modelled plant capacity, biomass supplies and costs, capital expenditures, and total project investment are among the choices. Bioenergy practitioners, energy policymakers, sustainability academics, and certification agencies will all benefit from the findings of this study.

3.3 Methods

3.3.1 Systematic review

Different types of reviews have been widely used in literature review which includes critical review, comprehensive review, scoping review, meta-analysis, and systematic reviews (Dastjerdi et al., 2021). A systematic literature review employs a systematic method to search, analyze and synthesize research evidence. The key feature of systematic literature reviews is the reduction of author bias in comparison with other types of reviews, which often support the authors' point of view (Mirkouei et al., 2017). The advantage of such studies is that they systematically answer the questions of what is known, and what remains unknown and propose recommendations for future research (Dastjerdi et al., 2021). A systematic review method is considered the most suitable tool for comparing and evaluating the techno-economic feasibility of producing biofuels via fast pyrolysis of lignocellulosic biomass.

3.3.2 Search strategy

This research study is based on the process to review techno-economic assessment studies of biofuel production from lignocellulosic biomass via fast pyrolysis. A review protocol was followed at each stage such as developing a search string, selection criteria, and data extraction. To produce scientifically sound results, four databases that include Web of Science, Scopus, Dimensions, and PubMed were examined to gather keywords, abstracts, and titles of relevant journal articles and international conferences between 2012 and 2022. The records were extracted using the following set of keywords: ("techno-economic analysis" OR "techno-economic assessment") AND ("biomass" OR "lignocellulosic biomass") AND (pyrolysis OR thermochemical conversion) AND (bio-oil OR bioenergy OR biofuel). The keywords were chosen by reviewing several review papers and journal articles on the techno-economic assessment of biomass to energy technologies.

To guarantee the quality of the review, only original peer-reviewed journal articles and state-of-art reviews on techno-economic assessment of biomass to energy technologies that were published in peer-reviewed academic journals were included. A flowchart illustrated in Figure 3.1 was developed to show the process undertaken in the selection of studies for this review. Initially, a total of 346 scientific articles were identified from a database search, and following the removal of duplicates, 253 scientific publications remained for further review. Titles, abstracts, and keywords were screened and a total of 146 scientific articles were excluded. In the final stage, full-text screening for eligibility was performed, yielding 78 articles for in-depth analysis.

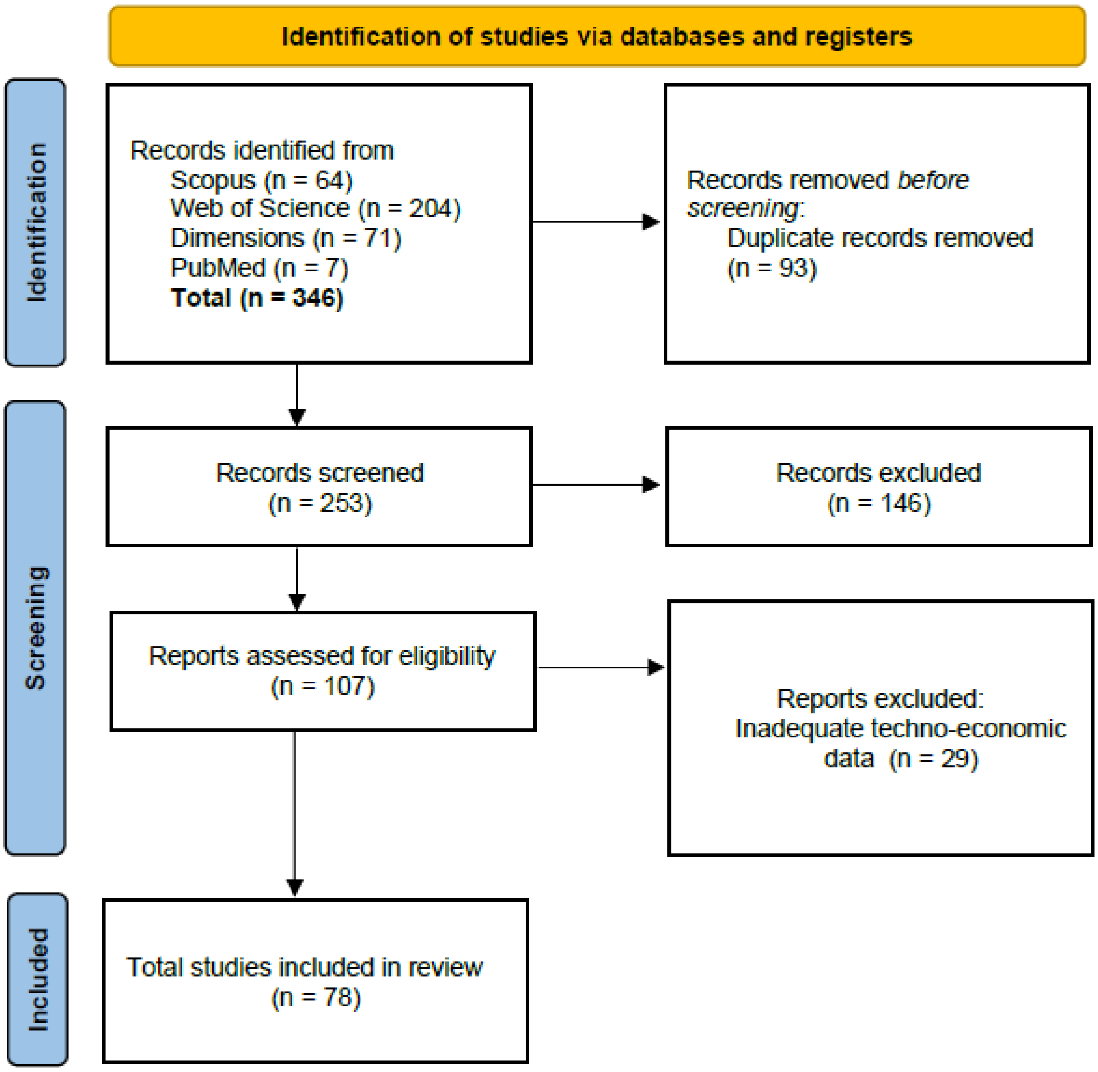


Figure 3.1: PRISMA flowchart for the identification and selection of studies for the inclusion process

3.4 Techno-economic analysis

3.4.1 Cost structure

The major inputs to the techno-economic model for estimating the production cost of biofuels include capital cost, feedstock cost, and operating and maintenance cost (Patel et al., 2019).

3.4.1.1 Capital cost

The total capital expenditure comprises the total direct and indirect cost (TDIC), cost of contingency (C_{Con}), and land cost (C_{Land}). The TDIC included total installed cost (TIC) and indirect cost. Table 3.3 depicts the detailed breakdown of TCAPEX.

3.4.1.2 Feedstock cost

The cost of feedstock can account for 40–50% of the total operating cost of a biomass plant. Agricultural wastes such as corn cobs and corn stover (Meyer et al., 2016), olive pomace (Ramos & Ferreira, 2022), rice husk (Liu & Wang, 2020), and sugarcane bagasse (Michailos et al., 2017; Ramirez & Rainey, 2019), on the other hand, are often associated with a lower feedstock acquisition costs. Feedstock cost encompasses all costs associated with the feedstock, from farming to transportation to the plant gate. A variety of factors are taken into account when calculating the feedstock cost: harvesting costs, transportation costs, silviculture costs, tertiary road construction costs, fertilizer distribution costs, and the premium provided to the owners above the cost of fuel (Patel et al., 2019).

3.4.1.3 Operating and Maintenance (OM) cost

The fixed and variable costs of running a biomass facility are referred to as operation and maintenance costs. The fixed operation and maintenance expenses can be defined as a proportion of the total capital costs. They usually vary from 1 to 6% of the initial capital cost per year for biomass facilities. Labour, scheduled maintenance, routine component/equipment replacement, and insurance are all fixed OM expenses. Variable OM expenses are expressed as a value per unit of production ($/kWh) and are dependent on the fuel's output. Non-biomass fuel expenditures such as unscheduled maintenance, equipment replacement, and additional service charges are included (Ramos & Ferreira, 2022). The cost of maintenance is considered to constitute 3% of the capital cost. Plant operating costs are estimated to represent 25% of operational labour costs, with plant overhead accounting for 50% of overall OM costs (Patel et al., 2019).

3.4.1.4 Annual cost

The annual cost method can be used to analyze the economics of biomass fast pyrolysis. The total annual cost of the pyrolysis process is the sum of the fixed and variable costs (Yahya et al., 2021).

3.4.1.5 Fixed cost

Several assumptions have been reported to determine the pyrolysis unit's annual fixed cost, as shown in Table 3.1 (Brown, 2015; Hu et al., 2016).

Table 3.1: Assumptions on determining the annual fixed cost of a pyrolysis unit (Patel et al., 2019)

Parameters	**Assumptions**
Financing	100% owned capital
Pyrolysis unit availability	82%
Pyrolysis unit depreciation	8 years
Interest on investment	10%
Total annual operating hours	7200 h

3.4.1.6 Variable cost

Repair and maintenance costs, labour costs, lignocellulosic biomass purchasing and transportation costs, energy costs for the pyrolysis unit and shredder, and nitrogen costs for induction into the reactor are all variable costs (Yahya et al., 2021). Assumptions are made on the miscellaneous chemical cost per ton of biomass.

3.4.2 Cost analysis methods

For the economic evaluation, the majority of the studies in this review used the internal rate of return (IRR), which is an indicator that measures the breakeven point when the project's net present value equals zero. The integrated pyrolysis biorefinery's IRRs are determined using a discounted cash flow rate of return (DCFROR) model over a 25-year timeframe. The primary assumptions and techniques utilized for cost assessment are summarized in Table 3.2 (Brown, 2015; Zhao, Brown, et al., 2015).

Table 3.2: Assumptions utilized for cost assessment (Patel et al., 2019)

Parameter	**Assumption**
Plant life	25 years
Equity	40%
Loan interest	7.5%
Loan term	10 years
Income tax rate	39%

The pyrolysis-bioenergy platform's economic performance is assessed using capital and operating costs, as well as the minimum fuel selling price (MFSP) (Li et al., 2019). Using the DCFROR technique, the MFSP is the breakeven selling price for the main product. Within a 25-year plant life-cycle, the rate of return is expected to be ten percent.

The total of material costs, energy costs and fixed operating costs are added to arrive at the total operating costs. The three fixed operational costs are insurance, maintenance, and salaries. To improve the project's economics, a complete analysis of the operating costs of an integrated biorefinery should address the interaction and integration of material streams. Many of the studies in this review calculate total material/energy costs by assigning a mass flow ratio to each material/energy stream that is equivalent to the bio-oil fraction under specified conditions. The majority of the research used Aspen Plus® material and energy balance simulation data to calculate material/energy prices. As an input, the IRR estimations require product selling prices from the biorefinery. Because there is limited industrial commercial data for bio-based products, we assume the final product pricing is the same as their comparable market commodities. We can calculate an IRR for 30-year plant life with a given combination of product yields by putting all of the collected price data into the economic model (Dang et al., 2016).

3.4.3 Capital cost estimates

The existing literature on biomass waste-to-energy techno-economic analyses uses a variety of capital cost estimation approaches. The first is the Lang factor method, which involves multiplying a project's total purchased equipment cost (TPEC) by a single factor based on the type of facility being built to arrive at a total capital investment (TCI) (Brown, 2015):

$$TCI = \sum (PEC) \times Langfactor \tag{3.1}$$

Originally, Lang factors were estimated for three types of facilities: solid processing, solid-liquid processing, and liquid processing. The following factors have been calculated for facilities in Africa that use biogas and fuel ethanol. Because of its simplicity, it has been used in comparative evaluations of bioenergy pathways as well as established fossil processes (Shabangu et al., 2014). Lang factors are also used as a model output rather than an input to quickly summarize the specific installation and indirect cost variables used by more sophisticated approaches (Dutta et al., 2012). The simplicity of the Lang factor cost estimation methodology can be a disadvantage because it requires the usage of factors generated from comparable facilities to be accurate. In the case of bioenergy pathways, this raises the question of whether next-generation biorefineries will have installation costs equal to those of existing chemical engineering facilities.

Individual factors for different equipment types inside the facility, rather than a single factor for the entire facility, are used in two alternative techniques to extend the adaptability of the Lang factor approach so that it copes with complex situations (Brown, 2015). Individual factors are used in the hand factor approach for eight different equipment kinds, but the Module factor method considers over 60 different equipment types. Both techniques determine total installed equipment cost (TIEC) by multiplying the purchased equipment cost by the relevant factor, which is then summed to produce the TCI:

$$TCI = \sum (PEC) \times Hand\ or\ Modulefactor \tag{3.2}$$

The Module factor technique is used in part in a more contemporary NREL design case TEA for the manufacture of cellulosic biofuels by gasification and mixed alcohols synthesis, as well as in an early NREL design case TEA on cellulosic ethanol production via enzymatic hydrolysis (Dutta et al., 2014).

The Percentage of Delivered Equipment Cost (PDEC) technique is the most commonly used methodology in the recent open literature on cellulosic biorefinery TEAs (Table 3.3) (Peters et al., 2003). This technique is comparable to the Lang factor method in that it divides processing into three categories: solid, solid-liquid, and liquid. It does, however, improve on the Lang factor approach in three respects. First, the PDEC technique divides the installation elements into seven 'direct' and five 'indirect' cost categories, allowing analysis to change the cost categories when the data justifies it. Second, the PDEC technique takes into account characteristics particular to three types of locations: grassroots (a new facility on an undeveloped site), battery-limit (a new facility on an established site), and expansion of an existing facility. Finally, the PDEC method explicitly models working capital, which is often treated differently than direct and indirect costs but still counts toward the TCI.

Table 3.3: PDEC methodology for calculating TCI of a grassroots solid-liquid processing plant (Peters et al., 2003)

Parameter	**Percent of delivered equipment cost (%)**
TPEC 100%	100
Purchased equipment installation	39
Instrumentation and controls	26
Piping	10
Electrical systems	31
Buildings (including services)	47
Yard improvements	12
Service facilities	55
TIEC	TPEC * 3.20
Engineering	32
Construction	34
Legal and contractors' fees	23
Contingency	15% of Fixed capital investment (FCI)
TIC	1.26 * TPEC
FCI	TIEC + TIC
Working capital (WC)	75
TCI	FCI + WC
TCI/TPEC	5.27

The capacity factor is the ratio between the total energy generated in a time and the total energy that could be created if the facility operated at maximum output for the same period without interruption. As a result, if the plant runs nonstop for 24 hours every day of the year, the capacity factor will be 100 percent. Most studies assumed a capacity factor of 60-85% for all plants (Ramos & Ferreira, 2022). Another important consideration is the plants' lifespan. The majority of studies report values between 15 and 25 years, with the majority reporting values equal to or greater than 20 years (Irena, 2012).

3.4.4 Net present value

The profitability of a project is determined by its net present value (NPV). It is the most effective way for deciding whether to accept or reject an industrial or financial investment. The rule in this assessment was that if the NPV was greater than zero, the project would be accepted, and if it was less than zero, it would be rejected (Abnisa & Wan Daud, 2014). In this context, Kuppens et al. (2010) found that flash co-pyrolysis of willow with any biopolymer was more economically attractive than pure willow pyrolysis, as the NPV of co-pyrolysis of biopolymers with willow resulted in positive cash flows for all types of biopolymers tested. Other estimates, such as the initial investment, cost of production, and potential income, also support the findings.

3.4.5 Internal rate of return

An investment project's IRR is the rate at which it is expected to make a profit throughout its life expectancy. It is the rate at which the project’s net cash inflows and outflows become equal. The IRR, in other words, is the discount rate at which the NPV of a project equals zero. The interest rate at which present equivalent revenues equal present equivalent costs determined on a before-tax basis is known as the prospective before-tax IRR on an investment.

3.5 Discussion

3.5.1 Biomass availability and cost of production

The cost of producing and transporting the biomass determines the delivered cost, and both are influenced by where the storage, biorefinery, and other facilities that handle the biomass are located. To pinpoint the locations of biomass acquisition and conversion facilities, research by Lan et al. (2021) used BioFLAME (Biofuels Facility Location Analysis Modelling Endeavor), a high-resolution spatial biorefinery sitting model using real geographic data with high precision. Site appropriateness, feedstock accessibility, and land conversion are the three elements that make up the decision support system of BioFLAME. In BioFLAME, the site appropriateness element is mostly focused on the proximity to infrastructure, including road networks, pipelines, and electricity lines, among others. The site appropriateness component has also steadily included additional geographical elements, such as soil properties and watershed conditions.

Using a 10-year life span for a stand of switchgrass, Lan et al. (2021) evaluated the expenses of generating perennial switchgrass via BioFLAME. The operations involved in the production include purchasing the land, establishing the switchgrass stand, maintaining it annually, harvesting the switchgrass each year with a huge rectangular baler, and transporting the biomass to the biorefinery for pre-processing. The costs that were modelled for the equipment were capital recovery, maintenance and repairs, taxes, insurance, and housing, as well as fuel and other consumable materials.

3.5.2 Capital investment and operating cost

Baral & Shah (2017) examined the use of stillage from a cellulosic butanol manufacturing process that produced 113.4 million litres per year using both a fast pyrolysis technology and a direct combustion system. The plant's total capital expenditure was anticipated to be $169.01 million for a direct combustion system and $171.87 million for a fast pyrolysis system, respectively. Due to the various levels of equipment needed for the solid stillage utilization processes, a fast pyrolysis system required higher initial capital investment. About 94% of the TCI for both systems went toward the direct fixed capital cost, which was the largest contribution. Working capital and starting expenses were next in line. It was discovered that the direct fixed capital cost of process equipment accounted for around 20.9% of it, with the remaining expenses of installation, building materials, engineering, and construction accounting for another 21.4%.

Costs associated with materials, labour, facilities, and utilities are all part of the yearly operating expenses of a biorefinery. Utilities, labour-dependent expenses, facility-dependent costs, and raw material costs are the other main contributors to operational costs. Depreciation, maintenance, and equipment insurance made up the majority of the facility-dependent expenses (Baral & Shah, 2017).

3.5.3 Fast pyrolysis techno-economics

3.5.3.1 Effects of feedstock pretreatment

The size reduction process is energy expensive due to the relatively small biomass size required. Torrefaction has been shown to improve biomass grindability, in addition to potentially improving the quality of pyrolysis bio-oil (Winjobi et al., 2017). As a result of including torrefaction before size reduction, the power demand of the size reduction stage may be reduced. Torrefaction takes place in an inert environment at lower temperatures and for a longer period than fast pyrolysis. It primarily destroys the hemicellulose part of the biomass, resulting in torrefied biomass, which is sometimes referred to as bio-coal because it is a substitute for fossil coal. Studies have investigated and observed the yield of better-quality bio-oil because of a torrefaction pretreatment of biomass before fast pyrolysis (Winjobi et al., 2017). A study by Winjobi et al. (2017) reported that the MFSP of hydrocarbon biofuel estimated for a fast pyrolysis production pathway is almost the same as the MFSP for a two-step torrefaction-fast pyrolysis pathway at 290 °C torrefaction. Hydrocarbon biofuel produced using the two-step process at elevated torrefaction temperatures, on the other hand, is expected to have higher minimum selling prices. However, based on the assumptions, designs, and parameters used in their study, torrefaction does not appear to be an advantage on the cost of production for hydrocarbon fuels compared to a one-step process at high torrefaction temperatures.

3.5.3.2 Techno-economics of bio-oil production

Brigagão et al. (2019) evaluated the economic aspects of producing bio-oil via fast pyrolysis of corncobs. Equipment sizing was utilized to estimate the FCI, and the Chemical Engineering Plant Cost Index was used to update equipment costs, with 2017 as the reference year. A project lifespan of 23 years was estimated, with 20 years of operation (as is typical for most chemical plants) after the first three years of building, providing a basis for comparing the NPV of different options. Fast pyrolysis was found to exhibit the lowest FCI among the thermochemical conversion processes, followed by combustion and gasification, due to the use of fewer process machinery with low power consumption and significantly smaller reactors for biomass conversion.

A study by van Schalkwyk et al. (2020) evaluated the economic feasibility of producing bio-oil from forest residues from different locations. The economic analysis results revealed a clear economy-of-scale benefit as biomass collection radius increased up to 300 km. The scenario where there was a biomass collection radius of 300 km was the most economically viable biorefinery scenario. By comparison, the MFSP (10% IRR) of upgraded bio-oil was more than double that of crude bio-oil. However, considering 22% IRR as the requirement for attracting private investors to an innovative project meant that both crude and upgraded bio-oil production were not economically viable.

The average MFSP of pyrolysis bio-oils is affected by the selling price of the by-products (biochar), feedstock price, fixed capital costs and product yields (Hu et al., 2016; Li et al., 2019). Li et al. (2019) reported that a higher biochar selling price leads to a more competitive

MFSP. MPSPs provide a criterion for product prices, but market prices are unpredictable throughout a project's 30-year existence. The maximum investment cost (MIC) and NPV will be affected by price fluctuations in commodities products. Uncertainty analysis enables the evaluation of MIC and NPV changes due to product price changes (Hu et al., 2016).

3.5.3.3 Techno-economics of bio-oil upgrading via hydroprocessing

In 2009, Pacific Northwest National Laboratory researchers published a conceptual case study of a 2000 metric tonnes per day (MTPD) biorefinery using fast pyrolysis and hydroprocessing (FPH) (Jones et al., 2009). According to the estimate, the total project investment (TPI) for the biorefinery was \$329 million, and the MFSP was \$2.21 per gge (\$0.58 per lge), based on the following assumptions: 10% IRR, a 20-year lifetime, and a \$60.50 MT^{-1} feedstock cost. Later, Iowa State University researchers published a TEA of the fast pyrolysis and hydroprocessing pathway at a biorefinery converting stover to fuel blend stocks under two scenarios: (i) the required hydrogen is produced at the biorefinery site through the process of steam-methane reforming of the bio-oil produced and (ii) hydrogen is acquired externally (Wright et al., 2010). The TPI for hydrogen produced at the biorefinery was \$311 million and \$217 million for hydrogen acquired externally. The analysis calculated MFSPs of \$3.35/gge and \$2.29/gge for the hydrogen produced at the biorefinery and hydrogen acquired externally, respectively, based on the following assumptions: 10% IRR, 20-year plant lifespan and \$90 MT^{-1} feedstock cost. The higher MFSP of the scenario with hydrogen production at the biorefinery results from the higher capital cost of the biorefinery and lower fuel yield, since a fraction of the bio-oil produced is utilized to produce hydrogen. Three years following the publication of the Wright et al. (2010) study, Brown et al. (2013) presented an updated analysis to take into account shifting market circumstances and route commercialization progress. A 2000 MTPD stover FPH facility using an external hydrogen source would result in an MFSP of \$2.57/gge according to the latest estimate, which forecasts a substantially higher TPI of \$429 million.

A study by Zhang et al. (2013) utilizes Aspen Plus to evaluate a 2000 MTPD fast pyrolysis and hydroprocessing biorefinery that uses a unique red oak feedstock pretreatment technique to generate the maximum yield of levoglucosan. Levoglucosan is hydrolyzed to glucose and bio-oil is hydroprocessed to diesel fuel utilizing on-site hydrogen generated from the bio-oil aqueous phase through steam reforming. The research determines a TPI of \$379 million and mentions hydroprocessing and reforming machinery as the major capital cost drivers. The analysis was based on the following assumptions: 20-year biorefinery lifespan, \$86.52 MT^{-1} feedstock cost, and a liquid fuel cost of \$2.82/gge (\$0.74/lge).

The expense of delivering raw bio-oil and lignocellulosic feedstock, which both restrict the FPH method's potential to benefit from economies of scale, has led to recent research on the logistics around the process. A mixed integer linear programming model is used by Yihua et al. (2014) to contrast two scenarios: one in which the hydrotreated bio-oil is processed in a new, centralized biorefinery in Iowa, and the other in which the biomass is pyrolyzed and hydrotreated at scattered facilities before being processed at an established petroleum refinery in Louisiana. According to the authors' calculations, the new biorefinery scenario produces gasoline with an MFSP of \$1.93/gge, compared to the old refinery scenario's \$3.31/gge. Although the current refinery scenario results in cheaper capital costs, they are more than compensated by the expenses associated with exporting bio-oil.

In contrast to prior TEAs of the fast pyrolysis and hydroprocessing route, Wright et al. (2012) focus solely on the expenses of the bio-oil hydrotreating stage. The trade-offs between using hydrogen generated locally through bio-oil reforming and hydrogen obtained from an external source for upgrading are determined by the authors using a response surface model. The research concludes that the on-site scenario should only be chosen when the market price of hydrogen is high in comparison to that of petroleum, even if it produces the least greenhouse gas emissions due to its slower upgrading rate. The authors also speculate that by restricting upgrading rates, the requirement to adhere to emission restrictions set by policymakers may raise the MFSP of blend stocks obtained from FPH.

Thilakaratne et al. (2014) investigated the economic aspects of the pyrolysis of biomass for the production of transportation fuels. The MFSP was estimated as a function of operational and capital costs using a DCFROR. From their study, the co-generation unit contributes the most to the capital cost, followed by hydrogen production, biomass pyrolysis, and bio-oil upgrading. The major operational expense is the cost of biomass feedstock, which accounts for 45% of the total operating costs. Due to the additional expense of acquiring hydrogen, a design that does not constitute a hydrogen generating unit would result in a higher MFSP. When natural gas is utilized to produce hydrogen instead of the off-gases from the process, the capital investment in the hydrogen generating unit is lowered since the mass flow rate of natural gas in the hydrogen generating unit is significantly lower than the mass flow rate of off-gases. Furthermore, in this case, the co-generation system grows to handle the process's surplus off-gases. This scenario results in a lower MFSP, owing to increased power generation and lower hydrogen plant costs. The co-generation facility is designed to create additional revenue by utilizing the excess heat generated throughout the operation. However, this benefit comes with a cost, which is comparable to introducing a power station to the system. Since the poor quality gas has a lower energy density, the off-gases from the system and NCGs can be re-sold to an external entity at an estimated price of \$20 per 1000m^3 when the co-generation unit is not included. In the absence of a co-generation plant, the process heating demand can be supplied with a smaller boiler costing \$35 million. Considering all of these variables, their analysis shows that eliminating the co-generation plant significantly reduces the MFSP and the TPI.

3.5.3.4 Techno-economics of bio-oil upgrading via gasification

Li & Hu (2016) compared the production of transportation fuels through two different pathways. The first pathway is biomass gasification, and the second pathway is bio-oil gasification. The biomass gasification pathway incorporates the gasification of biomass, syngas cleaning, fuel synthesis, and hydroprocessing. The process is illustrated in Figure 3.2. The second pathway incorporates biomass pyrolysis integrated with bio-oil gasification, followed by syngas cleaning, FT synthesis, and hydrocracking. The process is illustrated in Figure 3.3. Comparing the two pathways, the biomass acquisition cost for the bio-oil gasification pathway is very high because more biomass feedstock is consumed in the process due to low fuel conversion yield. Furthermore, the process complexity of bio-oil gasification makes the process' operation cost high. Li & Hu (2016) therefore concluded that the biomass pyrolysis pathway has higher efficiency of energy conversion than the bio-oil gasification pathway.

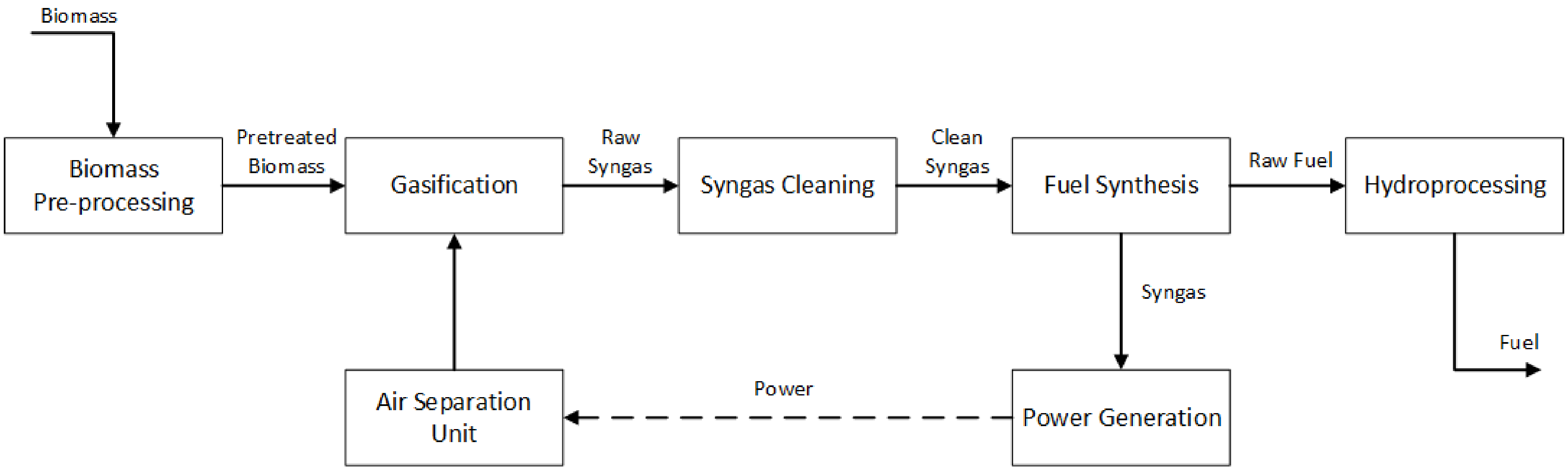


Figure 3.2: Biomass-fuel gasification pathway flow diagram (Li & Hu, 2016)

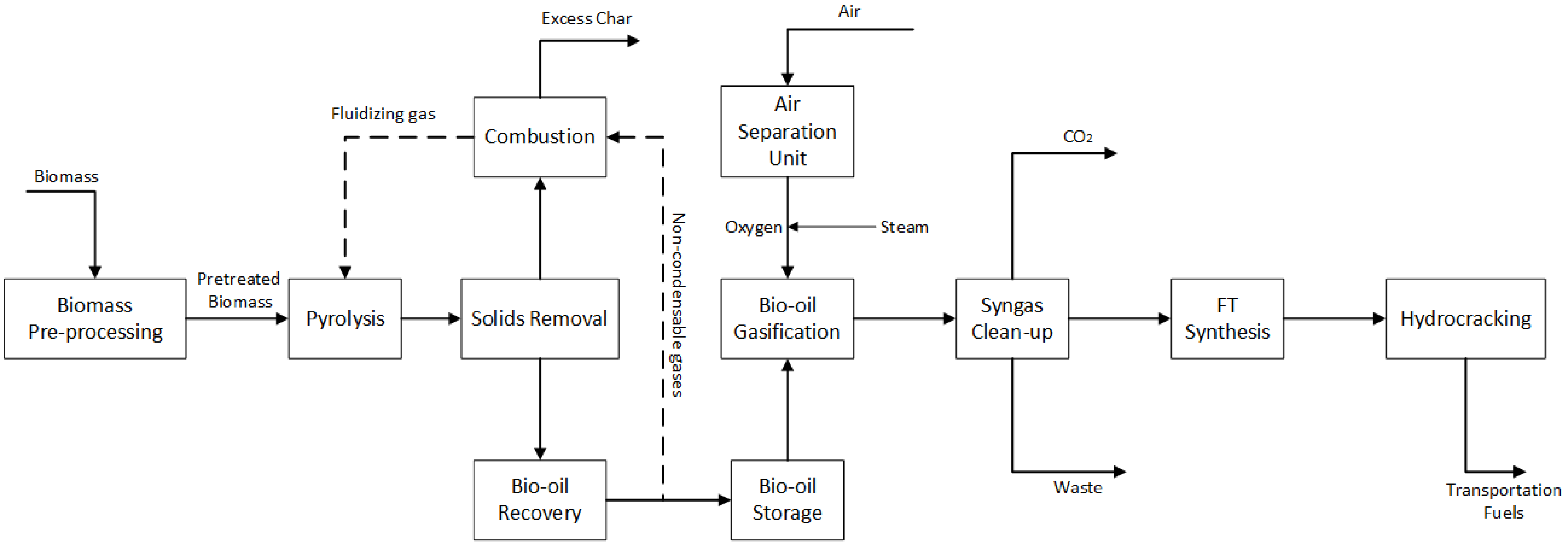


Figure 3.3: Bio-oil-fuel gasification pathway flow diagram (Li & Hu, 2016)

Ramos & Ferreira (2022) reported that the fast pyrolysis route for biomass conversion presented the best results as compared to gasification and direct combustion. Overall, the results from their study have shown that the scenarios with heat recovery have better results than the ones without, which indicates that the drying cost is a major factor for operating plants with biomass feedstocks of high moisture.

3.5.3.5 Techno-economics of integrated fast pyrolysis biorefineries

According to research by Dang et al. (2016), the integrated biorefinery's most lucrative portfolio under the highest historic price levels include upgrading bio-oil to produce bio-based goods, which has higher IRRs. The greatest IRR of 67.9% is attained if bio-based goods are offered to the market at their current high prices, while an IRR of 42.5% is produced at its average selling price. Biofuels and hydrocarbon chemicals, with IRRs of 18.5% and 27.0%, are more lucrative in low bio-based product market pricing conditions. These findings imply that improving the product distributions of an integrated biorefinery based on current market pricing may have substantial economic benefits. According to the findings, the biorefinery's chances of making money are better if it produces bio-based goods than hydrocarbon chemicals or biofuels. These results provide direction for choosing products to lower investment risk under known market conditions.

Zhao et al. (2015) evaluated the economic feasibility of eight different biofuel production pathways from lignocellulosic biomass which include pyrolysis, gasification, fermentation, and liquefaction. The breakeven pricing and cost breakdown of the eight different biomass conversion paths are shown in Figure 3.4. The various production pathways' breakeven prices ranged from $3.11-4.93/gallon of gasoline-equivalent (gge). Among all the biomass conversion processes, the FPH option had the lowest breakeven price. Furthermore, with an NPV of -53.83 million dollars, an IRR of 9.64%, and a benefit-cost ratio of 0.96, the FPH pathway proved to be the most economically viable biomass conversion pathway, followed by the methanol to gasoline pathway with an NPV of -236.3 million dollars and a benefit-cost ratio of 0.78 (Zhao et al., 2015)

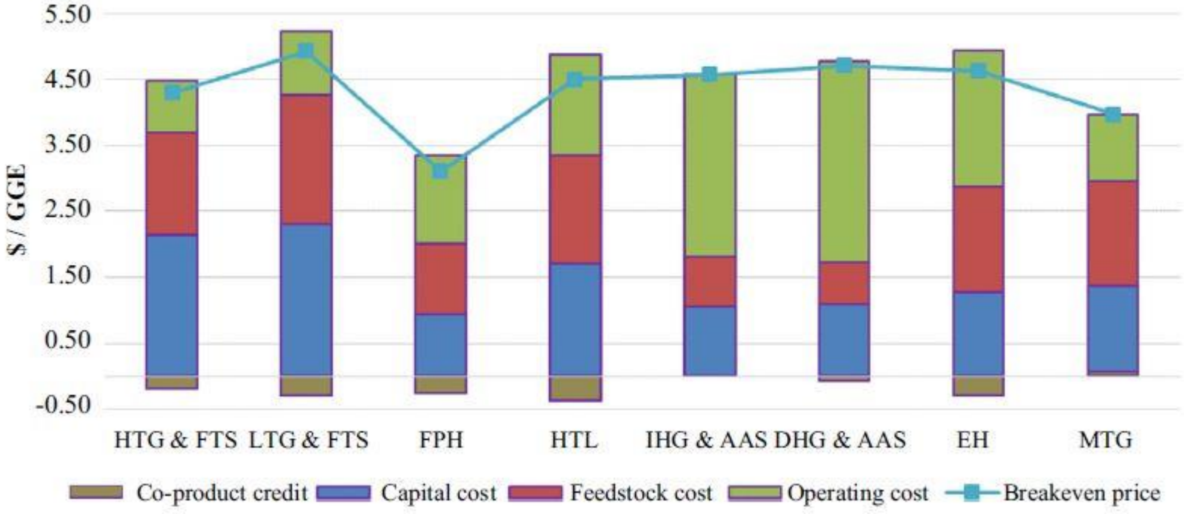


Figure 3.4: Breakeven and breakdown fuel price for cellulosic biofuel pathways. The line indicates the breakeven price level after balancing out the negative co-product credit. Reprinted from (Zhao et al., 2015), with permission from Elsevier

Patel et al. (2022) evaluated the economics of three production scenarios, (i) producing biofuels only, (ii) biofuels and potash fertilizer, and (iii) biofuels, potash fertilizer, and activated carbon. Negative values of NPV for only biofuel production and the biofuel and potash fertilizer scenario were obtained. This indicated that the production pathways were not economically feasible. The biofuels, potash fertilizer, and activated carbon production scenario was the only production pathway that proved to be profitable. The synthesis of activated carbon from spent char after potash fertilizer recovery has remarkably improved the profitability of the plant. However, biorefineries can produce value-added products from process waste to improve the economic feasibility of the process. Patel et al. (2019) evaluated the economic competitiveness of concentrated solar gasification of empty cotton boll handling the same capacity. A comparative analysis was carried out on the two technologies. Concentrated solar gasification produced more liquid biofuels as compared to fast pyrolysis, but potash fertilizer production was approximately 1.6 times higher for fast pyrolysis. The total capital expenditure for setting up a concentrated solar gasification plant was reported to be five times higher than for fast pyrolysis, making fast pyrolysis a more attractive thermochemical conversion technology.

3.5.3.6 Techno-economics of electricity production from fast pyrolysis bio-oil

Pighinelli et al. (2018) compared the economics of producing electricity from a pyrolysis-oil-fired boiler with a bagasse-fired boiler. Sugarcane and ethanol production industries in Brazil use residual bagasse to generate steam for use during the sugar production process and in a boiler-steam turbine system for electricity production. Carpio & Simone de Souza (2017) evaluated the cost of producing electricity from sugarcane bagasse on a plant with a processing capacity of 130 MT of bagasse. Based on their research findings, 3MWh of electricity per ton of sugarcane bagasse with 70% available for export was produced. A total electricity production cost of 60 US$/MWh was estimated in a scenario where 91% of the sugarcane bagasse is used for electricity generation and 9% for second-generation ethanol production. Considering the electricity production efficiency, a bagasse-fired boiler-turbine system is much more efficient when compared to a wood pyrolysis oil-fired boiler-turbine system (Pighinelli et al., 2018). In a study carried out by Pighinelli et al. (2018), 1.32 MWh/ton of wood can be obtained, and only 40% of energy is available for export as a result of high energy consumption processes during the grinding and drying of wood. Pighinelli et al. (2018) estimated the TCI of a tail gas pyrolysis system as US$ 314.4 million, which is higher than the TCI of a fast pyrolysis and gasification facility for electricity production (US$ 273 million) (Li et al., 2015) and biomass pretreatment and pyrolysis plant (US$ 87.4 million) of the same capacity (Carpio & Simone de Souza, 2017).

3.5.3.7 Techno-economics of fast pyrolysis and combined heat and power integrated system

Yang et al. (2018) concluded that integrating a pyrolysis system with a combined heat and power system is a more efficient waste-to-energy recovery technique. In their study, pyrolysis bio-oil was blended with diesel and utilized in a diesel internal combustion engine to provide electricity and the pyrolysis gases were used to fuel a gas engine-based generator. Both engines produced electricity and heat in the form of hot water. According to the economic analysis, the plant's levelized electricity cost was $0.084/kWh, which is within the range of UK electricity costs as determined by the UK government. For the specific facility under consideration, the capital investment was assessed to be $8.26 million per megawatt. The capital cost was the largest part of the levelized cost of energy, according to the breakdown analysis of the production cost. The costs of biodiesel fuel, trash disposal, labour, utilities, plant maintenance, and overheads were then added on. In comparison to product sales, income from feedstock gate fees and renewable incentive payments were more important in offsetting production costs.

3.5.4 Uncertainty analysis

In the context of second-generation biofuel and chemicals production, several uncertainties may be identified that could affect the viability of the project. Uncertainties may stem from the assumptions made during the process of design and model creation, or they may be connected to external characteristics (Hytönen & Stuart, 2011). Analysis of uncertainties may be crucial, especially in process system engineering where circumstances and process variables are constantly changing. As a result, quality control is becoming increasingly important in all process operating plants. However, the uncertainties may be well understood to avoid any unanticipated outcomes that could result in process failure or a loss of revenue.

3.5.4.1 Capital cost uncertainty

Due to variables including fluctuating equipment costs, unanticipated construction circumstances, shifting regulatory policies, and economic instability, TCI estimates can demonstrate considerable variability when contrasted with actual project costs. Royal Dutch Shell observed its capital cost estimate for the project increase from $4 billion to $19 billion when production for a gas-to-liquids plant began several years later (Wood et al., 2012). In another instance, Fulcrum Sierra Biofuels, a gasification and Fischer-Tropsch synthesis firm, increased their estimate of the capital cost for an 11 million gallon per year facility from $120 million in 2011 to $266 million in 2014 (Brown, 2015). Due to a lack of past information, this cost uncertainty is particularly likely to exist for the TCI calculation of a facility using a novel technology approach, for instance, a cellulosic biorefinery. To account for this uncertainty, several techno-economic evaluations of lignocellulosic biorefineries portray the TCI as a probability distribution as opposed to a deterministic point estimate. A cumulative distribution function for economic viability is created by combining the probability distribution with distributions reflecting other factors.

3.5.4.2 Crude oil price uncertainty

The analysis of the crude oil market's dynamics is crucial since it enables the forecasting of the financial markets and the costs of commodities. Because of the historical and economic reasons influencing crude oil prices, there is uncertainty surrounding the pricing of other commodities and instability on a worldwide scale. Consequently, several pieces of research have been carried out in the area, including analyses to get the probability distribution for predicting the future price of oil (Shih & Yu, 2009; Yuan et al., 2014). According to the literature, a Gaussian distribution cannot adequately reflect the empirical distribution of crude oil price returns (Shih & Yu, 2009; Yuan et al., 2014). As an alternative, Yuan et al. (2014) developed a stable Levy distribution, which more accurately captures the distribution returns for this variable.

3.5.4.3 Uncertainties of biomass supply chain

1. Biomass Availability

There are several biomass harvesting seasons, which is one factor that accounts for the biomass's availability (Martinkus et al., 2018). According to Lim et al. (2019), the unpredictable pattern of biomass availability is caused by a variety of factors (such as seasons, logistics, etc.) that would need accounting for alternate options (such as importing biomass from outside sources) in the event of a biomass shortage. This will increase the need for logistics, which will further lower the price competitiveness of products generated from biomass. El-Halwagi et al. (2013) took into account the aforementioned potential alternatives by supposing that 200 tonnes per day of biomass are available locally. If additional biomass is required, it will be transported from other sources, which will increase the cost of transportation. Tanzer et al. (2019) asserted that the chosen biomass must be plentiful to satisfy the need. Researchers have discovered that the worsening climate change has had a severe negative impact on biomass agriculture, especially by 2100 (PATERSON et al., 2017). Climate change will have an impact on the dispersion of plant species, including biomass, according to Paterson et al. (2015). As a result, they conducted climate projections as part of their study to look at how climate change may affect the growth of oil palm. The effects of the availability of biomass being unclear are further exacerbated by this.

2. Biomass quality

Each biomass attribute has an impact on the final product or the biomass conversion process, such as physical characteristics (which affect the logistics and segregation of the conversion process), elemental characteristics (which affect the heating value and NOx, SOx, and CO emission), etc (Van Ommen & de Jong, 2014). The significance of researching the qualities of biomass for the conversion process was highlighted by Lim & Lam (2016). They suggested looking at the issue more closely, i.e., the ideal biomass quality needed for each technology, as opposed to examining the suitability of each feedstock in each technology. The quality of biomass is the most critical characteristic that will eventually affect the economics of biorefineries, according to Baral et al. (2019). Their findings show that using high-quality biomass can improve economic feasibility even when a larger initial expenditure is required. Additionally, the quality of the biomass has a considerable impact on its applicability for different conversion processes (such as gasification, anaerobic digestion, etc) (Kataki et al., 2015). Lim et al. (2019) highlighted the fact that a wider range of biomass quality will cause more variation in both technological performance and product production. For instance, lignin decomposes at a rate of around 0.1 wt.%/℃ under identical pyrolysis conditions, but hemicellulose and cellulose decompose at a rate of 1.0-2.8 wt.%/℃ (Bayu et al., 2019). This results in the production of several products, such as biochar and bio-oil. Product yields are the primary determining element in the total economic viability of the biomass conversion process (Tanzer et al., 2019). In addition to affecting product output, Bussemaker et al. (2017) noted that reducing the moisture content of biomass would result in a 40% cost decrease in terms of both transportation and drying costs (i.e., reducing the amount of moisture of biomass from 60% to 40%). Before the biomass-based business is commercialized, it is necessary to have a more thorough understanding of the quality of the biomass and the operational circumstances.

3. Total transportation cost

One of the essential elements of successful supply chain management is the efficient conveyance of the feedstock or product to the intended destination. The length of the voyage, the cost of travel based on distance, and the weight of the transported biomass are just a few of the variables that affect overall transportation costs (Ashtineh & Pishvaee, 2019). One of the biggest challenges in the biomass supply chain is logistics management since the high-moisture and low-density biomass requires more expensive transportation (How et al., 2019). Numerous studies have been undertaken by researchers to show the major effect of the aforementioned. For instance, Bussemaker et al. (2017) showed that reducing the moisture levels of biomass from 60% to 30% lowers the entire transportation cost (by around 40%). Additionally, An (2019) investigated the ideal biomass transportation schedule and found that using fully loaded trucks would result in increased transportation efficiency. Even though it has been asserted in several works that the fuel price fluctuation is unaffected by logistics choices (i.e., mode of transportation) (How et al., 2019), this does not mean that the biomass industry cannot become unprofitable if the income is no longer adequate to cover the high transportation costs and other investment costs.

4. Raw material and product market price

According to Gui et al. (2008), the cost of edible feedstocks (soybean and rapeseed oil) accounts for roughly 70–80% of the total cost of producing biodiesel. This fact motivates researchers to consider potential combinations of bioethanol with biodiesel to maximize profitability. Compared to food feedstocks, biomass is a more affordable feedstock. For instance, it was discovered by Mohammed et al. (2019) that the cost of biomass accounts for 8% of the overall operating cost.

The majority of studies included fixed prices for the product when conducting techno-economic analyses (for example, AlNouss et al. (2019) performed an economic analysis on biomass-based poly-generation systems with the fixed cost assumptions for all considered products; How et al. (2019) evaluated the financial performance of the proposed biomass corridor with the incorporation of static pricing for the involved products). However, the cost of materials for goods often varies over time. Khatiwada et al. (2016) indicated that the overall process feasibility has been greatly impacted by the sharp fluctuations in the price of power produced from biomass. In agreement, AlNouss et al. (2019) compared the total supply chain costs for different end-products of the biomass conversion process and discovered a noteworthy finding whereby the product's market pricing (for example, ammonia is priced at $ 375/tonne while liquid fuels are priced at $775/tonne) influences the supply chain's financial outcome. In addition, the final product's quality, such as its purity or the elemental makeup, plays a significant part in determining the product's market price. For instance, Lin et al. (2013) emphasized that the chemical nature of biofuels would affect the product's final profitability due to the cost of raw materials as well as the quality of biofuels. Therefore, using a set price in the techno-economic study is less preferable.

5. Wages

The cost of labour has a significant impact on how technically efficient bioenergy production is (Bakhtiar et al., 2020). According to Mohammed et al. (2019), labour costs account for around 48% of overall operational expenses. Therefore, it shouldn't be overlooked when doing the techno-economic evaluation. Additionally, the overall cost is impacted by the number of employees. According to Lo et al. (2021), elements that might effect employee compensation include the geographic location of the company, demand for the profession, prior job experiences, and educational level. Furthermore, it was noted by Lo et al. (2021) that the government is a significant factor in the amount of salaries provided to employees (i.e., laws and policies regarding minimum wages and allowance). The use of sophisticated mechanisms and artificial intelligence might reduce the previously indicated technical efficiency by Bakhtiar et al. (2020). In contrast to artificial intelligence, which is trained to respond to various situations, human weariness can impair judgment and result in tiny errors, especially in a setting where long hours are worked. There is still research employing artificial intelligence to analyze the biomass process, even though the direct use of mechanization and AI in the biomass business is still in its infancy. For instance, Flores-Asis et al. (2018) investigated the predictions of biogas generation through anaerobic digestion using artificial neural networks, and then investigated the effects of different input factors (such as pH, organic load, etc.) on the anaerobic process.

3.5.5 Other factors in techno-economic analysis

In addition to the aforementioned factors, additional factors may have an impact on the likelihood of assessing and reducing the risk provided by the factors.

3.5.5.1 Regulatory risk

Government policies are crucial in making sure the projected biomass supply chain can be industrialized. For instance, government policies (such as tax breaks and requirements for renewable fuels) increased the output of bioethanol from nothing in 1980 to almost 60.57 billion litres in 2016 (Herath & Tyner, 2019). Additionally, numerous governments have started several legislation and programs to encourage the use of renewable sources of energy (Lo et al., 2021). The implementation of these rules and guidelines would expose the biomass industries to regulatory risk, putting stakeholders at risk of noncompliance and increasing operating costs (How et al., 2019). As a firm grows, it becomes increasingly difficult to create and implement compliance initiatives, and failing to do so might result in severe penalties, costly security breaches, and even significant public embarrassment (Lo et al., 2021). Furthermore, the top-down strategy (from higher levels like the federal government to lower levels like the state government) during policy development to implementation is judged inefficient since it takes too long to get permission, which causes project delays, greater costs, and even cancellation (Yatim et al., 2016). According to How et al. (2019), stakeholders must be educated and trained on the many standards they must follow to reduce the impact of regulatory risk.

3.5.5.2 Company's profile

The customer's decision to purchase from a company is influenced by the reputation or profile of the business. Investors are still hesitant to make investments in the biomass business, even though a lot of current activities and research are being done to study the techno-economic viability of processes that convert biomass into value-added products. This is mostly because investing in biomass sectors has a high financial risk, making many people wary of doing so (Bufoni et al., 2016). Salm (2018) stated that a lack of investors makes it difficult to acquire essential facilities, technology, and equipment. Due to the intense competition with conventional fuels, the local fuel price also has a considerable impact on the economics of biofuels (Tanzer et al., 2019). According to stakeholders who participated in interviews, insufficient economic conditions and high technical investment costs are the main barriers to expanding the use of biomass (Vukasinovic et al., 2019). The use of renewable energy sources, such as hydrogen, is still hindered by several significant obstacles, including the fact that its costs are still unaffordable and that it is not as generally accepted as other conventional fuels (Lo et al., 2021).

3.5.5.3 Big Data and predictive aspects

Due to intense competition in the biomass business, knowledge and thorough supply chain analysis might give an unfair advantage over rivals. Waller & Fawcett (2013) argued that through deepening functional prediction, data-driven optimization, analytical methods, data analysis, as well as other supply chain analytics, Big Data may transform supply chain management. The power of Big Data may also speed up operations in strategic sourcing, supply chain network design, product creation, sales forecasting, procurement, production, storage, and logistics management (Wang et al., 2016). Hazen et al. (2014) asserted that analytical specialists are needed for the adoption of such technologies to test, monitor, and manage data quality to deliver beneficial supply chain analytics. Due to the frequent inaccuracies in data created by the supply chain, the work also offered a viewpoint for regulating the quality of the data employing statistical process monitoring approaches.

The ability of Big Data to synthesize biomass supply chain networks offers one of the most attractive benefits: the ability to construct biomass networks optimally while taking uncertainties into account (Hu et al., 2017). Big Data may be used to accurately perform TEA for biomass supply chains. For instance, research by Vondra et al. (2019) examined the viability of biomass digestion treatment technology along the supply chain using Monte Carlo modelling, decision trees, and neural networks. Next, De Laporte et al. (2016) also examined how Big Data may support precision agriculture inside the biomass supply chain and have a favourable impact on supply chain architecture and feedstock pricing. The study looked at information such as biomass pricing, supply chain architecture, location, and quality of biomass supplies and used a biomass supply chain case study in Ontario to illustrate their point of view. But another difficulty is acquiring Big Data from the supply chain itself. To deliver Big Data on geographical data based on cyberinfrastructure and e-science, a CyberGIS system is presented by Hu et al. (2017) as a solution. A system like this is advantageous because it makes Big Data from the biomass supply chain accessible to all academics, allowing them to investigate biomass network optimization at a large scale, conduct uncertainty analysis, and give in-depth analysis with geodesign characteristics. There is exciting research potential with the combination of Big Data and the biomass supply chain.

3.6 Challenges and prospects of biomass pyrolysis

The advantages of biomass pyrolysis and associated products in terms of economy and the environment have previously been established. There has been a lot of research done on the pyrolysis of biomass to produce useful products, both on a laboratory and demonstration scale. The industrialization and commercialization of biomass pyrolysis are being supported by a large number of businesses worldwide. However, biomass pyrolysis is only beginning to be commercialized, and engineers and researchers still face several obstacles in the next phase (Umar et al., 2021).

Pretreatment is crucial for the creation of high-quality products because of the raw biomass's high moisture content, nonuniformity, and strong molecular structure. However, the need for significant amounts of energy, additives, and specialized equipment results in extremely high pretreatment costs. To validate the cost-competitiveness of biomass pretreatment on an industrial scale, the advantages of biomass pretreatment should be contrasted with pretreatment costs (Mong et al., 2021).

Although using bio-oils can help the environment by lowering CO_2 emissions, their poor quality, which includes thermal instability, high acidity and viscosity, and low heating value prevents them from being utilized in drop-in fuel applications (Zhang et al., 2021). For instance, pyrolysis bio-oil has a water content (15–30 wt.%) that is significantly higher than petroleum crude oil (1 wt.%). In addition to the oil's much-decreased energy level, a high water content might interfere with engine ignition. The oxygen concentration in fast pyrolysis bio-oil is also substantially higher (35–50 wt.%) than that of petroleum crude oil (1 wt.%). Because of its high oxygen content, bio-oil mixes poorly with fossil fuels but dissolves in polar solvents like acetone and methanol. In addition, bio-oil's high oxygen content causes it to be unstable and very acidic or corrosive, which has an adverse effect on how the oil is transported and stored (Saber et al., 2016). Therefore, upgrading treatment is required before using bio-oil as a drop-in fuel.

Techniques for upgrading bio-oil have been developed, which include hydrotreatment, steam reforming, catalytic cracking, and supercritical fluids treatment. When crude bio-oil is hydrotreated, oxygen is removed through the formation of water, while N and S are removed as NH_3 and H_2S, respectively. It should be emphasized that since the majority of bio-oils don't have high concentrations of N and S, hydrotreatment of crude bio-oil is effectively hydrodeoxygenation, which eliminates the oxygen from the crude bio-oil. Although catalytic hydrodeoxygenation has been widely shown to be successful and shows potential for upgrading bio-oil, the main barriers to its utilization are the high H_2 consumption, coke production, and limited catalyst lifetime (Zhang et al., 2021).

Using steam reforming, Lan et al. (2010) upgraded the bio-oil obtained from fast pyrolysis of rice husk, obtaining the greatest H_2 yield of 75.88% at 700–800 °C and a steam/carbon molar ratio of 15–20. The main difficulties in steam reforming bio-oil are coke formation, catalyst deactivation, high reaction temperature, and high operating costs (Saber et al., 2016).

At temperatures above 350 °C and relatively high pressures (up to 14 MPa), oxygen is removed from bio-oil by the creation of H_2O, CO_2, and CO during the process of catalytic cracking, which is a method of upgrading bio-oil (Xiwei et al., 2012). In a study by Zhao et al. (2015), camelina oil was upgraded using catalytic cracking over a Zn/ZSM-5 catalyst at 550 °C; however, as is a common drawback of upgrading bio-oil using catalytic cracking, there was significant coke formation during the process, which could deactivate the zeolite catalyst.

The energy content of bio-oil may be increased by supercritical fluid processing, which also significantly lowers the oil's acid number, heteroatom concentration, and viscosity (J.-H. Lee et al., 2019). More intriguingly, after supercritical fluid treatment, the properties of upgraded bio-oil may resemble those of petroleum oil (Saber et al., 2016). Nevertheless, the high cost of the solvent and the generally high temperature/pressure are two major technical obstacles to the industrial-scale application of this upgrading approach.

Despite these difficulties, pyrolysis is typically thought of as a cost-effective method in thermochemical platforms (Sharifzadeh et al., 2019). However, considering the current state of the technology, further work is required to bring pyrolysis technology to a stage where it is also competitive with technologies powered by fossil fuels (Arbogast et al., 2012, 2013). Additionally, there is still a need for thorough techno-economic studies to assist the research community in focusing their future efforts on the main cost factors that are most likely to have a beneficial influence on the process economy as a whole (Zacher et al., 2014). In an integrated biorefinery, value-added co-products in particular may be taken into account. Hu et al., (2016) observed that the co-production of biochemicals, such as aromatics and olefins, and biomaterials, such as bio-cement, is expected to stay viable in 100% of scenarios tested, but only found that biofuel production was profitable in 18% of the situations. Another approach that might assist improve the overall economics by lowering production costs and the environmental impact is to utilize the existing infrastructure wherever it is technically and logistically possible to do so (Talmadge et al., 2014). To determine the best process configurations, more research is required. For instance, a recent study (Zhang & Wright, 2014) discovered that fast pyrolysis bio-oil upgrading is more economically advantageous, contrary to a prior study's (Brown et al., 2012) observation that the phase-separated bio-oil upgrading was economically more favourable. This could be caused by the various technologies and finished products that were taken into account.

Hu & Gholizadeh (2019) pointed out that the biomass pyrolysis process's high requirements (such as low moisture content feedstock, etc.), lack of adequate kinetic and reaction processes, and other factors make it difficult to commercialize. The cooperation of all players is crucial for the biomass supply chain to be viable. One of the factors holding back the development of biomass usage, according to stakeholders interviewed by Vukasinovic et al. (2019), is a lack of knowledge about biomass. This will ultimately have an impact on how harvesters and consumers behave. Therefore, studies on the valorization of biomass should be conducted in greater depth, with a focus on the impact of biomass quality on the yield and quality of the end product. Additionally, qualitative approaches (such as focus groups, interviews, questionnaires, and so on) may be used to completely understand the perspective and concerns of stakeholders. In addition, risk analysis for the biomass supply chain may be carried out to give investors a complete understanding of the financial results associated with the examined biomass supply chain.

3.7 Conclusions

The review identified several factors that affect the economic performance of fast pyrolysis systems, such as capital costs, feedstock acquisition costs as well as OM costs. The average selling price of pyrolysis oils is greatly dependent on the selling price of the by-products, feedstock price, fixed capital costs, and product yields. Uncertainties and risks associated with the biomass conversion process that hinders further commercialization of the biomass industry has been discussed comprehensively. Overall, this review showed that there is room for the deployment of alternative transportation fuels, but further development of both technology pathways and energy plans is still required.

CHAPTER FOUR: MICROWAVE-ASSISTED PYROLYSIS OF PINE SAWDUST (PINUS PATULA) FOR BIO-OIL PRODUCTION AND EVALUATION OF ITS CONVERSION INTO BIODIESEL

4.1 Chapter overview

This chapter aims to thermochemically convert pine sawdust to crude bio-oil via the MAP technique with subsequent bio-oil transesterification. ASTM D410-84, D3173-5 and D5373 standards were followed in the characterization of the feedstock and pyrolysis products. The thermal degradation behaviour of pine sawdust was studied using thermogravimetric analysis. The components in the bio-oil organic phase were upgraded to fatty acid methyl esters via the transesterification process. Compositional analysis of the organic phase and the fatty acid methyl esters were analyzed using Gas Chromatography–Mass Spectrometry (GC-MS) and Fourier Transform-Infra Red (FTIR). The thermal degradation behaviour of pine sawdust showed three distinct phases of weight loss. These stages include the drying stage (30-200 °C), the devolatilization stage (200-450 °C), and the char formation stage (>450 °C). The process yielded 42.28 wt.% of bio-oil, constituting 24 wt.% and 76 wt.% of the organic and aqueous phases, respectively. GC-MS and FTIR compositional analysis identified various organic compounds and functional groups with phenolics contributing a greater percentage. Transesterification improved the bio-oil properties by converting the organic acids and oxygenated compounds to methyl esters with a 510.05 mg/L concentration. The bio-oil has proven to be a promising sustainable raw material for the production of biofuels and value-added biochemicals.

This chapter is based on an original research paper published in the journal Biofuels. A microwave-assisted pyrolysis experiment was designed to produce bio-oil, which was further upgraded to biodiesel, fulfilling objectives 1 and 2.

Makepa, D. C., Chihobo, C. H., & Musademba, D. (2023). Microwave-assisted pyrolysis of pine sawdust (Pinus Patula) with subsequent bio-oil transesterification for biodiesel production, Biofuels, DOI: https://doi.org/10.1080/17597269.2023.2239543

4.2 Introduction

The unreliability of fossil fuels, as well as the challenges related to their use, has prompted a search for cleaner energy sources. Biomass is a promising sustainable renewable energy source that can be used as a feedstock in thermochemical conversion processes. Biomass can be thermochemically transformed into biochar, bio-oil, and combustible gases (Ayub et al., 2022). The timber industry in Zimbabwe generates biomass waste of over 70,000 tons annually. Due to rising industrialization and urbanization, the quantity of biomass waste generated is anticipated to quadruple by 2030. The need for timber supplies has increased as a result of the rising demand for residential housing in Zimbabwe, while the regional demand has been steadily growing over time (Makepa et al., 2023b).

The harvesting and processing of timber produce approximately 45% offcuts and chips, 10% bark, and 5% sawdust. The current sawdust disposal practices include dumping at municipal landfills, sawmills, plantation property, and open-air incineration. Open-air burning as a method of disposal results in the release of particulate matter and anthropogenic air pollutants that affect air quality and public health (Okedere et al., 2017). The outdoor stockpiles produce a wood residue leachate containing high levels of metals and dissolved organic matter during the wet season. The leachate is potentially hazardous and toxic to water bodies that receive the runoff. Commonly identified organic compounds in wood leachate including phenols, acid resins, tannins, volatile fatty acids, and tropolones contribute to the observed toxic effects of the leachate (Liu et al., 1999). Besides its toxic effects, the wood leachate can contribute to low pH, acidity and oxygen depletion in the receiving water. An urgent need exists for a waste processing technology that can effectively eliminate the environmental problems and public health risks associated with current disposal practices.

Research and development into various thermochemical, biochemical and chemical conversions of biomass into biofuels and value-added materials have been done by several authors (Bharath et al., 2020; Costa et al., 2016; Khelfa et al., 2020; Makepa et al., 2023b, 2023a; Naureen et al., 2015; Sınağ et al., 2011).

Biomass pyrolysis has emerged as a viable option for converting biomass to a composite mixture of organic compounds, biochar fractions, and gas. Pyrolysis is a thermal decomposition process that involves the breakdown of carbonaceous materials by heating them in an inert atmosphere.

The process can be classified into three categories based on the heating rate and biomass retention time, namely flash, fast, and slow pyrolysis. The biomass pyrolysis process can convert between 60-75 % of the original biomass waste into bio-oil, which can be utilized in both internal combustion engines and turbines. Bio-oil can be economically transported to biorefineries located within a radius of 250 km from the bio-resources for processing to obtain value-added products (Pootakham & Kumar, 2010).

An alternative to conventional heating commonly used during fast pyrolysis is the use of microwave radiation. The process is commonly known as MAP. This process has been proven to be fast and energy-efficient. Furthermore, current research reported that MAP technology is easy to use and control. MAP produces high-quality liquid products that can be utilized as feedstock in the manufacture of biochemicals and biofuels sustainably, and the energy balances for the process are favourable (Mutsengerere et al., 2019). Uniform heating in MAP permits the direct utilization of large-sized particles as feedstock (Fernández et al., 2009). Microwave-absorbing agents such as silicon carbide, activated carbon, and biochar are normally added to facilitate heating in MAP processes because not all materials can absorb microwaves.

The major obstacle which limits the application of bio-oil is its instability. Bio-oil constitutes a high percentage of oxygenated compounds, making it prone to oxidation and degradation. Additionally, bio-oil is comprised of large amounts of carboxylic acids, which can cause corrosion and fouling in processing equipment. To counter these effects, various upgrading techniques have been developed to reduce the acidity of bio-oil. The transesterification of bio-oil has proven to be a cheaper and viable route to reduce the acidity of bio-oil. Transesterification involves reacting the carboxylic acids in bio-oil with an alcohol to form methyl esters (Pinheiro Pires et al., 2019). This process reduces the acidity of bio-oil and produces a more stable product that is easier to store and transport.

Previous studies have reported the thermochemical conversion of pine sawdust to bio-oil through catalytic liquefaction (Cheng et al., 2017) and pyrolysis (Nomanbhay et al., 2017; Xiong et al., 2023; Zhang et al., 2016). One of the major drawbacks of conventional pyrolysis methods is the low heating rates, which may lead to the formation of unwanted by-products and reduced conversion efficiencies. This study focuses on the application of microwave heating, which offers faster heating rates and improved product quality. The main challenge in commercializing pyrolysis biorefineries is the high costs associated with bio-oil upgrading techniques. However, there is a need to develop cost-effective bio-oil upgrading methods. Extensive research has been done on transesterification for biodiesel production using vegetable oils, but there has been no research on its application to pyrolysis bio-oil. The objective of the current research was to examine the use of MAP of pine sawdust for the production of bio-oil, followed by transesterification to produce biodiesel. The obtained products were subjected to physicochemical characterization, FTIR Spectroscopy, and GC-MS analysis. The pyrolytic bio-oil obtained from the MAP process was used as feedstock for the transesterification process to produce biodiesel.

4.3 Materials and methods

4.3.1 Sample collection and preparation

The study utilized pine sawdust collected from selected sawmills in the eastern region of the country. To ensure uniformity in particle size distribution for further analysis, the feedstock was passed through ISO Retsch test sieves with a mesh size of 2 mm in accordance with ASTM D 410-84. This process was necessary to eliminate oversized wood chips in the pine sawdust. The samples utilized in this study are shown in Figure 4.1.

Figure 4.1: Pine sawdust samples

4.3.2 Physicochemical characterization

The physicochemical characterization of pine sawdust before using it as a feedstock is crucial. The modified procedure (ASTM D3173-5) was used to conduct the proximate analysis, while the ultimate analysis was performed using the Thermo Scientific Flash 2000 Organic Elementary Analyzer and based on ASTM D5373 (2014).

4.3.3 Thermogravimetric analysis (TGA)

The Setaram Simultaneous Thermal Analyzer Labsy Evo-TG-DSC 1600 was utilized to conduct a thermogravimetric analysis of pine sawdust. An alumina crucible containing approximately 25 ± 0.5 mg of pine sawdust was heated at a rate of 5 ℃ min^{-1} from ambient temperature to 600 ℃, while the weight loss was recorded as a function of temperature and time. To provide an inert atmosphere, nitrogen gas with a purity of 99.999% and at a flow rate of 100 ml/min was used during the non-isothermal decomposition process.

4.3.4 MAP experiment

The MAP experiments of pine sawdust were performed using a modified Defy microwave oven, model DMO 356, with an operating frequency of 2450 MHz and a rated microwave output of 950 Watts. The microwave had a cavity volume of 42 litres. As shown in Figure 4.2, a 500 ml three-neck borosilicate reactor was used, and in each experimental run, 100 g of pine sawdust and 10 g of activated charcoal were placed into the reactor. The reactor was purged with helium at a flow rate of 3 LPM to maintain an inert atmosphere. The samples were then subjected to microwave heating at maximum power for 30 minutes. During the pyrolysis process, volatiles were produced and passed through a condensing system that utilized water as a coolant. Resultantly the condensable compounds condensed from the gaseous vapour as bio-oil which was collected in a volumetric flask. At the end of the experimental run, the yield of the bio-oil, biochar and non-condensable gases was calculated on a mass basis. A pictorial view of the experimental setup and the bio-oil samples are shown in Figures 4.3 and 4.4, respectively.

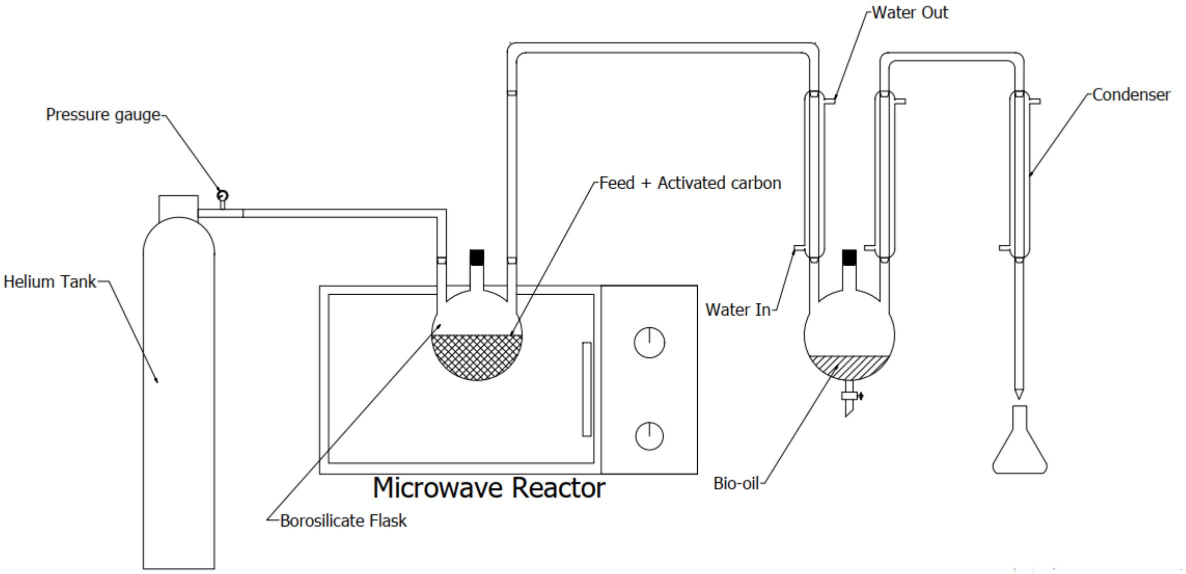


Figure 4.2: MAP experimental setup

Figure 4.3: Microwave-assisted pyrolysis experimental setup

Figure 4.4: Bio-oil samples

4.3.5 Crude bio-oil phase separation

The crude bio-oil produced from the pyrolysis reaction was stored overnight at 4 ºC, followed by centrifugation using a globe centrifuge, model HKSC 220 at 6000 rpm for 30 minutes to promote phase separation. After centrifugation, the bio-oil aqueous phase which was on top was separated from the heavy organic phase at the bottom. The separated fractions were weighed and their weights were expressed as percentages of the original sample.

4.3.6 Characterization of bio-oil

The water content, ash content, viscosity, total acid number (TAN) and flash point of the bio-oil were evaluated. The water content of the bio-oil was determined according to ASTM D4377 using a BIOBASE Coulometric Karl Fischer Titrator. The ash content of the bio-oil was determined according to ASTM D482. The viscosity was determined according to ASTM D445 using a Shambavi Impex Saybolt Viscometer. The TAN was determined by titrating bio-oil in a solution of water, isopropyl alcohol, and toluene (volumetric ratio of water: isopropyl alcohol: toluene = 1: 99: 100) with 0.1 M KOH isopropyl alcohol solution to an end-point of pH 11 (ASTM D664). A Corning 320 digital pH meter was used to determine the pH of the bio-oil sample. The bio-oil density was determined using ASTM D4052 standards. The Cleveland Open-Cup Flash Point

Tester was used to find the bio-oil's flashpoint (ASTM D92–18). The pour point of the bio-oil was measured according to ASTM D97-17b. All the experimental analyses were done in triplicate, with average results reported.

4.3.7 Upgrading bio-oil via transesterification

Transesterification is one of the methods used to upgrade bio-oil. Transesterification converts the organic acids in bio-oil to esters. The chemical reaction occurring during transesterification reduces the viscosity and acidity of the bio-oil while at the same time increasing the volatility and heating value. The transesterification of bio-oil was performed by reacting 20 g of bio-oil with 50 % w/w of ethanol in the presence of 2 wt.% sulphuric acid as a catalyst. The mixture was refluxed for 240 minutes at 60 ºC using a BIOBASE RE-501 Rotary Evaporator. After the transesterification process, 0.1 N KOH was added to the reaction mixture to separate methanol and the unreacted catalysts, followed by decanting and filtration. The transesterification of bio-oil is guided by Equations 4.1-4.5 (Adeniyi et al. 2019). The upgraded bio-oil was characterized using GC-MS. Figure 4.5 illustrates the procedure followed in the transesterification of bio-oil.

Oleic acid ($C_{18}H_{34}O_2$) + Methanol (CH_3OH) ↔ Methyl-Oleate ($C_{19}H_{36}O_2$) + water (H_2O) (4.1)

Palmitic acid ($C_{16}H_{32}O_2$) + Methanol (CH_3OH) ↔ Methyl-Palmitate ($C_{17}H_{34}O_2$) + water (H_2O) (4.2)

Linoleic acid ($C_{18}H_{32}O_2$) + Methanol (CH_3OH) ↔ Methyl-Linoleate ($C_{19}H_{34}O_2$) + water (H_2O) (4.3)

Acetic acid ($C_2H_4O_2$) + Methanol (CH_3OH) ↔ Methyl-Acetate ($C_3H_6O_2$) + water (H_2O) (4.4)

Formic acid (CH_2O_2) + Methanol (CH_3OH) ↔ Methyl-Formate ($C_2H_4O_2$) + water (H_2O) (4.5)

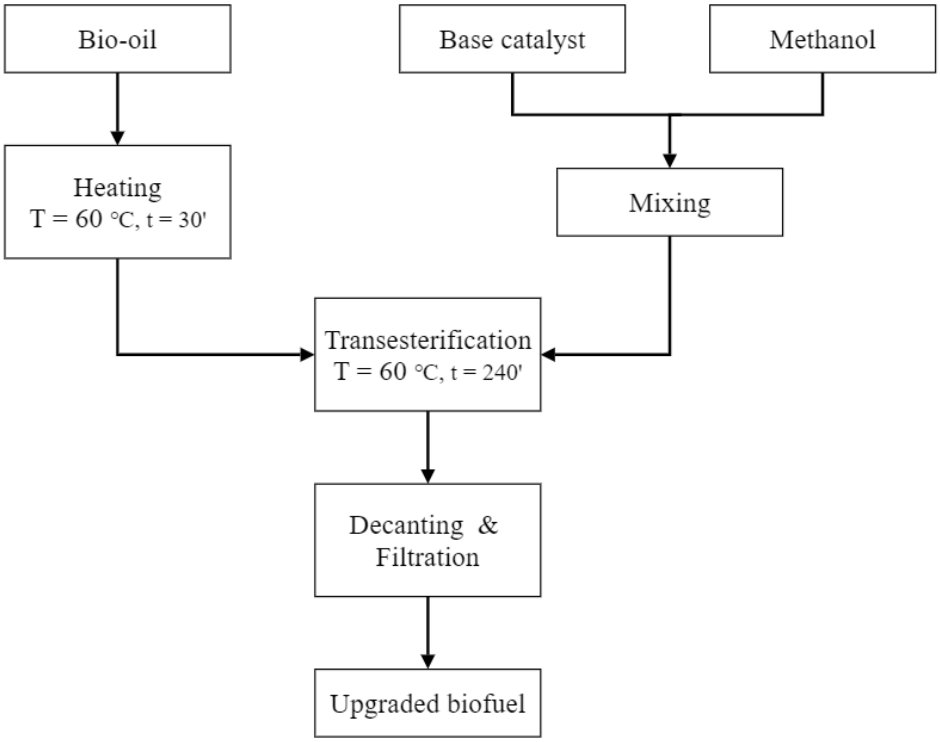


Figure 4.5: Transesterification procedure for upgrading bio-oil

4.3.8 GC-MS compositional analysis

The GC- MS analysis was carried out in a high-performance Shimadzu GC-MS QP2010 Ultra. For the bio-oil sample, the analysis complied with ASTM methods D5134, D6729, D6730 and D6733 which use single-column GC to group the hydrocarbon components by structure. A splitless injection mode was used to introduce bio-oil aliquots of 1µL into the column. A 30 m long DB-5MS capillary column with an internal diameter of 0.25 mm and 0.25 µm film thickness was used. The oven's initial temperature was set to 50 ℃ and held for 1 minute and then ramped to 310 ℃ at 20 ℃ min^{-1} and held for 10 minutes. The carrier gas utilized in the analysis was helium, which was maintained at a constant pressure of 93.17 kPa and a consistent flow rate of 1 ml/min throughout the experiment. For the biodiesel sample, the EN 14103 standard that specifies a GC method for the determination of the fatty acid methyl ester content in diesel fuel was employed. By comparing the mass spectra obtained with the ones in the NIST14 Mass Spectral Library, the chemicals in the bio-oil were identified.

4.3.9 FTIR analysis

An INFRALUM FT-12 FTIR by Lumex Instruments was utilized to conduct Fourier Transform Infrared (FTIR) Spectroscopic analysis on the bio-oil samples at room temperature. The purpose of this analysis was to identify the functional groups present in the bio-oil. The scanning range for the analysis was set at 400-4000 cm^{-1} wavenumbers.

4.4 Results and discussion

4.4.1 Pine sawdust properties

The characterization of pine sawdust is important to check its suitability for thermochemical conversion. The proximate and ultimate analysis results are presented in Table 4.1. The high volatile matter (76.39 wt.%) is mainly due to the thermal decomposition of hemicellulose in the pine sawdust. Bio-oil production is enhanced by the presence of volatile matter in the feedstock (Abnisa et al., 2013). The highly volatile matter improves volatility and reactivity, essentially required for liquid fuel production (Omar et al., 2011). The volatile matter of pine sawdust is comparable to other biomass feedstock materials as shown in Table 4.1. A low ash content of 2.08 % was found in the pine sawdust is a desirable characteristic. Generally, a low ash content is associated with a low alkali metal content. Alkali metals found in ash have been reported to act as mediators in pyrolysis depolymerization pathways, altering the composition of pyrolysis products (Mullen & Boateng, 2008). The deviation in the comparative results in Table 4.1 is mainly due to the differences in the physical environment (e.g., climate and soil) in which the biomass was grown. The desired characteristic of biomass thermal pyrolysis is the highly volatile matter with low ash content (Parascanu et al., 2017). The pyrolytic conversion efficiency and heating values of the derived liquids are greatly influenced by the moisture content of the biomass (Eke et al., 2020). The pine sawdust has a moisture of 7.29 %. This low moisture content feedstock is due to its natural solar drying at the dump site.

The elemental analysis showed that pine sawdust has a high carbon content of 51.6 %. The nitrogen and sulphur content were found to be 0.34 % and 0.02 % respectively. The low nitrogen and sulphur content implies that the thermochemical conversion of pine sawdust is thus not likely to produce noxious NO_x and SO_x emissions to the environment. The H/C of pine sawdust was found to be 1.20 and comparable to other biomass materials (Du et al., 2011; Mullen & Boateng, 2008;

Omar et al., 2011). A high H/C molar ratio (greater than 1) for biomass implies that the resulting bio-oil will have a higher HHV and higher yield of liquid products (El Bassam, 2010). The O/C of pine sawdust was found to be 0.62. The O/C molar ratio was comparable to other biomass materials (Mullen & Boateng, 2008; Omar et al., 2011), except for microalgae which had a low oxygen content (Du et al., 2011). Low O/C ratios (less than 0.2) favour the production of biochar with little bio-oil and syngas. This is because there is not enough oxygen to react with the carbon in the biomass to form volatile compounds. On the other hand, high O/C ratios (greater than 1.0), favour the production of syngas with little biochar and bio-oil. This is because there is too much oxygen to form stable carbon compounds. An O/C ratio of 0.62 is considered optimal for producing high-quality bio-oil with moderate yields of biochar and syngas (Chen et al., 2014). The HHV of pine sawdust was 20.23 MJ/kg. A high HHV indicates that the resulting products have a high energy content and can be used as a source of renewable energy.

Table 4.1: Pine sawdust properties and comparison with other biomasses

Composition (wt.%, dry basis)	**Pine sawdust (present study)**	**Empty fruit bunch (palm oil)** (R. Omar et al., 2011)	**Switchgrass** (Mullen & Boateng, 2008)	**Microalgae** (Du et al., 2011)
		Proximate analysis		
Moisture Content	7.29	-	-	13.70
Volatile matter	76.39	71.20	83.41	68.40
Ash content	2.08	7.54	2.61	7.80
Fixed carbon	14.24	18.30	13.98	10.10
		Elemental composition		
C	51.60	45.0	47.53	49.70
H	5.20	6.40	6.81	6.98
N	0.34	0.25	0.51	10.92
S	0.02			
O	42.84[a]	47.30	42.54	24.60
H/C molar ratio	1.20	1.69	1.71	1.67
O/C molar ratio	0.62	0.69	0.62	0.36
HHV (MJ/kg)	20.23	18.1	-	-

[a] Calculated from difference

4.4.2 Thermal degradation profile of pine sawdust

Figure 4.6 illustrates the TG and DTG curves for the thermal degradation of pine sawdust under an inert atmosphere and a linear heating rate of 5 ℃/min. The TG curve of pine sawdust shows three distinct weight loss stages, mainly the drying stage (30-200 °C), the devolatilization stage (200-450 °C) and the char formation stage (>450 ℃). The devolatilization stage consists of the decomposition of hemicellulose (200-315 °C) and cellulose and lignin decomposition (315-400 °C) and lignin degradation (>400 °C) Lignin usually degrades thermally at a slower rate over a significantly larger temperature range of 200-600 ℃ (Chong et al., 2019).

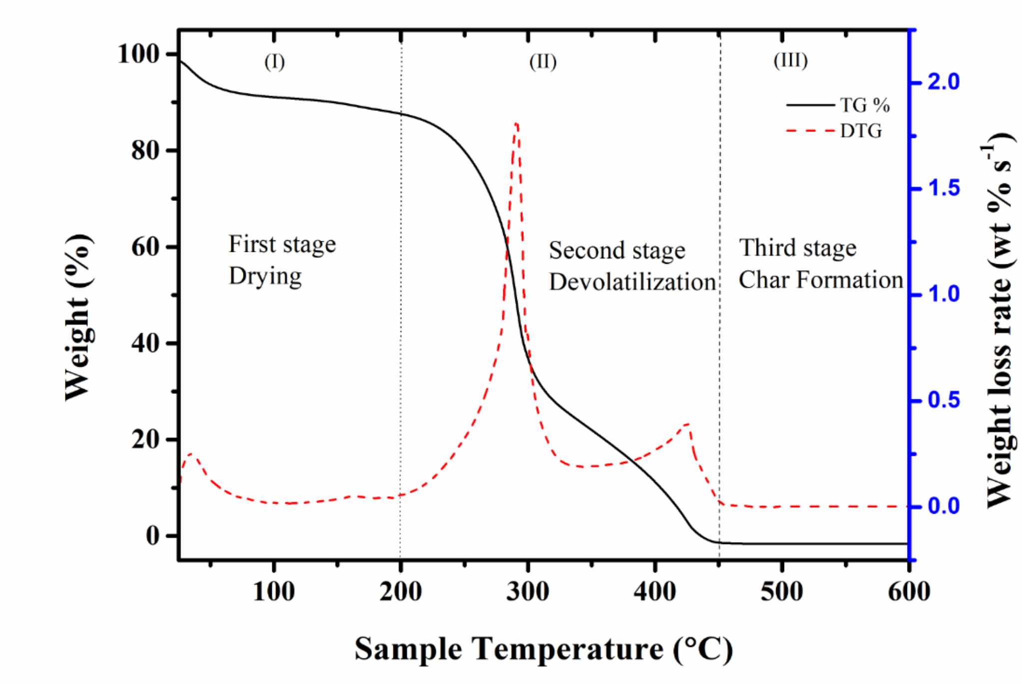


Figure 4.6: TG and DTG curves of pine sawdust at a linear heating rate of 5 °C/min

The first stage occurred at the temperature range of 30-200 ℃ where 11.09 % of the mass was lost, which can be associated with the loss of intracellularly retained and surface-adsorbed moisture and light volatile components (Chihobo et al., 2016). Costa et al. (2016) and Marangwanda et al. (2021) reported weight losses in the range of 4-19 % for pine wood samples at temperatures <200 ℃ corresponding to the drying of the biomass samples. However, the differences in the weight losses during the drying stage are mainly attributed to the moisture content of the biomass sample.

The second stage (devolatilization) is demarcated by a temperature range of 200-450 ℃ with a maximum mass loss and mass loss rate of 88.99 % and 1.81 wt.% s^{-1} respectively. This is related to the formation of stronger and more stable bonds as a result of the thermal dissociation of weak bonds in the polymeric structure of the primary components of pine sawdust. Hemicelluloses, cellulose and lignin are recognized to be the primary constituents of lignocellulosic biomasses such as pine sawdust (Marangwanda et al., 2021), and it has been demonstrated that the devolatilization region mostly corresponds to the degradation of these constituents. The positions of the peaks on the DTG curves reflect the temperatures at which the greatest rate of weight loss occurred. Two distinct peaks are shown on the DTG curve of pine sawdust during the second stage (which is demonstrated by a noticeable change in the slope of the TG curve). The degradation of hemicellulose is responsible for the first peak at 291.96 ℃, whereas cellulose degradation is responsible for the second peak between 350 and 450 ℃.

The third stage (char formation) begins at 450 °C and corresponds to the decomposition of lignin and the formation of biochar (Laougé & Merdun, 2021), and exhibits a small mass loss (0.23 %) as a result of the decomposition of carbonaceous materials in the solid residue (Bach & Chen, 2017). A study by Koskela et al. (2021) stated that the investigation of lignin pyrolysis demonstrates that the benzene bonds from lignin are broken at temperatures over 450 ℃, leading to the production of new aromatic clusters and favouring char formation.

4.4.3 Pyrolysis process yields

The composition on a weight basis of the MAP products is represented in Table 4.2. The products presented in the current study were derived from pine sawdust feedstock. The bio-oil yields were higher than biochar and non-condensable gas yields. Abnisa et al. (2013) reported the same tendencies in the pyrolysis of palm oil wastes, and Mullen et al. (2010) also reported the same in the pyrolysis of corn stover and corn cobs. Higher bio-oil yields could be owing to the feedstock's highly volatile matter and low ash content.

The study gave a bio-oil yield of about 42.28 wt.% of the parent biomass. This bio-oil yield is approximately half of what Lam and Chase (2012) reported for waste-to-energy processes involving MAP. However, this yield is almost double the one which was reported by Raheem et al. (2015) in the microwave co-pyrolysis of microalgae and scum (municipal solid waste). This variance in yield could be a result of differing parent biomass's chemical composition. This assumption is confirmed by research done by Echresh Zadeh et al. (2020) on the elemental analysis of bio-oil samples derived from two different biomass feedstocks, where the carbon, oxygen, and sulphur contents of the bio-oils were different. However, co-feeding pine sawdust may aid to boost bio-oil yield. The weight fractions of the other products biochar and NCGs (non-condensable gases) were 36.11 wt.% and 21.61 wt.% respectively.

Table 4.2: Pyrolysis process yields and comparison with other biomasses and technologies

Feedstock	Pyrolysis Technology	Yields (wt.%)			Reference
		Bio-oil	Biochar	NCGs	
Pine sawdust (Present Study)	MAP	42.28	36.11	26.61	-
Pine sawdust	MAP	24.00	26.90	49.10	(Khelfa et al., 2020)
Microalgae	MAP	48.00	28.50	23.50	(Du et al., 2011)
Softwood lignin	Fixed-bed pyrolysis	24.40	48.30	27.40	(Echresh Zadeh et al., 2020)
Hardwood lignin	Fixed-bed pyrolysis	30.20	58.00	12.00	(Echresh Zadeh et al., 2020)
Palm shells	Fixed-bed pyrolysis	47.43	35.26	17.31	(Abnisa et al., 2013)
Empty fruit bunch	Fixed-bed pyrolysis	45.75	29.05	25.20	(Abnisa et al., 2013)
Mesocarp fiber	Fixed-bed pyrolysis	43.87	29.80	26.33	(Abnisa et al., 2013)
Cynara cardunculus L	Fixed-bed pyrolysis	43.74	18.55	37.71	(Encinar et al., 2000)
Wood sawdust	Fixed-bed pyrolysis	60.90	18.80	20.20	(Oyebanji et al., 2017)
Corn cobs	Fluidized bed pyrolysis	40.90	18.90	14.70	(Mullen et al., 2010)
Corn stover	Fluidized bed pyrolysis	58.20	17.10	5.30	(Mullen et al., 2010)

4.4.4 Bio-oil and biodiesel characterization

After centrifugation, the crude bio-oil was split into two distinct fractions. The precipitate or particles deposited at the bottom of the centrifuge tube were referred to as the bottom phase (organic phase). The top phase (the aqueous phase) refers to the supernatant after the centrifugation. The aqueous phase predominantly consisted of water, while the organic phase concentrated on the organic molecules. The crude bio-oil yielded 24 wt.% of the organic phase and 76 wt.% of the aqueous phase. These values compare well with a study done by Cha et al. (2016) on bio-oil derived from switchgrass pyrolysis. Drying and co-pyrolysis of pine sawdust with highly lignocellulose biomass can significantly increase the organic phase yield and reduce water in the aqueous phase (Makepa et al., 2022).

Table 4.3 presents the physical characteristics of crude bio-oil and biodiesel. The biodiesel parameters were compared to the quality requirements of biodiesel used as a blend component for automotive fuels (EN 14214). The density of the crude bio-oil obtained was 1170.57 kg/m^3. Because of the presence of a considerable amount of water and macromolecules such as oligomeric phenolic chemicals, hemicelluloses, and cellulose, the density of bio-oil generated from MAP of pine sawdust is higher than that of gasoline and diesel (Xu, Hu, et al., 2011). The density of the biodiesel was 965.26 kg/m^3, which makes bio-oil a promising biofuel for compression ignition engines when upgraded. According to Sakthivel et al. (2018), pyrolysis derived biofuels can have densities around 980 kg/m^3, which is comparable to the values obtained in this study.

The flashpoint of the bio-oil was found to be 214 ℃. In a comparison with diesel fuel (54 °C) and biodiesel derived from vegetable oil (165 °C), bio-oil has a greater flashpoint The flash point was greatly improved for the biodiesel. The viscosity of bio-oil was found to be 39.20 cSt (40 ℃) indicating that the bio-oil has a relatively high resistance to flow. The biodiesel has a low viscosity of 4.5 cSt (40 ℃) which makes it suitable for use as a fuel. The water content of the biodiesel was greatly reduced from 35.66 wt.% to 4.7 wt.%. High water contents make crude bio-oil undesirable for use as a fuel as it can lead to instability, corrosion, and reduced heating value of the bio-oil (Lahijani et al., 2022). High-ash fuels are undesirable as they have a tendance to produce more ash when burned, which can lead to increased maintenance costs and reduced efficiency in combustion systems (Hariana et al., 2023). However, the transesterification of crude bio-oil reduced the ash content from 0.37-0.04 wt.%. The crude bio-oil TAN of 103.2 mg KOH/g indicated a relatively high concentration of acidic compounds. These acids can be corrosive and can cause damage to engines and other equipment. However, upgrading the bio-oil via transesterification has significantly reduced the TAN to 33.8 mg KOH/g. The biodiesel has an HHV of 32.40 MJ/kg, which is significantly lower than the HHV of conventional fuels such as gasoline, diesel and natural gas. This lower HHV limits the use of bio-oil in most energy applications, however, it is higher than the HHV of crude bio-oil, wood and straw (Wang et al., 2020).

Table 4.3: Physical characteristics of crude bio-oil and biodiesel

	Crude bio-oil	**Biodiesel**	**EN 14214**	
			Test method	**Limits**
Density (kg/m^3)	1170.57	965.26	EN ISO 3675/ EN ISO 12185	860-900
Flash point (℃)	214	107	EN ISO 3679	101 (min)
Viscosity at 40℃ (cSt)	39.20	4.50	EN ISO 3104	3.5-5.0
Water content (wt.%)	35.66	4.7	-	-
Ash content (wt.%)	0.37 ± 0.01	0.04	EN ISO 6245	0.05 (max)
TAN (mg KOH/g)	103.2	33.8	ASTM D 5558-95	370 (max)
HHV (MJ/kg)	18.70	32.40	-	-

4.4.5 Bio-oil pH and stability trend

The variation of bio-oil pH with time is represented graphically in Figure 4.7. The pH of the bio-oil was 2.87 and conforms with reported values of other bio-oils from various biomass feedstock which ranged from 2.0 to 3.7. The low pH indicated the presence of acidic organic compounds in high concentrations in the bio-oil. As stated by Sınağ et al. (2011), significant levels of acidic compounds in bio-oil can be linked to the pyrolysis process's breakdown of hemicellulose and lignin. The pH is dependent on the feed material. For example, according to Liu et al. (2014) wood-based oils were more acidic than switchgrass-based oils.

Bharath et al. (2020) compared the chromatograms of fresh and aged bio-oil obtained from fast pyrolysis of date tree wastes. In their study, it was apparent that the number of certain hydrocarbons increased over time, showing that the bio-oil underwent hydrolysis and oxidation as it aged, producing new by-products. A comparison of the constituent compositions has shown that native alcohols and aldehydes present in the bio-oil were oxidized to acids. Alsbou & Helleur (2014) observed similar trends in the investigation of accelerated ageing on bio-oil produced from fast pyrolysis of hardwood. In this regard, raw bio-oil as a fuel has several undesirable properties due to its chemical composition, which makes it corrosive and thermally unstable. Acids present in bio-oil are the principal cause of material corrosion during storage and application. As a result, upgrading is required to meet the fuel requirements before application through various bio-oil upgrading methods.

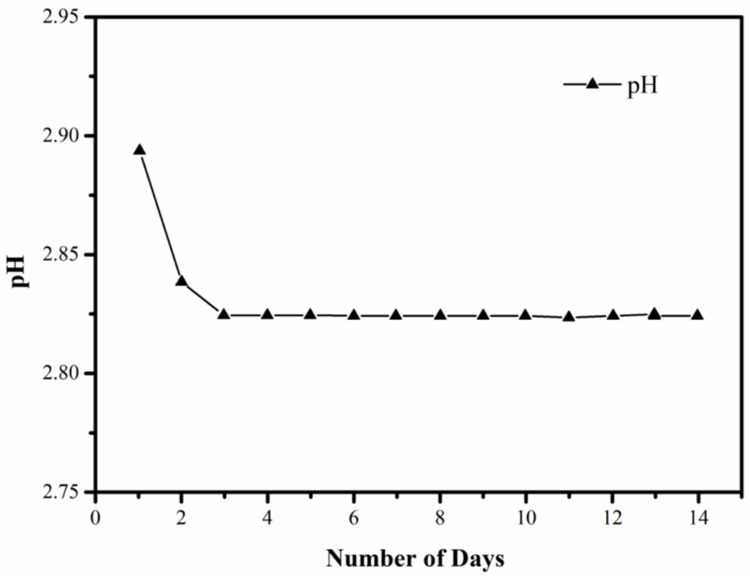


Figure 4.7: Bio-oil pH variation over time

4.4.6 FTIR results

The functional groups contained in the organic phase of the bio-oil were identified using FTIR. The FTIR spectra of the bio-oil organic phase are shown in Figure 4.8, and Table 4.4 shows the peaks of the functional groups present in the bio-oil that have strong and moderate intensities of different bond types. The presence of carboxylic acids, phenols and alcohols is indicated by the C=O and O-H stretching vibrations at the broad peak between 3700 and 3200 cm^{-1}. The carboxylic acids are the ones that contribute to the low pH values of bio-oil (Lu et al., 2008). The presence of alkanes in the bio-oil was linked to the C-H stretching vibrations from 2800 cm^{-1} to 3000 cm^{-1}. The presence of alkenes and aromatic compounds in the bio-oil was linked to the C=C stretching vibrations from 1700 cm^{-1} to 1600 cm^{-1}. The C-H bending vibrations from 1500-1400 cm^{-1} also indicated the presence of alkanes. Because bio-oil contains alkanes and alkenes, it can be used to generate petroleum-based range fuels (Makarfi Isa & Ganda, 2018). The C-O stretching and deformation vibrations from 1300-1200 cm^{-1} indicated the presence of ester and ether functional groups. The O-H stretching and C-H stretching vibrations from 1200-1000 cm^{-1} also indicated the presence of alcohol and phenol functional groups in the bio-oil. Furthermore, the absorbance peaks between 950-550 cm^{-1} indicated the presence of alkenes, mono and polycyclic substituted aromatics groups. The presence of cellulose, hemicellulose and lignin in pine sawdust is clearly shown by the considerable quantity of aliphatic compounds and a few aromatic compounds present in the bio-oil.

Table 4.4: Main functional groups of the bio-oil organic phase

Wavenumber (cm^{-1})	**Functional groups**	**Compound class**
3403.48	O-H stretching	Alcohols, Phenols, carboxylic acids
2929.72	C-H stretching	Alkanes
1695.38	C=C stretching	Aromatic compounds, alkenes
1429.69	C-H bending	Alkanes
1235.32	C-O stretching	Alkyl aryl ethers
1026.27	C-O stretching	Alcohol, Phenols
742.95	C=C bending	Alkenes

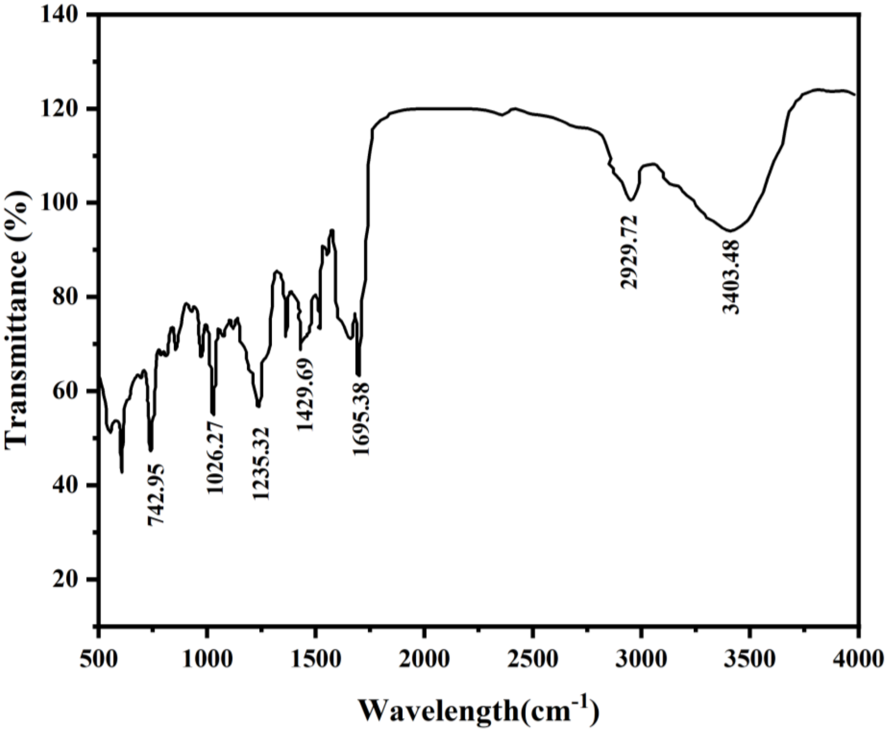


Figure 4.8: FTIR spectra of the bio-oil organic phase

4.4.7 GC-MS analysis of bio-oil

The main components identified through GC-MS analysis are listed in Table 4.5. The bio-oil composition contained a wide range of oxygenated molecules and hydrocarbons, including saturated and unsaturated, straight-chain and cyclic organic compounds. According to the findings of the qualitative analysis, acetic acid is the main acidic component of bio-oil, while furfural and furfural alcohol are the main products produced from furans. Hexadecanoic acid and tetradecanoic acid are the main carboxylic acids identified in the bio-oil. The major constituent of ketones identified is 1-hydroxy-2-propanone, along with several cyclopentanones and cyclopentadiones. Levoglucosan, a characteristic pyrolysis by-product from cellulose pyrolysis, shows inadequate carbohydrate decomposition. A significant number of methylated or methoxylated phenolic compounds, including 2-methoxy-phenol, 2-methoxy-4-methyl-phenol, 2-methoxy-4-vinylphenol, eugenol, and vanillin, were also identified.

Table 4.5: Main compounds identified in bio-oil obtained from pine sawdust

RT	**Compound name**	**MW**	**Formula**
8.064	1-hydroxy-2-propanone	74	$C_3H_6O_2$
10.717	Butanediol	86	$C_4H_6O_2$
11.270	Acetic acid	90	$C_2H_4O_2$
11.485	Furfural	96	$C_5H_4O_2$
17.945	1,2-cyclopentanedione	98	$C_5H_6O_2$
18.879	3-methyl-1,2-cyclopentanedione	112	$C_6H_8O_2$
19.395	2-methoxy-phenol	124	$C_7H_8O_2$
20.791	2-methoxy-4-methyl-phenol	138	$C_8H_{10}O_2$
21.795	4-ethyl-2-methoxy-phenol	152	$C_9H_{12}O_2$
22.498	4-ethyl-phenol	122	$C_8H_{10}O$
23.529	Eugenol	164	$C_{10}H_{12}O_2$
23.859	2-methoxy-4-vinylphenol	150	$C_9H_{10}O_2$
24.582	*Z*)-isoeugenol	164	$C_{10}H_{12}O_2$
25.624	(*E*)-isoeugenol	164	$C_{10}H_{12}O_2$
26.415	4-hydroxy-3-methoxycinnamaldehyde	178	$C_{10}H_{10}O_3$
27.294	5-hydroxymethylfurfural	126	$C_6H_6O_3$
20.013	Vanillin	152	$C_8H_8O_3$
28.438	2-methoxy-4-propyl-phenol	166	$C_{10}H_{14}O_2$
28.894	3-methoxy-4-hydroxyacetophenone	166	$C_9H_{10}O_3$
35.231	4-hydroxy-3-methoxybenzeneacetic acid	182	$C_9H_{10}O_4$
36.745	Levoglucosan	162	$C_6H_{10}O_5$
36.833	Tetradecanoic Acid	228	$C_{14}H_{28}O_2$
36.894	Neophytadiene	27	$C_{20}H_{38}$
36.917	Hexadecanoic acid	256	$C_{16}H_{32}O_2$
36.917	n-Hexadecanoic acid	256	$C_{16}H_{32}O_2$

4.4.8 GC-MS analysis of biodiesel

To confirm the complete conversion of bio-oil to its fatty acid methyl esters (FAMEs), the biodiesel produced was subjected to GC-MS analysis. Table 4.6 provides a list of the principal methyl ester compounds identified. The GC-MS analysis revealed that Hexadecanoic acid, 1,2-Benzenedicarboxylic acid, 2-ethyl-6-hydroxyhexyl methyl ester, Methyl 2-ethylhexyl phthalate, 9,12 Octadecenoic acid, methyl ester, (E,E)-, 9-Octadecenoic acid, 9-Octadecenoic acid(Z), Octadecanoic acid, 1,2-Benzenedicarboxylic acid, 2-ethyl-5-hydroxyhexyl methyl ester and 1,2-Benzenedicarboxylic acid, 2-(2-hydroxyhexyl)hexyl methyl ester, Bis(2-ethylhexyl)phthalate (S)-2,4-dimethyl-2-carbomethoxy-1,2- were the most dominant FAMEs present in the synthesized biodiesel. The total concentration of the identified FAMEs was 510.05 mg/L. Xiong et al. (2023) identified thirteen FAMEs in biodiesel obtained from the transesterification of corn straw bio-oil. The yield of FAMEs was improved by co-pyrolyzing corn straw with other feedstocks. Mohamad et al. (2017) identified nine major FAMEs obtained from the transesterification of vegetable palm oil. However, the FAMEs identified in biodiesel synthesized in this study are consistent with those reported in the production of biodiesel from vegetable oils (Elango et al., 2019; Naureen et al., 2015). The GC-MS analysis of biodiesel has proved the successful conversion of organic acids and oxygenated compounds in bio-oil to methyl esters, therefore, the biodiesel can be stored easily and utilized in internal combustion engines.

Table 4.6: FAMEs identified in the bio-oil from the thermal conversion of pine sawdust

RT	**Identified FAME**	**MW**	**Formula**	**Concentration (mg/L)**
20.147	Hexadecanoic acid, Methyl Ester	270	$C_{17}H_{34}O_2$	26.3
20.609	1,2-Benzenedicarboxylic acid, 2-ethyl-6-hydroxyhexyl methyl ester	308	$C_{17}H_{24}O_5$	13.35
21.606	Methyl 2-ethylhexyl phthalate	292	$C_{17}H_{24}O_4$	13.78
22.287	9,12 Octadecenoic acid, methyl ester, (E,E)-	294	$C_{19}H_{34}0_2$	88.83
22.353	9-Octadecenoic acid, Methyl Ester	296	$C_{19}H_{36}O_2$	15.36
22.353	9-Octadecenoic acid(Z), Methyl Ester	296	$C_{19}H_{36}O_2$	15.31
22.632	Octadecanoic acid, Methyl Ester	299	$C_{19}H_{38}O_2$	10.47
23.397	1,2-Benzenedicarboxylic acid, 2-ethyl-5-hydroxyhexyl methyl ester	308	$C_{17}H_{24}O_5$	14.73
23.682	1,2-Benzenedicarboxylic acid, 2-(2-hydroxyhexyl)hexyl methyl ester	308	$C_{17}H_{24}O_5$	22.33
26.508	Bis(2-ethylhexyl)phthalate (S)-2,4-dimethyl-2-carbomethoxy-1,2-	391	$C_{24}H_{38}O_4$	289.59

4.5 Conclusion

The study's goal was to convert pine sawdust into biodiesel through waste-to-energy recovery. The MAP technique was employed and the product yield for bio-oil, biochar, and NCGs was 42.28 wt.%, 36.11 wt.%, and 21.61 wt.% respectively. The bio-oil physical properties concur with other bio-oils produced from different lignocellulosic biomass feedstocks. The thermal degradation behaviour of pine sawdust showed three distinct weight loss stages, mainly the drying stage (30-200 °C), the devolatilization stage (200-450 °C) and the char formation stage (>450 °C). GC-MS analysis was employed in the determination of the chemical composition of the bio-oil and FTIR methods and the main chemical families that were identified include phenolics, furan, carboxylic acids, and aromatics. Phenols were found to be the major chemical identified. They can be extracted by solvent methods for use in different industries, including the production of chemicals, antioxidants, and antimicrobials. They also improve biofuel properties and prevent degradation during storage.

Bio-oil is corrosive because of its low pH value, and the oxygenated components in it make it reactive and unstable. Bio-oil transesterification has been shown to improve the bio-oil properties by converting the organic acids and oxygenated compounds in bio-oil to methyl esters with a concentration of 510.05 mg/L. The properties of the biodiesel obtained were within the limits stipulated by the EN 14214 (a European standard that describes the quality requirements and test methods for biodiesel). Converting bio-oil to biodiesel might be an alternate strategy for improved energy recovery because bio-oil is a complex product that needs further upgrading or distillation to separate distinct energy molecules. It is important to note that the bio-oil's high fatty acid content increases its acidity, necessitating further upgrading for pH neutralization, which raises the cost overall. Thus, the post-upgrading stage might be avoided by converting bio-oil into biodiesel. However, the biochemicals in the bio-oil can be extracted by solvent extraction methods and they have many applications in the chemical, pharmaceutical, and food industries. MAP of pine sawdust has proved to be a viable waste-to-energy recovery method in the valorization of pine sawdust. It is noted that the pyrolysis of biomass can enhance global energy security and help in mitigating the negative effects of climate change.

CHAPTER FIVE: PROCESS MODELLING, PERFORMANCE OPTIMIZATION, AND ECONOMIC EVALUATION OF MICROWAVE-ASSISTED PYROLYSIS OF PINE SAWDUST

5.1 Chapter overview

This chapter presents the optimization of the process conditions to extract maximum yields of bio-oil from pine sawdust using MAP. Aspen Plus® V11 was used to model the thermochemical conversion of pine sawdust to pyrolysis products, and response surface methodology (RSM) based on a central composite design (CCD) was employed in the optimization of the process parameters. The mutual effects of pyrolysis temperature and reactor pressure on the product distribution were investigated. The findings have shown that the optimal operating conditions for producing the highest amount of bio-oil (65.8 wt.%) were achieved at 550 ℃ and 1 atm. The product distribution of the simulated model was more significantly influenced by linear and quadratic terms of the reaction temperature. In addition, a high determination coefficient (R^2=0.9883) was obtained for the developed quadratic model. A set of three published experimental results acquired under circumstances comparable to the simulations' operating limitations were used to further validate the simulation results. The process's economic viability was assessed in order to establish the bio-oil minimum selling price (MSP). A MSP of $1.14/L of liquid bio-oil was evaluated. An economic sensitivity analysis has shown that the annual fuel yield, required rate of return, annual income tax, annual operating costs and initial capital investment have a substantial impact on the MSP of bio-oil. It was inferred that using the optimized process parameters may improve the process' competitiveness on an industrial scale due to its better product yields and improved sustainability in biorefineries, as well as assure waste reduction.

This chapter is based on an original research paper published in the journal Heliyon. A process simulation was developed in Aspen Plus and the economic viability of bio-oil production was evaluated, fulfilling objective 3 and part of objective 4.

Makepa, D. C., Chihobo, C. H., Ruziwa, W. R., & Musademba, D. (2023). Microwave-assisted pyrolysis of pine sawdust: Process modelling, performance optimization and economic evaluation for bioenergy recovery. Heliyon, 9(3), e14688. https://doi.org/10.1016/j.heliyon.2023.e14688

5.2 Introduction

Due to the rapid increase of the world's population and the emergency of new technologies, the energy demand is rising rapidly, while the reserves of the currently available energy supplies are depleting (Isahak et al., 2012). The relevance of renewable and sustainable energy sources is simultaneously raised by environmental concerns and a potential crisis in energy production and sustainability (Pattiya et al., 2010). Biomass has received a lot of attention recently amongst other renewable energy resources since it is the only renewable source of fixed carbon (Makepa et al., 2022).

Each year, a large amount of forestry and agro-industrial waste is dumped; nevertheless, it can be collected and transformed into energy using thermochemical or biological conversion techniques (Li et al., 2019). The Zimbabwe timber industry depends on timber plantations located in the Eastern Highlands, occupying about 0.025% of dry land in Zimbabwe, comprising 130,000,000 m^2 of wattle, 240,000,000 m^2 of eucalyptus, and 810,000,000 m^2 of pine. The industry generates over 70,000 tons of pine sawdust every year with an energy potential estimated at 232 kt_{Oe} (Jingura et al., 2013). The quantity of pine sawdust produced is anticipated to double in the next five years due to rapid industrialization and urban growth. The growing demand for residential housing in Zimbabwe has boosted the demand for timber supplies, while regional demand has been continuously expanding over the years. In general, securing a sustainable supply of raw materials for pyrolysis is made feasible by the continuous annual output of pine sawdust.

Pine sawdust was often thought to have little economic value by millers and was frequently burned in open fields or dumped in the ground, polluting the environment (Bakar et al., 2016). Researchers are investigating various methods of utilizing waste biomass as fuel as a result of the rise in demand for waste-to-energy usage. Most experts agree that biomass pyrolysis is a competent way to produce bioenergy from a range of wastes (Faraji & Saidi, 2021). This method increases the effectiveness of waste management and has great potential for generating renewable and low-carbon energy (Kumar & Samadder, 2017).

Among the thermochemical conversion processes, pyrolysis, which is the breakdown of organic material without the presence of oxygen, is a potential method for utilizing waste biomass. It has been extensively utilized to transform biomass into gaseous, liquid (tar or oil), and solid (char) fuels (Tsai et al., 2006). The product composition is often related to the pyrolysis operating conditions. Low process temperatures and long vapour residence periods promote char creation, high process temperatures and long vapour residence periods promote the conversion of biomass to gas, while intermediate process temperatures and short vapour residence periods are ideal for liquid production (Bridgwater, 2012). Due to its high energy content, the solid product is mainly used either directly as an energy source in boilers, or as a feedstock to create activated carbon. Even though the generated gas is a by-product, its main constituents are carbon monoxide and methane, which makes it usable as fuel when burnt. The liquid product known as tars may be added to the feedstock used in petroleum refineries, improved by catalysts to generate premium-grade refined fuels, or it may have potential use as a chemical feedstock.

The simulation of biomass pyrolysis has made use of a variety of commercially available computer-based modelling and simulation programs, including ChemCAD, Fluent, Aspen HYSYS®, and Aspen Plus®. Aspen Plus® is the most popular of these programs for biomass pyrolysis simulations because it comes with a built-in library model for determining the solid properties. As a result, it is more adept at identifying solid components than other applications. Additionally, FORTRAN code, an imperative programming language, is used in conjunction with Aspen Plus® to facilitate the creation of modifications and numerical computations.

Aspen Plus® simulator has been used to model the biomass pyrolysis process for the generation of bio-oil in several in-depth investigations. For instance, Liu et al. (2022) simulated the thermochemical conversion of sugarcane bagasse and rice straw. The influence of pyrolysis temperature on product yield was examined by changing the temperature from 300-800 °C. Rosha et al. (2022) simulated the pyrolysis of biomass using Aspen Plus® for the production of renewable fuel. The authors carried out a sensitivity analysis to find out the optimum operating conditions by varying the operation temperature, feed residence time and reactor volume. Xianjun et al. (2015) modelled the pyrolysis of rice husk using Aspen Plus® to determine the non-condensable gas (NCG) yield and properties obtained by varying temperatures between 350-600 °C.

The method that has been widely researched is heating biomass with an external heat source. The benefit of pyrolysis is that the end product yield may be changed depending on the operating conditions; such as process temperature and heating rate (Wu et al., 2014). In recent years, MAP has emerged as a viable alternative to conventional pyrolysis, primarily due to its fast-heating rate, selective heating, volumetric heating, and uniform heating, which speed up reaction rates and boost energy efficiency. Instant on/off control made possible by microwave heating makes operation simple and improves product quality and yield. Additionally, it limits pollution emissions and decreases the production of hazardous products, making the process environmentally beneficial (Li et al., 2016). According to research by Yu et al. (2020) on the interactions between microwaves and starch, microwave-assisted hydrolysis uses 47% less energy than traditional conductive heating to produce equivalent product yields. Li et al. (2018) performed pyrolysis studies in the presence and absence of microwave irradiation in a fixed-bed pyrolysis reactor. The outcomes demonstrated that microwave heating enhanced the liquid product yield and composition, which merits further exploration in the future. Lam et al. (2019) observed that microwave pyrolysis may be economically feasible for processing used cooking oil and waste plastics. It also showed potential as a viable method for bioenergy production, offering better process characteristics and effective synthesis of renewable liquid fuels.

The majority of past research has reported the effects of certain parameters while holding other process variables constant at stated levels. This method fails to capture the overall impact of all process factors. Finding the ideal amounts takes time and needs several tests, some of which may be inaccurate. By jointly optimizing all the process parameters using statistical experimental design, such as RSM, these drawbacks of a traditional method may be overcome (Abnisa et al., 2011). The RSM is an effective instrument for investigating the relationships between two or more factors. It primarily consists of a specific combination of mathematical and statistical methods for experimental planning, model creation, analyzing the impacts of variables, and looking for the best combinations of variables to predict certain outcomes (Ghani et al., 2011).

This study aims at optimizing the process conditions to extract high yields of the desired product from used pine sawdust. A reliable numerical simulation model for the MAP of pine sawdust was created. To understand the connection between reaction temperature and pressure and product yield, and to come up with the optimal operating conditions for producing the highest amount of bio-oil from pine sawdust by MAP, simulations were carried out by RSM based on CCD. This may therefore be used to forecast the viability of producing bio-oil from low-cost biomass sources like pine sawdust using MAP, increasing the effectiveness of its utilization.

5.3 Materials and methods

5.3.1 Experimental data

The pine sawdust samples employed in this study were obtained at selected sawmills processing the same wood species in the eastern region of the country. The feedstock was oven dried at 110 °C and sieved through ISO Retsch test sieves of 2 mm mesh size according to ASTM D 410-84. This step was necessary to remove oversized wood chips in the pine sawdust to achieve a uniform particle size distribution. The proximate analysis was carried out according to modified procedures (ASTM D 3173, ASTM D3175 and ASTM D 3174). The ultimate analysis was carried out in accordance with ASTM D5373 (2014) and a Thermo Scientific™ FLASH 2000 CHNS/O Analyzer was employed in the analysis. In the experimental runs, 100 g of pine sawdust was mixed with 10 g of microwave absorbent activated carbon. The microwave reactor used has a cavity volume of 42 litres, a rated microwave output of 950 Watts and an operating frequency of 2450 MHz. Helium at a flowrate of 3 LPM served as carrier gas and to create an inert environment in the reactor. The samples were subjected to microwave heating at maximum power for 30 minutes. A very short residence time of ~2 s was maintained to control the further conversion of large molecules in bio-oil into small molecules which are more stable under a thermodynamic equilibrium state. The volatiles that evolved during the pyrolysis process were forced to pass through a condensing system utilizing water as a coolant. When the vapours go through the cooling lines the condensable compounds condense from the gaseous vapour forming bio-oil which is collected in a collection flask. Both the reactor and the condensing system were weighed before and after the pyrolysis experiments to measure the liquid and solid yields. The gas yield was determined by difference.

5.3.2 Simulation model

Aspen Plus® V11 software was utilized for the modelling and simulation of the pyrolysis of pine sawdust. It has built-in tools to enable the calculation of process energy and mass balances, reaction kinetics, chemical equilibrium and process optimization. Complicated and comprehensive systems can be modelled from the extensive databases, physical properties and thermodynamic models in the software. The ability to handle conventional and non-conventional solids, liquids and gaseous compounds makes it ideal for modelling chemical processes (Shoaib Ahmed Khan et al., 2022). There are two types of components in Aspen Plus®: conventional and non-conventional. Conventional components have recognized molecular structures and may be found in several Aspen Plus® databanks. The representation of non-conventional components is based on proximate and ultimate analysis as they lack a molecular formula (Ward et al., 2014).

5.3.2.1 Model component specification

The simulation contains mixed streams of conventional and non-conventional solids, liquids and gaseous compounds; therefore, the global stream class is set to MIXCINC (meaning both conventional and nonconventional solids are present, but there is no particle size distribution. For non-conventional components, only enthalpy and density are estimated; these variables are determined by empirical correlations. The HCOALGEN (a model used to calculate enthalpy) and DCOALIGT (a model used to calculate density) methods, which depend on ultimate and proximate analyses, respectively, were selected as specified property methods for enthalpy and density for pine sawdust. Proximate and ultimate analyses are needed to model non-conventional components and the data required to model the pine sawdust in Aspen Plus® is presented in Table 4.1.

Table 5.1: Pine sawdust composition (wt.%, dry basis)

Proximate analysis		**Ultimate analysis**	
Moisture Content	7.29	C	51.60
Volatile Matter	78.19	H	5.20
Ash Content	0.28	N	0.04
Fixed Carbon	14.24	O	43.16[a]

[a] Calculated from difference

The conventional and non-conventional components added to the simulation model are presented in Table 5.2. H_2O was included in the components specification to accommodate for the feedstock's moisture content. Since pine sawdust is a non-conventional component, it is decomposed to lignin, hemicellulose and cellulose species during the simulation and modelling process. Cellulose is denoted by its monomer $C_6H_{10}O_5$ (Adeniyi et al. 2019) and hemicellulose is represented by glucomannan and xylan monomers ($C_5H_8O_4$). Lignin is a complex organic polymer made up of phenolic monomers. Tannin ($C_{15}H_{12}O_7$), C-rich lignin ($C_{15}H_{14}O_4$), O-rich lignin ($C_{20}H_{22}O_{10}$) and H-rich lignin ($C_{22}H_{28}O_9$) are used as monomers for lignin. The pyrolysis intermediate products and end products modelled in the simulation are listed in Table 5.2.

Table 5.2: Model component specifications

Component ID	**Type**	**Component**	**Molecular Formula**
C	Solid	Carbon graphite	C
TANN	Solid	Tannin	$C_{15}H_{12}O_7$
METHY-01	Solid	Carbon-rich lignin	$C_{15}H_{14}O_4S$
LIGO	Solid	Oxygen-rich lignin	$C_{20}H_{22}O_{10}$
LIGH	Solid	Hydrogen-rich lignin	$C_{22}H_{28}O_9$
GMSW	Solid	Hemicellulose-glucomannan	$C_5H_8O_4$
XYHW	Solid	Hemicellulose- xylan	$C_5H_8O_4$
CELL	Solid	Cellulose	$C_6H_{10}O_5$
ASH	Solid	Calcium oxide	CaO
LIG	Solid	Secondary lignin intermediate	$C_{11}H_{12}O_4$
METHY-02	Solid	Carbon-rich lignin intermediate	$C_{15}H_{14}O_4S$
LIGOH	Solid	Hydrogen/Oxygen-rich lignin intermediate	$C_{19}H_{22}O_8$
HCE1	Solid	Activated hemicellulose 1	$C_5H_8O_4$
HCE2	Solid	Activated hemicellulose 2	$C_5H_8O_4$
CELLA	Solid	Activated cellulose	$C_6H_{10}O_5$
ITANN	Solid	Tannin intermediate	$C_8H_4O_4$
CHAR	Solid	Carbon graphite	C
HMWL	Solid	High-molecular weight lignin	$C_{24}H_{28}O_4$
CH4	Conventional	Methane	CH_4
H2	Conventional	Hydrogen	H2
CO2	Conventional	Carbon dioxide	CO_2
CO	Conventional	Carbon monoxide	CO
HE	Conventional	Helium	He
H2O	Conventional	Water	H_2O
H2S	Conventional	Hydrogen sulphide	H_2S
O2	Conventional	Oxygen	O_2
CH3OH	Conventional	Methanol	CH_4O
N2	Conventional	Nitrogen	N_2
HCOOH	Conventional	Formic acid	CH_2O_2
CH2O	Conventional	Formaldehyde	CH_2O

COUMARYL	Conventional	Ethyl-benzoate	$C_9H_{10}O_2$
ANISOLE	Conventional	Methyl-phenyl-ether	C_7H_8O
HMFU	Conventional	1,2,3-benzenetriol	$C_6H_6O_3$
PHENOL	Conventional	Phenol	C_6H_6O
LVG	Conventional	Levoglucosan	$C_6H_{10}O_5$
XYLAN	Conventional	Xylosan	$C_5H_8O_4$
FURF	Conventional	Furfural	$C_5H_4O_2$
C3H6O2	Conventional	1,3-dioxolane	$C_3H_6O_2$
ALD3	Conventional	Propylene-oxide	C_3H_6O
ACROL	Conventional	Acrolein	C_3H_4O
C2H5OH	Conventional	Ethanol	C_2H_6O
GLYCO-01	Conventional	Glycol-aldehyde	$C_2H_4O_2$
ACETI-01	Conventional	Acetic acid	$C_2H_4O_2$
CH3CHO	Conventional	Acetaldehyde	C_2H_4O
C2H4	Conventional	Ethylene	C_2H_4
GLYOX	Conventional	Glyoxal	$C_2H_2O_2$
FFA	Conventional	Cyclotetradecane-1,8-dione-ethylene-ketal	$C_{18}H_{32}O_4$
FE2MACR	Conventional	Sinapyl aldehyde	$C_{11}H_{12}O_4$
BIOMASS	Non-conventional		
DRY-BIOM	Non-conventional		

The Peng-Robinson-Boston-Mathias (PR-BM) method was chosen as the property's technique for the simulation. This property method is employed when the model consists of hydrocarbons and light gases (Unlu & Hilmioglu, 2020). When temperatures are extremely high, the temperature-dependent parameter alpha enhances the correlation of pure component vapour pressure (Adeniyi & Ighalo, 2020). All solid components must have values for their molecular weight, solid molar heat capacity, solid molar volume and standard solid heat of formation model parameters to employ the PR-BM technique. These values are presented in Table 5.3. All conventional fluid components must have values for their molecular weight, ideal gas standard state heat of formation, critical pressure and temperature, vapour pressure, acentric factor, and ideal gas molar heat capacity characteristics. These values are presented in Table 5.4.

Table 5.3: Estimated solid property model parameters for conventional solids (Gorensek et al., 2019)

Component name	Molecular weight, kg/kmol	Standard solid enthalpy of formation, kJ/kmol	Heat capacity model coefficients		Solid density, kmol/m^3
			C_1, kJ/kmol-K	C_2, kJ/kmol-K^2	
		Tannin and lignin			
Secondary lignin intermediate	208.21388	-729310	13.2251	0.82834	7.3002
Carbon-rich lignin	258.27376	-759390	16.4048	1.02749	5.8852
Carbon-rich lignin intermediate	258.27376	-759390	16.4048	1.02749	5.8852
Hydrogen-rich lignin	436.45892	-1722700	27.7226	1.73636	3.4826
Oxygen-rich lignin	422.38868	-1847500	26.8289	1.68039	3.5986
Hydrogen/Oxygen-rich lignin intermediate	378.37888	-1429200	24.0335	1.50530	4.0171
High-molecular weight lignin	380.48392	-958260	24.1672	1.51386	3.9949
Tannin intermediate	164.11736	-616980	10.4242	0.65291	9.2617
Tannin	304.25608	-1079700	19.3254	1.21042	4.9958
		Cellulose species			
Cellulose	162.1424	-1019000	-1.5328	0.67527	9.3745
Activated cellulose	162.1424	-1019000	-1.5328	0.67527	9.3745
		Hemicellulose species			
Hemicellulose-xylan	132.11612	-759200	-1.2489	0.55022	11.5050
Hemicellulose-glucomannan	132.11612	-759200	-1.2489	0.55022	11.5050
Activated hemicellulose 1	132.11612	-759200	-1.2489	0.55022	11.5050
Activated hemicellulose 2	132.11612	-759200	-1.2489	0.55022	11.5050

Table 5.4: Estimated fluid property model parameters for conventional fluids (Gorensek et al., 2019)

	1,3-dioxolane	Ethyl-benzoate	Sinapyl aldehyde	Xylosan
Molecular weight, kg/kmol	74.07944	150.1772	208.21388	132.11612
Ideal gas enthalpy of formation, kJ/kmol	-345300	-193500	-483800	-642300
Critical temperature, K	605.0	791.4	837.9	744.3
Critical pressure, bar	56.36	56.90	29.25	2.134
Acentric factor	1.133	1.198	0.981	0.292
Ideal gas heat capacity estimates, J/mol-K:				
$Cp^{*,ig}$(298K)	91.46	177.30	240.85	142.76
$Cp^{*,ig}$(400K)	109.33	225.11	302.37	179.06
$Cp^{*,ig}$(500K)	126.37	264.73	357.37	215.39
$Cp^{*,ig}$(600K)	141.02	296.16	402.54	240.55
$Cp^{*,ig}$(800K)	164.75	342.81	471.36	281.03
$Cp^{*,ig}$(1000K)	182.00	374.75	520.31	307.48
Aly-Lee $Cp^{*,ig}$ equation coefficients:				
$C_{CP,1}$, J/kmol-K	77793.84	128972.6	190226.6	115298.4
$C_{CP,2}$, J/kmol-K	106997.7	342667.4	491979.1	224458.5
$C_{CP,3}$, K	814.165	1575.222	1728.691	824.2086
$C_{CP,4}$, J/kmol-K	66750.56	266861.9	371592.3	59411.96
$C_{CP,5}$, K	2048.402	728.2816	797.2112	2302.592
$C_{CP,6}$, K	298	298	298	298
$C_{CP,7}$, K	1000	1000	1000	1000
Extended Antoine equation coefficients, K/Pa:				
$C_{PL,1}$	136.9781	286.7075	286.6149	135.2637
$C_{PL,2}$	-13924.84	-25124.63	-25391.53	-14336.53
$C_{PL,3}$	-15.46495	-37.26739	-37.28766	-15.74501
$C_{PL,4}$	1.303768e-17	1.48627e-5	1.36118e-5	2.245921e-18
$C_{PL,5}$	6	2	2	6
$C_{PL,6}$	261.15	406.15	406.15	455.4
$C_{PL,7}$	605	791.4	837.9	744.3

5.3.2.2 Reactor model description

Three reactor blocks, the RSTOIC (a stoichiometry-based reactor with specified extents of reaction), RYIELD (a reactor based on specified yields), and RGIBBS (a rigorous reactor which includes phase equilibrium using Gibbs freeenergy minimization) reactors, were used in conjunction to simulate the pyrolysis process. Stoichiometric equations are used in the RSTOIC block, a stoichiometric reactor. This served as a model for the drying of pine sawdust before heating. The conversion of pine sawdust to conventional simulation components takes place in the RYIELD reactor. By minimizing Gibbs free energy, the RGIBBS reactor determines the product components' distribution and phase equilibrium. The chemical equilibrium may be expressed as Equation 5.1 for a system operating at constant temperature and pressure (Adeniyi et al., 2019):

$$dG = \sum_{i=1}^{k} \mu_i n_i dn_i \tag{5.1}$$

where k is the sum of chemical species present in the reaction, G is the Gibbs free energy, μ_i is the chemical potential of species i and n_i denotes the number of moles of species i. The goal is to identify the values of n_i that will reduce the value of the Gibbs free energy. Aspen Plus® employs a non-stoichiometric method to determine the solution. If the mass balance is assumed, the expression, known as the objective function, can be expressed as Equation 5.2 (Adeniyi et al., 2019).

$$G = \sum_{i\,=\,1}^{k} n_i \Delta G_i^{\circ} + RT \sum_{i\,=\,1}^{k} n_i Iny_i + RT \sum_{i=\,1}^{k} n_i InP \tag{5.2}$$

where T denotes the temperature, P denotes the pressure, y_i denotes the mole fraction and G_i° denotes the standard Gibbs free energy of formation. This serves as the foundation for the computations carried out by the software to find thermodynamically viable results. Stoichiometric equations are not necessary for the Gibbs reactor or the yield reactor to be specified. The descriptions of each unit used in the simulation are listed in Table 5.5. The assumptions that were considered in developing the model are:

- The Aspen Plus® pyrolysis model is a steady-state, isothermal model that makes use of sequential-modular computing. Time-dependent factors like heating rate and residence time cannot be directly investigated since the model is not transient or dynamic.

- 95% of the moisture in the biomass is evaporated during the drying process.
- Biochar produced is assumed to be made up of elemental carbon.
- All components except for helium, which is regarded as inert, participate in the chemical process.

Table 5.5: Model block description

Aspen Plus® ID	**Block ID**	**Description**
RSTOIC	DRYER	Models the removal of moisture from the raw pine sawdust.
SEP	SEP-1	Models the separation of water vapour and dry pine sawdust.
MIXER	MIXER-01/02	Merges several streams to form one stream.
CRUSHER	CRUSHER	Models the particle size reduction of dried biomass.
SCREEN	SCREEN	Utilized to remove oversized biomass particles.
RYIELD	DECOMP	Models the decomposition of pine sawdust to conventional components.
RGIBBS	PYROLY	Determines the distribution of the pyrolysis products using the Gibbs free energy minimization approach.
CYCLONE	CYCLONE	Separates the biochar from the gaseous stream.
HEATX	HEX	Lowers the vapour stream temperature, causing the pyrolysis liquid products to condense.
FLASH2	SEP-2	Separates the condensable and non-condensable fractions of the pyrolysis products.

5.3.3 Description of the process model

The process flow chart developed in Aspen Plus® is demonstrated in Figure 5.1 and the stream information is presented in Table 5.6. Raw biomass at 200 kg/hr (25 ℃ and 1 atm) enters the RSTOIC reactor and is dried at 125 ℃ to remove moisture in the biomass based on Equation 5.3 (Adeniyi et al., 2019). A biomass fractional conversion of 1 has been specified (Liu et al., 2022; Tauqir et al., 2019) and the drying of biomass was modelled using the stochiometric equation in Equation 5.3. The separator block is used to remove the water vapour that evolves during the drying process. A crusher was modelled to reduce the biomass particle size to 2mm and the screen separates the oversized biomass particles which are then recycled into the crusher. The pine sawdust is transformed into conventional simulation components by the RYIELD reactor at 500 ℃ and 1 atm. Helium gas at 16 kmol/hr is added to the stream to maintain an inert environment in the pyrolysis reactors.

Table 5.6: Aspen Plus® model stream information

Stream ID	**Description**
RAW-FEED	Raw biomass feed (pine sawdust) enters the RSTOIC block for drying at 25℃ and 1 bar.
S6	A mixture of dried pine sawdust and moisture.
H2O-VAPO	The stream consists of moisture separated from the pine sawdust.
DRY-FEED	The stream consists of dried biomass feed.
S5	Particles >2mm are recycled to the crusher.
HELIUM	The stream consists of helium gas at 16 kmol/hr. Helium served a carrier gas and provided an inert environment in the pyrolysis reactors.
AC	The stream consists of activated carbon which acts as a microwave absorbent.
S2	The stream consists of decomposed biomass components from the RYIELD reactor.
S4	The stream consists of the pyrolysis products from the RGIBBS reactor.
S9	A mixture of the non-condensable and condensable vapour fractions.
CHAR	The stream consists of the by-product of pyrolysis, char.
H2O	Cooling water is used in the heat exchanger.
S13	A mixture of the condensed fraction and the non-condensable fraction of the pyrolysis products from the heat exchanger.
NCG	The stream is composed of non-condensable gases.
BIO-OIL	The stream constitutes the condensable fraction of the pyrolysis products, bio-oil.

Activated carbon acts as a microwave absorbent when pyrolysis is taking place. The yield fractions of pine sawdust are specified based on research by(Caudle et al., 2020) Caudle et al. (2020) and the decomposition fractions are presented in Table 5.7. The RGIBBS reactor estimates the distribution of the products by minimizing Gibbs free energy. Helium gas was defined as an inert component in the RGIBBS reactor. The operating pressure and temperature of the RGIBBS reactor was specified at 1 bar and 500 ℃ respectively. The relationship between the bio-oil output and the operating temperature was examined by varying the temperatures of the RYIELD reactor. The solid fraction (char) was separated from the product stream with the aid of a cyclone. The rest of the product stream is condensed to ambient temperature to separate the gaseous products from the liquid fraction (bio-oil).

$$BIOMASS \rightarrow 0.95\, DRY\ BIOMASS + 0.0027754\, H_2O \tag{5.3}$$

Table 5.7: Biomass decomposition yield fractions

Component	Basis	Yield
CELL	Mass	0.4385
GMSW	Mass	0.2191
METHY-01	Mass	0.0471
LIGH	Mass	0.1199
LIGO	Mass	0.1084
TANN	Mass	0.0125
ASH	Mass	0.0046
XYHW	Mass	0.0499

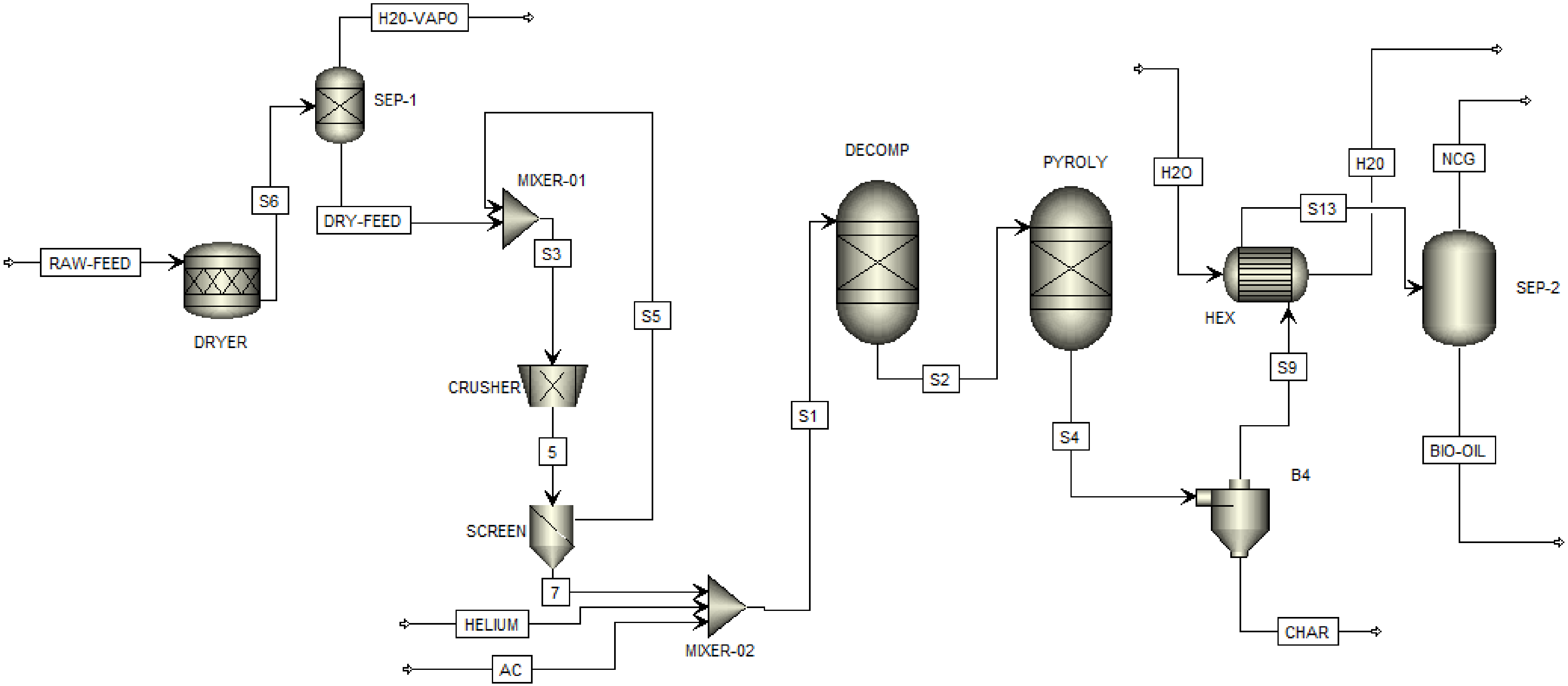


Figure 5.1: Aspen Plus® simulation flow diagram for the conversion of pine sawdust to pyrolysis products

5.3.3.1 *Process sensitivity analysis*

The process sensitivity analysis was performed using the developed simulation model by adjusting reactor pressure from 1-3.3 bar and temperature from 340 to 700°C. The distribution of the product was then examined in relation to temperature and pressure.

5.3.3.2 *Response surface methodology*

The main objective of this analysis was to come up a regression model that would evaluate system performance by taking into account how the key parameters interacted. Design-Expert® Software was used to develop a design matrix using the Aspen Plus® simulated data. The parameters for biomass fast pyrolysis were optimized using RSM based on CCD. A second-order model has been fitted using the CCD, a standard RSM design. CCD is an excellent approach for fitting a quadratic surface and aids in minimizing the number of tests required to maximize the effective parameters and examine how the parameters interact.

Analysis of variance (ANOVA) was evaluated using statistical analysis of the model. ANOVA enables determining the significance of the effect and interaction of the examined parameters in relation to the experimental error. To evaluate the significance of the effects, statistical F-tests were utilized. It is applied to compare statistical models that have been fitted to data sets to determine which model better represents the population that the data were sampled. By doing an ANOVA at a 95% confidence level and assessing the model's quality, the objective response regression models were developed. According to the second-order quadratic equation shown in Equation 5.4, the response variable interaction was established (Kombe et al., 2022).

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=1}^{n} \beta_{ij} x_i x_j + \epsilon \tag{5.4}$$

Where y denotes the output response, x denotes the decision parameter, β_i denotes the coefficient, n denotes the total sum of the variables, and ϵ is the statistical error.

The constructed regression model's accuracy was measured using the regression coefficient (R^2) and the adjusted regression coefficient (R_{adj}^2) values. These variables were determined using Equation 5.5 (Kombe et al., 2022):

$$R_{adj}^2 = 1 - \left[\frac{\left(\frac{SS_R}{n-p} \right)}{\left(\frac{SS_T}{n-1} \right)} \right] = 1 - \frac{(1 - R^2)(n-1)}{1-p} \tag{5.5}$$

Where SS_R and SS_T are determined using Equations 5.6 and 5.7.

$$SS_R = \sum_{i=1}^{n} \left(y_i - y_j\right)^2 \tag{5.6}$$

$$SS_T = \sum_{i=1}^{n} y_i^2 - \frac{\left(\sum_{i=1}^{n} y_i^2\right)}{n} \tag{5.7}$$

Where y_i and y_j, respectively, denote the observations and the fitted observations.

The p-value, a key parameter in the model, is usually perceived as insignificant if its value surpasses 0.05 (Roy et al., 2020). The degree of fit is measured by R^2, which was calculated using Equation 5.8 (Kombe et al., 2022).

$$R^2 = 1 - \frac{SS_R}{SS_T} \tag{5.8}$$

The values of R^2 and R_{adj}^2 were between 0 and 100%. A value of more than 90% means the model is accurate (Kombe et al., 2022; Zaman & Ghosh, 2021). Further evidence for a good model is provided by the less than 0.2 difference between R^2 and R_{adj}^2 (Zaman & Ghosh, 2021).

5.3.3.3 Model validation

Model validation was performed using the product distribution results attained from the experimental setup described in section 2.1. A set of three published experimental results acquired under circumstances comparable to the simulations' operating limitations were used to further validate the simulation results. The initial validation was performed using Ningbo et al. (2015) experimental findings. In their experimental work, fast pyrolysis of pine wood was performed in a screw reactor to examine the influence of solid residence time and pyrolysis temperature on the distribution of products and energy. Secondly, the comparison employed DeSisto et al. (2010) experimental findings. In their study, pine sawdust was pyrolyzed between 400 and 600℃ in a fluidized bed pyrolysis reactor. Lastly, the comparison employed Zhang et al. (2017) experimental findings. The study employed fluidized bed pyrolysis to carry out the pyrolysis of pine wood.

The deviation of the simulation results from the experimental results from the literature was measured using the root mean square error (RMSE). This was established using Equation 5.9.

$$\mathrm{RMSE} = \sqrt{\sum (\mathrm{X_s} - \mathrm{X_e})^2 / \mathrm{N}} \tag{5.9}$$

Where X_s is the simulated result, X_e is the experimental result and N is the number of data sets.

5.3.4 Economic evaluation

The Aspen Plus Economic Analyzer was employed in determining the equipment costs. Scaling and installation factors were used to adapt the price of the purchased machinery to the required size, operating pressure, and building materials. Using a Chemical Engineering Plant Cost Index (CEPCI) of 699.0, installed equipment costs were then updated for the year 2022. Peters and Timmerhaus' approach was employed in the determination of the TPI, as presented in Table 5.8 (Makepa et al., 2023a; Peters et al., 2003). The MSP of bio-oil, described as the minimum market price which provides a NPV equal to zero at a set IRR; 10% nominal or 22% desired, was determined in this study using a DCFROR analysis. Table 5.9 lists the assumptions used in the DCFROR analysis. A 25% change in an economic parameter's impact on the MSP of bio-oil was taken into account while conducting economic and process sensitivity analysis to determine which economic parameters provide the most investment risk.

Table 5.8: TPI estimation method (Makepa et al., 2023a; Peters et al., 2003)

Parameter	**Factor**
TPEC	TPEC
TIC	3.02*TPEC
Indirect cost (IC)	0.89*TPEC
TDIC	TIC + IC
Contingency	0.2* TDIC
FCI	TDIC + contingency
Location factor (LF)	0.1*FCI
TPI	**FCI + LF**

Table 5.9: DCFROR assumptions

Parameter	**Assumption**
Plant life	25 years
Equity	40%
Loan interest	7.5%
Loan term	10 years
Income tax rate	39%

5.4 Results and discussion

5.4.1 Validity of the model

Based on data from MAP, simulations for the fast pyrolysis of pine sawdust were performed in Aspen Plus® software. The experimental results and the output of bio-oil, biochar, and NCGs were compared to assess the validity of the proposed microwave-assisted fast pyrolysis model. Using input and output variables including reactor temperature, biomass properties, and absorbent and inert gas flow rates, among others, the fast pyrolysis process was simulated under similar conditions described in the experimental setup.

The simulation was carried out at 500 °C using Aspen Plus® to estimate the output of bio-oil, biochar, and NCGs. This simulation was run after specifying the physical and chemical parameters of each component utilized in the proposed model. Figure 5.2 compares experimental data with the product yield results that were obtained. The RMSE illustrates how closely simulated results match experimental data. The product distribution of the simulated model and the experimental results matched satisfactorily with an RMSE of 3.55%, 2.24% and 1.31% for bio-oil, char and NCGs respectively.

In addition, the model was compared with three sets of published experimental results as shown in Figure 5.3. The model product distribution was fairly consistent with the experimental works of DeSisto et al. with an RMSE of 0.8% for bio-oil. However, lower bio-oil outputs of 51.7 wt.% and 50.1 wt.% were obtained from the experimental works of Ningbo et al. (2015) and Zhang et al. (2017) respectively. The lower bio-oil yields attribute to higher temperatures (600 °C) employed during the pyrolysis process. At higher pyrolysis temperatures, the long-chain macromolecules are broken down into smaller fragments and the pyrolysis vapours undergo secondary cracking. Lower char yields may be the result of a more extensive primary breakdown of biomass and subsequent decomposition of the solid product at higher temperatures (Ningbo et al., 2015). Both Lu et al. (2015) and Heidari et al. (2014) observed comparable trends in the product distribution temperatures between 500 and 800 ℃.

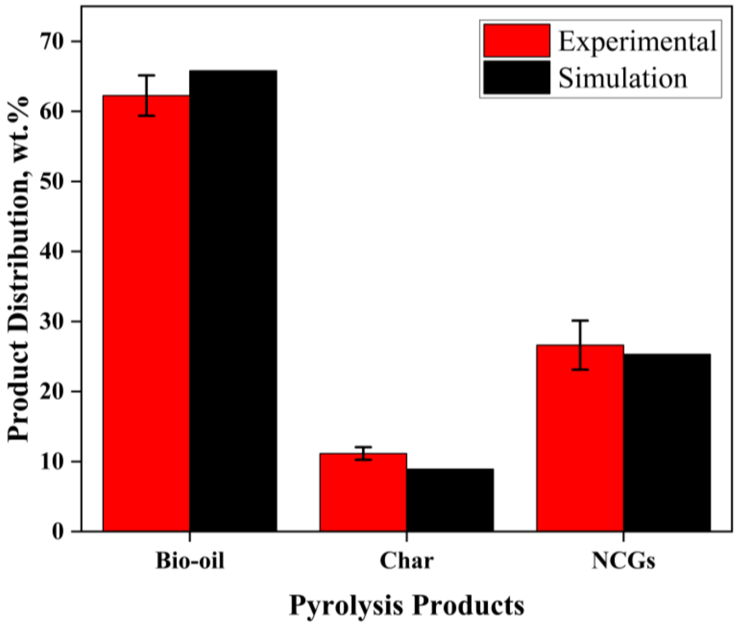


Figure 5.2: Comparison between experimental findings and Aspen Plus® model results

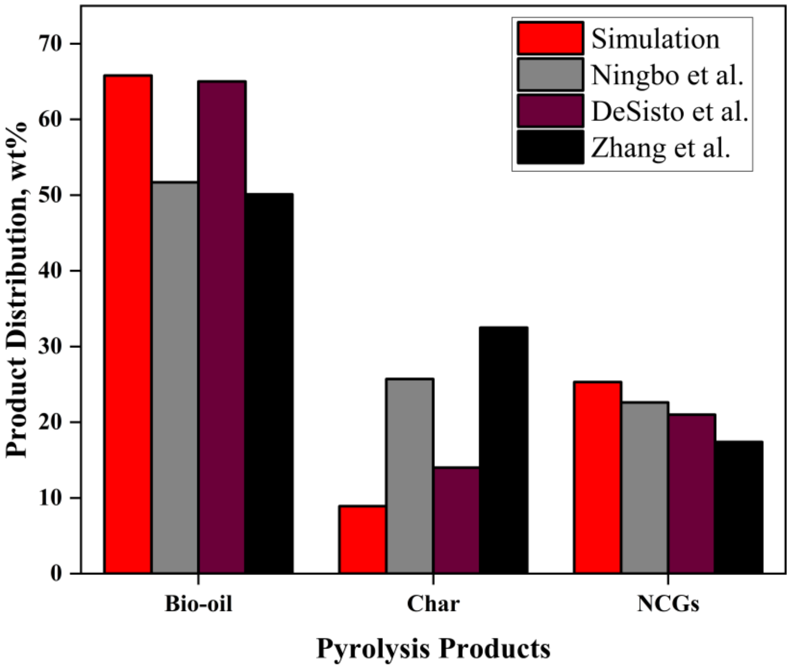


Figure 5.3: Comparison between published works and Aspen Plus® model results

5.5 Effects of process parameters on product distribution

Table 5.10 shows the pyrolysis product distribution at various pyrolysis temperatures and pressures. The influence of pyrolysis temperature on the product distribution is illustrated in Figure 5.4. The production of char was favoured at low pyrolysis temperatures because lower temperatures tend to favour charring processes that produce coke. The bio-oil product yield increases with increasing pyrolysis temperature, but only until a certain point, at which point it begins to fall (Mutsengerere et al., 2019). At temperatures between 500-550 °C, the bio-oil product yield reached its maximum; as temperatures are further increased, the yield gradually declined. The observed decrease in bio-oil production was attributed to subsequent thermal cracking reactions between pyrolysis vapours and tar fragments to produce true vapours, which enhanced the yield of NCGs. In addition, regardless of the heating technique utilized, Binti Mohd found that the formation of NCGs often rises as the pyrolysis temperature rises (Binti Mohd, 2017). Thus, at higher temperatures, both tar and char are transformed into lighter hydrocarbons like syngas. The bio-oil product yield has regularly been observed to improve initially with temperature increase up to a particular temperature, where the production would decrease as temperatures are further increased. Additionally, comparable results were obtained regarding the effect of temperature on the rapid pyrolysis of biomass feedstock in a fluidized bed reactor by Lu et al. (2015) and Heidari et al. (2014).

The influence of reactor pressure on product distribution was also investigated. The effects of reactor pressure on product distribution are shown in Figure 5.5. The reactor pressure has no significant effect on pyrolysis product distribution. However, because of its inverse relationship to the volumetric density of the vapour phase, it indirectly affects the reactor's residence time (Caudle et al., 2020).

Table 5.10: Distribution of pyrolysis products at various pyrolysis temperatures and pressures

Variable modified	Process inputs		Product distribution (wt.%)		
	Temperature (°C)	**Pressure (atm)**	**Bio-oil**	**Char**	**NCGs**
Baseline	500	1	65.8	8.9	25.3
Reactor Temperature	340	1	30.4	64.3	5.3
	400	1	47.4	40.1	12.5
	600	1	57.5	8.7	33.8
	700	1	52.7	9.6	37.8
Reactor Pressure	500	1.3	60.1	19.0	20.9
	500	1.8	53.7	11.1	25.3
	500	2.8	64.9	8.3	26.9
	500	3.3	63.6	8.1	28.3

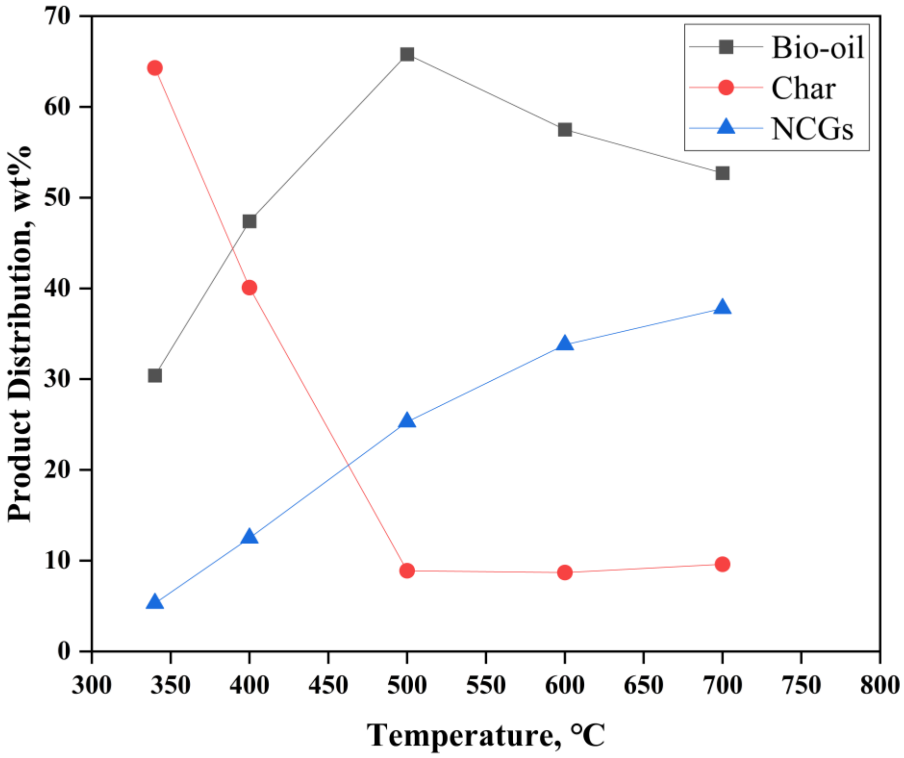


Figure 5.4: Effect of temperature on pyrolysis product output

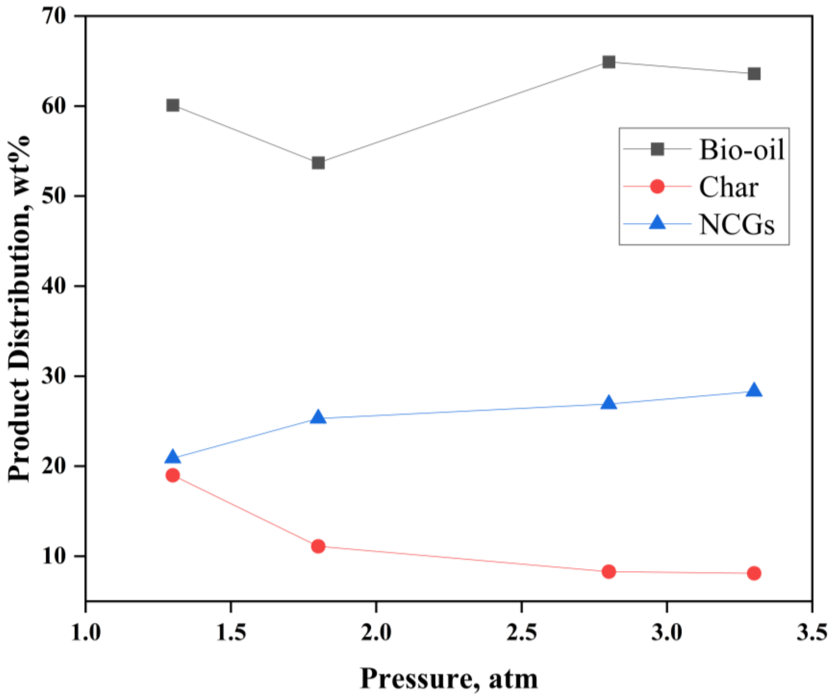


Figure 5.5: Effect of reactor pressure on pyrolysis product output

5.6 Regression models and ANOVA

In terms of the coded factors with significant variables, the final model regression equations for bio-oil, char, and NCGs yield are shown in Equations 5.10-5.12, respectively.

$$Bio - oil\ Yield\ (\%) = -133.27464 + (0.671978A) + 4.16109B - 3.99303^{-16}AB - 0.000579A^2 - 0.967696B^2 \qquad (5.10)$$

$$Char\ Yield(\%) = 291.49722 - 0.907127A - 5.1692B + 7.85616^{-16}AB + 0.00072A^2 + 1.20214B^2 \qquad (5.11)$$

$$NCGs\ Yield\ (\%) = -51.22833 + 0.208476A + 1.74404B - 1.50616^{-16}AB - 0.000119A^2 - 0.405592B^2 \qquad (5.12)$$

Where A is the temperature and B is the pressure.

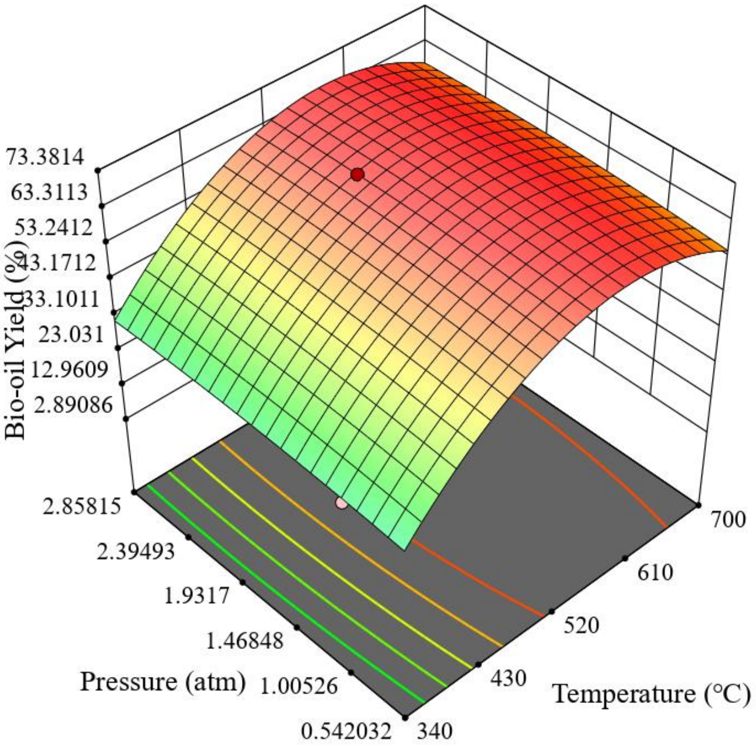
Table 5.11 presents the results of the ANOVA for the output of bio-oil, char, and NCGs. The significance of the models is demonstrated by the low p-values (less than 0.0001) and high F-values (74.94, 156.55, and 174.52, respectively) for the bio-oil, char, and NCGs yield regression models. A high F-value indicates that the model is significant and there is only a 0.01% likelihood that F-values this big are caused by noise. The linear and square terms are significant, based on the ANOVA results. However, the effect of reactor pressure on the output of bio-oil is insignificant. The correlation coefficient (R^2) measures how much the independent factor variables in the model's response have been able to reduce the response's variability. $R^2 = 0$ denotes that the fit does not predict the response any better than the mean response as a whole, and $R^2 = 1$ denotes that the fit is perfect (the errors are all zero). Regression models for the product distribution of bio-oil, char, and NCGs had R^2 values of 98.17%, 99.11%, and 99.20%, respectively. The high R^2 values indicate that the bio-oil, char, and NCGs yield regression models fit the experimental findings with a level of acceptable precision. Additionally, the adjusted R^2 values of 96.86%, 98.48%, and 98.64% for the respective yields of bio-oil, char, and NCGs are reasonably close to the corresponding R^2 values. The difference of less than 0.2 between the Predicted R^2 values and the Adjusted R^2 values for all the regression models further implies the significance of the model. These findings indicate that there is very little probability of including an insignificant term in the model. As a result, the response variables may be precisely determined by the regression models

Table 5.11: ANOVA results for pyrolysis products yield

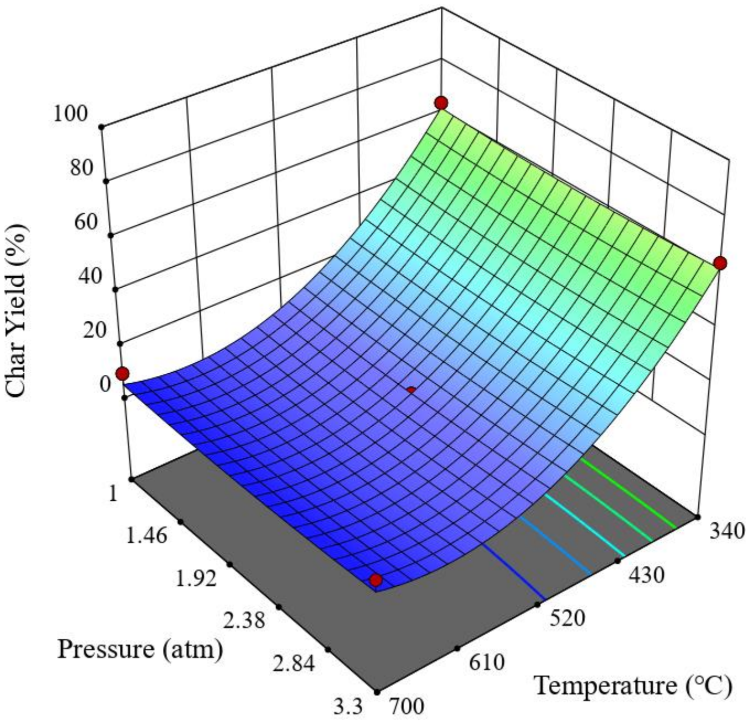
Constant	df	Bio-oil Yield				Char Yield				NCGs Yield			
		Sum of Squares	Mean Squares	F-value	p-value	Sum of Squares	Mean Squares	F-value	p-value	Sum of Squares	Mean Squares	F-value	p-value
Model	5	3729.33	745.87	74.94	< 0.0001	10315.4	2063.08	156.55	< 0.0001	1983.77	396.75	174.52	< 0.0001
A-Temperature	1	1273.88	1273.88	127.99	< 0.0001	6517.19	6517.19	494.53	< 0.0001	1881.14	1881.14	827.44	< 0.0001
B-Pressure	1	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000
AB	1	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	1.0000
A^2	1	2445.83	2445.83	245.74	< 0.0001	3783.28	3783.28	287.08	< 0.0001	102.62	102.62	45.14	0.0003
B^2	1	11.39	11.39	1.14	0.3202	17.58	17.58	1.33	0.2860	2.00	2.00	0.8804	0.3793
Residual	7	69.67	9.95			92.25	13.18			15.91	2.27		
Lack of Fit	3	69.67	23.22			92.25	30.75			15.91	5.30		
Pure Error	4	0.0000	0.0000			0.0000	0.0000			0.0000	0.0000		
Total	12	3799.00				10407.6				1999.69			
Coefficient of determination													
R^2		0.9817				0.9911				0.9920			
Adjusted R^2		0.9686				0.9848				0.9864			
Predicted R^2		0.8696				0.9370				0.9434			

Three-dimensional (3D) response surface plots of two factors were represented in this study. The purpose of the 3D-surface plot is mainly to classify the surface shape for various parameters used and show the effectiveness of each parameter on the output of bio-oil, char and NCGs (Kılıç et al., 2014). The operating point at which the highest production of pyrolysis products may be achieved is investigated using the synchronized effects of the crucial parameters. Figure 5.6 presents the combined effects of reactor temperature and pressure on the production of bio-oil, char, and NCGs. Bio-oil yield increased with increased temperature from 340-600 ℃ and eventually decreased with temperatures exceeding 600℃. Temperatures between 520 and 600 ℃ result in a high amount of bio-oil output, with 550℃ and atmospheric pressure as the optimum operating conditions. The effect of reactor pressure bio-oil yield is insignificant, as illustrated in Figure 5.6 (a). Maximum char yields are obtained at the lowest temperature (340 ℃) (Figure 5.6 (b)) as low temperatures tend to favour the charring process that produces coke. Incomplete or unpyrolyzed biomass might be the result of the increased char output at lower temperatures (DeSisto et al., 2010). It is evident from Figure 5.6 (c) that the yield of NCGs increases with increasing temperatures. As the NCGs yield increases, the bio-oil yield is observed to decrease with increasing temperature, owing to the secondary cracking reactions of the gaseous and liquid products with rising temperature (Heidari et al., 2014; Mutsengerere et al., 2019). From the 3D surface plots, the maximum yields of bio-oil were archived at temperatures of 550 ℃ and atmospheric pressure. Therefore, it can be inferred that reaction temperature has a substantial effect on the conversion of biomass into bio-oil.

However, other parameters such as residence times and heating rate are known to affect the mass yields of the pyrolysis products. The heating rate is crucial in the pyrolysis process since it affects the amount and quality of the end product to some extent. The likelihood of secondary reactions can be eliminated or minimized at low heating rates. A low heating rate also prevents the thermal cracking of biomass, increasing the production of biochar. High heating rates support biomass fragmentation and boost gas and liquid production, which reduces the likelihood of biochar formation (Tripathi et al., 2016). According to Chen et al. (2016), enhanced heating rates gave rise to higher mass yields of the liquid product, and the influence of heating rate on biochar being more noticeable at lower temperatures. The mass yield of NCGs is not significantly influenced by the heating rate, but the yield rises with temperature, mainly because of the secondary cracking reactions of the volatiles (Chen et al., 2016). Short residence times favour bio-oil production by rapid removal of organic vapours from the reactor, minimizing secondary reactions (Kan et al., 2016). A longer residence time gives the biomass components sufficient time to react and promotes repolymerization of the biomass components (Tripathi et al., 2016).



(a)



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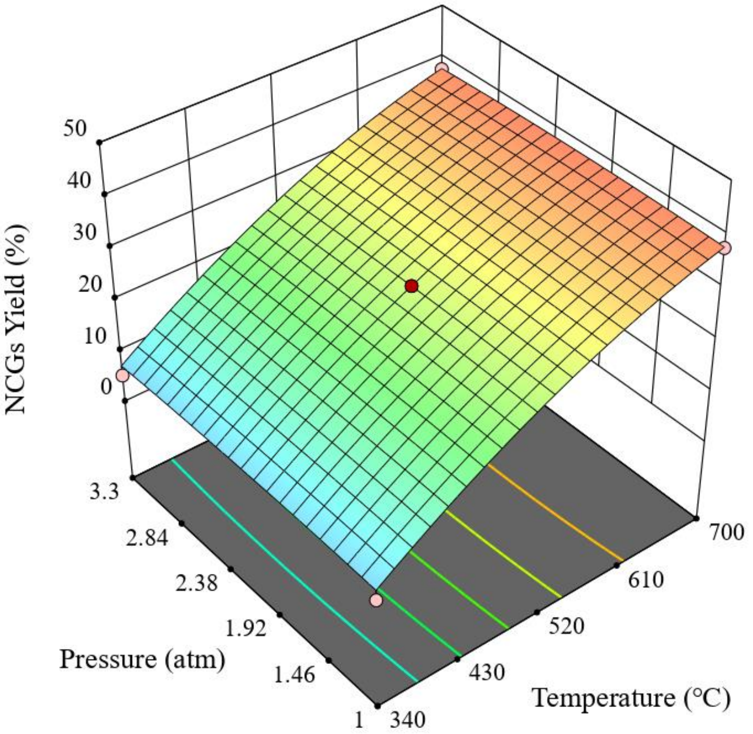


(c)

Figure 5.6: 3D response surface plots of the effect of operating temperature and reactor pressure on (a) bio-oil yield, (b) char yield, and (c) NCGs yield

5.6.1 Economic evaluation

5.6.1.1 Capital cost estimation

The findings of the process modelling were utilized to estimate and calculate the cost of the process equipment. The pyrolysis unit contributes between 37.9% to the TIEC. In a study by van Schalkwyk et al. (2020), pyrolysis contributes between 39.8 and 44.1% to the TIEC of each biorefinery scenario. Although pyrolysis contributed 31.1% to the TIEC in the study by Dutta et al. (2015), the TIEC on an annual biorefinery throughput basis was significantly higher than in this study. Due to economies of scale, pretreatment (biomass grinding and drying) accounts for 21.4% of the overall installed equipment cost, while product recovery accounts for 17.1% of the TIEC. The result for product recovery reported by Dutta et al. (2015) accounted for 11.4% of the TIEC. This agrees with the results reported by van Schalkwyk et al. (2020), where pretreatment contributed between 15.4 and 21.4% of the TIEC and product recovery contributed 17.1% of the TIEC.

5.6.1.2 Economic sensitivity analysis

The economic sensitivity analysis given in Figure 5.7 assesses the impact of a 25% change in the economic parameters of bio-oil production. The MSP shows the highest sensitivity to variations in annual fuel yield, required rate of return, annual income tax, annual operating costs and initial capital investment. Carrasco et al. (2017) and van Schalkwyk et al. (2020) also found that the MSP of the liquid product is sensitive to a variation in the initial capital investment. The MSP of bio-oil was estimated at \$1.14/L. This agrees with a value of \$1.11/L obtained by Li et al. (2015) in an analysis of biomass pyrolysis for the production of biofuels. A 25% increase in the required rate of return, annual income tax, annual operating costs and initial capital investment increases the MSP of bio-oil to \$1.40/L, \$1.35/L, \$1.31/L and \$1.25/L, respectively. However, increasing the annual fuel yield by 25% decreases the MSP to \$0.91/L. Furthermore, a 25% reduction in the required rate of return, annual income tax, annual operating costs and initial capital investment decreases the MSP to \$0.97/L, \$0.98/L, \$0.97/L and \$1.02/L, respectively. Correspondingly, for a 25% reduction in annual fuel yield, the MSP of bio-oil increases to \$1.52/L.

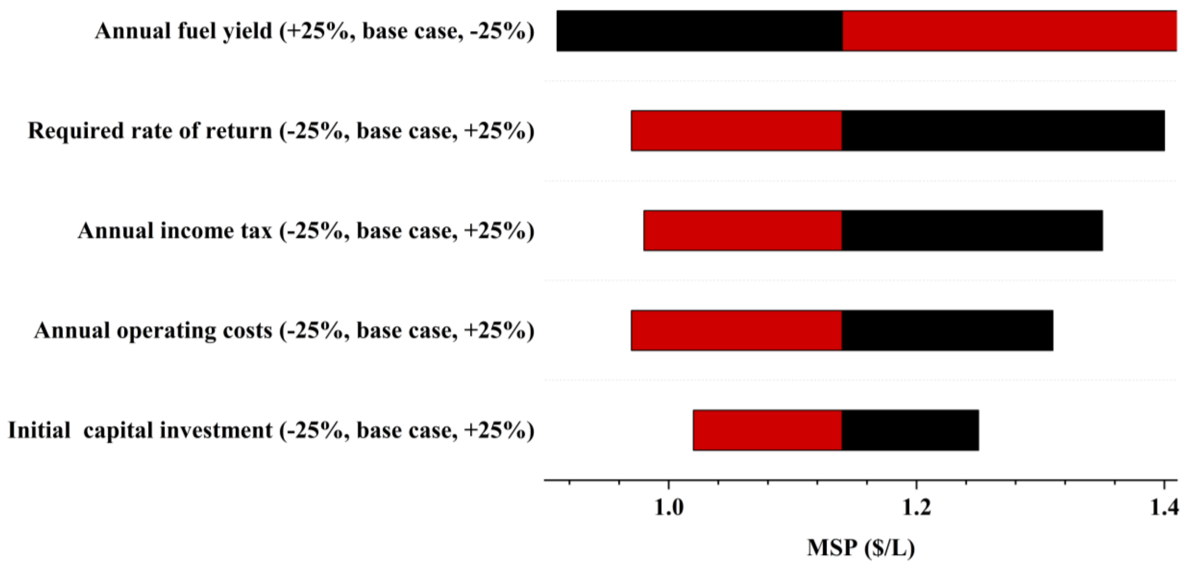


Figure 5.7: Economic sensitivity analysis bio-oil production

5.7 Conclusions

The main aim of the study was to model the MAP of pine sawdust and to optimize its process variables. Aspen Plus® V11 was used to model the MAP of pine sawdust, and a CCD with RSM was employed in optimizing the process variables. The RSM findings showed that the generation of bio-oil was more influenced by operating temperature. Additionally, the findings showed that the output of bio-oil was more significantly influenced by linear and quadratic terms of the reaction temperature. The maximum yield of bio-oil (65.8 wt.%) was achieved at the optimized condition. The optimized values of experimental variables were 550°C and 1 atm for operating temperature and reactor pressure respectively. The pyrolysis product yield may be predicted using quadratic models created based on the regression analysis. Reactor pressure does not significantly influence the distribution of the end products, according to the quadratic model developed for the pyrolysis product yield. With an overall high determination coefficient (R^2=0.9883), the developed quadratic model fits the data well to predict the response. A MSP of $1.14/L of bio-oil was estimated from the economic evaluation of the model. A sensitivity analysis revealed that the annual fuel yield, required rate of return, annual income tax, annual operating costs and initial capital investment have a significant impact on the MSP. As a result, it can be inferred that using the optimized process parameters may improve the pyrolysis process' competitiveness on an industrial scale due to its better product yields and improved sustainability in the biorefinery, as well as assure waste reduction.

CHAPTER SIX: TECHNO-ECONOMIC ANALYSIS

6.1 Chapter overview

Pyrolysis is one of the most promising biomass conversion technologies for bio-oil production. It is essential to upgrade bio-oil before it can be used as a fuel in internal combustion engines. This study aimed at evaluating the economic feasibility of MAP of pine sawdust for biodiesel production. Aspen Plus® was used to simulate a facility that processed 2000 metric tonnes of pine sawdust per day. The MFSP of biodiesel was established through the use of a DCFROR analysis. The findings of the process modelling revealed that the pyrolysis section yielded 65.8 wt. % bio-oil, 8.9 wt. % biochar, and 25.3 wt. % NCGs. The biodiesel product yield was 48 wt. % of the raw bio-oil, yielding 631.7 tonnes per day of biodiesel. With the cost of methanol playing a significant role, the overall capital investment was $216.7 million (MM) and the total yearly operating expenses were $164.9 MM. The predicted MFSP for biodiesel is $2.31/L, with yearly operational expenses and biodiesel output being the most important factors. With an anticipated MFSP that is competitive with traditional diesel fuel, the study concludes that the method is economically viable. The results underline how crucial it is to optimize crucial process variables in order to increase the process's economic viability.

This chapter is an original research manuscript submitted to the journal Heliyon (Under review). A comprehensive techno-economic analysis was performed, fulfilling objective 4.

6.2 Introduction

Over the past few decades, the development of biofuels has drawn a lot of interest as a viable replacement for conventional fossil fuels. This is primarily because biofuels have the potential to improve sustainability, minimize greenhouse gas (GHG) emissions, and improve global energy security (Mat Aron et al., 2020). Worries over climate change and the environmental impact of non-renewable fuels have sparked interest in producing sustainable biofuels with lower carbon footprints. Biofuels are made from a variety of feedstocks including municipal waste, forestry waste, and agricultural waste, which are renewable sources of biomass. The development and use of biofuels can reduce GHG emissions by offsetting carbon emissions. Furthermore, boosting domestic production of biofuels lowers or reduces reliance on foreign oil imports, improving energy security (Prasad et al., 2020).

Pyrolysis is a practical method for transforming biomass into crude bio-oil that can be utilized in an integrated biorefinery to produce various biofuels and value-added chemicals. Pyrolysis, is the thermal degradation of carbonaceous biomass feedstocks in the absence of oxygen. In this process, complex organic molecules are broken down into less complicated ones (Mutsengerere et al., 2019). The pyrolysis technology is advantageous in that it utilizes a variety of feedstocks, including municipal solid waste, agricultural leftovers, and forestry residues (Makepa et al., 2022). Depending on the process parameters and the feedstock, pyrolysis can result in a variety of products including bio-oil, biochar, and NCG. This enables versatility in the development of biofuels with particular qualities that can satisfy a variety of market demands (Mutsengerere et al., 2019). Despite these benefits, pyrolysis does have certain drawbacks. For instance, depending on the feedstock and process parameters employed, the process is known to be energy-intensive and the quality of the bio-oil generated can vary (Amalina et al., 2023).

The synthesis of bio-oil from biomass feedstocks can be optimized in yield and efficiency using MAP (Makepa et al., 2023a). Compared to conventional pyrolysis techniques, MAP can reduce processing times and boost bio-oil production because microwaves can quickly and evenly heat biomass feedstock (Mutsengerere et al., 2019).

Despite having characteristics that are comparable to those of petroleum-based diesel, bio-oil cannot be utilized directly as a fuel due to its instability, high acidity, and high water content (Sánchez-Borrego et al., 2021). As a result, bio-oil requires upgrading to improve its quality characteristics for use as fuel.

Several techniques including esterification, hydrotreating, hydro-deoxygenation, and fractionation can be employed to upgrade bio-oil to enhance its physical and chemical characteristics, such as lowering its acidity, enhancing its stability, and raising its energy density (Kumar et al., 2020).

Bio-oil is highly acidic, it can cause corrosion in storage tanks and engines, resulting in high maintenance costs (Lahijani et al., 2022). Bio-oil's potential as a fuel source is constrained by its low energy density. Increasing the energy density of bio-oil can make it more cost-effective and efficient for use in engines and other applications (Hu & Gholizadeh, 2020). Finally, improving bio-oil can make it more compatible with the fuel distribution and infrastructure already in place.

Bio-oil can be upgraded or transformed to biodiesel through transesterification. Transesterification is a process that involves reacting the bio-oil with an alcohol, such as methanol, to produce FAMEs, respectively (Hadhoum et al., 2019). Bio-oil transesterification can potentially reduce the acidity of bio-oil, improve its stability, and increase its energy density. The resulting FAMEs can be further purified for use or blended with conventional diesel.

While large-scale commercialization of advanced biofuel production technologies utilizing bio-oil remains elusive, there is potential for biomass-derived products to replace fossil-fuel-based alternatives, provided they can be produced sustainably and cost-effectively. One approach to assessing the economic feasibility of biomass conversion pathways is through TEA (Makepa et al., 2023a). Several studies have utilized TEA to investigate the economics of various fast pyrolysis pathways. For example, Wright et al. (2010) estimated a product price of \$2.11 and \$3.09 per gallon of gasoline-equivalent for a pyrolysis plant that converted biomass to diesel-range fuels and naphtha under internal hydrogen production and merchant hydrogen purchase cases, respectively. Li et al. (2015) projected MFSPs ranging between \$1.11 and \$1.13/L for catalytic pyrolysis of biomass for the production of transportation fuel, respectively. Brown et al. (2012) assessed the techno-economic viability of different pathways that produced bio-chemicals through the integrated catalytic fast pyrolysis process, while Hu et al. (2016) evaluated the economics of biofuels, bio-chemicals, and hydrocarbon chemicals production through a fast pyrolysis biorefinery. Hu et al. reported minimum product selling prices of \$0.82/L for biofuels, \$773.5 per metric ton for hydrocarbon chemicals, and \$433.7 per metric ton for bio-chemicals. These studies demonstrate the potential for cost-effective production of biofuels and other value-added products derived from biomass- through fast pyrolysis technology. However, challenges such as equipment costs, process optimization, and uncertainties in market demand and pricing must be addressed to achieve large-scale commercialization.

Most previous studies focused on traditional biofuel production systems (Hu et al., 2016; Sangeetha et al., 2023; Zhang et al., 2016) and have not explored the economics of upgrading bio-oil via the esterification route. A few studies have attempted to upgrade bio-oil via esterification (Hu & Gholizadeh, 2019; Prasertpong et al., 2020), but information on the economics of this process is scarce. A thorough TEA of bio-oil esterification for biodiesel synthesis can aid in the development of sustainable and affordable biodiesel production pathways. This information may be used to identify opportunities for cost reduction and process optimization, create novel catalysts and process conditions, and guide policy choices relating to the production of biofuels. Researchers, decision-makers, and industry stakeholders can collaborate to develop and promote the adoption of more sustainable and economical biodiesel production technologies, which can lessen reliance on non-renewable fossil fuels and slow down climate change, by utilizing the insights gained from TEA.

The central goal of the study was to evaluate the techno-economic viability of producing biodiesel using bio-oil obtained from the MAP of pine sawdust to inform future efforts to create environmentally friendly and economically viable fossil fuel substitutes. The study also sought to evaluate the sensitivity of the MFSP to these factors and to determine the critical process variables that influence the economic feasibility of the process.

6.3 Methods

6.3.1 Pine sawdust characterization

To ascertain the input characteristics of the biomass feedstock in Aspen Plus®, proximate and ultimate analysis of the pine sawdust was conducted. Samples of pine sawdust were taken at specified sawmills that only process Pinus Patula wood. The proximate analysis was carried out according to modified procedures (ASTM D 3173, ASTM D3175 and ASTM D 3174). The elemental analysis was carried out following ASTM D5373 (2014) and the test employed a Thermo Scientific Flash 2000 Organic Elementary Analyzer. Table 6.1 contains the necessary information for modelling pine sawdust in Aspen Plus®.

Table 6.1: Pine sawdust composition (wt.%, dry basis)

Proximate analysis		**Ultimate analysis**	
Moisture Content	7.29	C	51.60
Volatile Matter	78.19	H	5.20
Ash Content	0.28	N	0.04
Fixed Carbon	14.24	O	43.16[a]

[a] Calculated from difference

6.3.2 Process modelling

The microwave-assisted fast pyrolysis process of pine sawdust for bio-oil, char and syngas production, with subsequent bio-oil transesterification to biodiesel is developed using Aspen Plus® V11 assuming an nth plant design. The model assumes the conversion of 2000 metric tonnes of pine sawdust on a daily basis. The model is comprised of four major processing steps: feedstock pre-processing, fast pyrolysis, pyrolysis product recovery and bio-oil transesterification. A process flow diagram of the microwave-assisted fast pyrolysis process is presented in Figure 6.1.

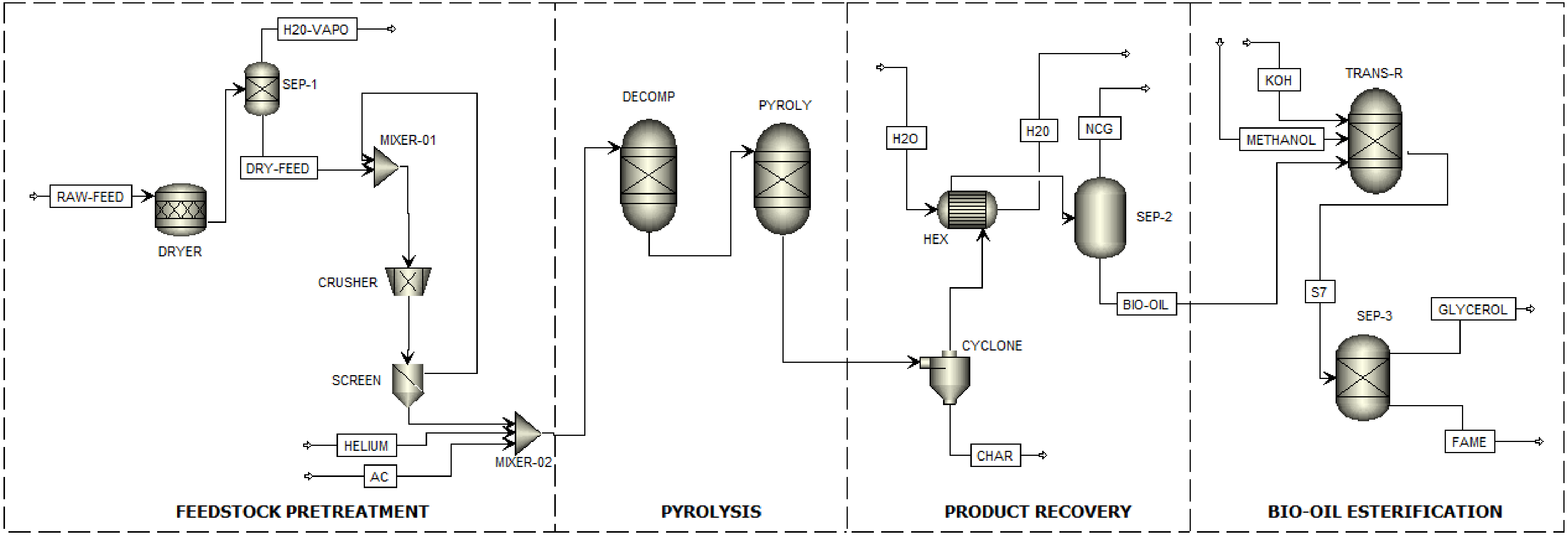


Figure 6.1: MAP flow diagram for the MAP of pine sawdust

6.3.2.1 Feedstock pre-processing

During feedstock pre-processing, the pine sawdust is sent to a drier operating at 125 ℃ and 1 atm to remove excess moisture. Effective drying of the feedstock is crucial in thermochemical processes as the presence of moisture in the feedstock consumes process heat resulting in decreased product yields. The drier was modelled in Aspen Plus® using an RSTOIC reactor. The drying process is necessary as low moisture content enhances the pyrolysis process and improves product quality (Tavares et al., 2020). The dried biomass is then sent to a crusher where the biomass particle size is reduced to approximately 2 mm and passes through a screen. It was essential to carry out this step to eliminate pine sawdust particles that were larger than the required size. The ground pine sawdust is sent to a feed/adsorbent mixer where it is mixed with activated carbon at a ratio of 1:50. Activated carbon is an effective microwave absorbent (Negi et al., 2021) and also catalyzes the pyrolytic cracking of biomass.

6.3.2.2 Fast pyrolysis

Fast pyrolysis is known as the thermochemical degradation of organic matter in an oxygen-free environment, at temperatures ~500 ℃, atmospheric pressure and short residence time ~1s (Makepa et al., 2022). The microwave-assisted fast pyrolysis process was simulated using two sets of reactors in Aspen Plus®. A RYIELD reactor (DECOMP) was employed to model the decomposition of pine sawdust into conventional components, based on the proximate and elemental analysis of the pine sawdust (Table 6.1), and a RGIBBS reactor (PYROLY) was employed in modelling the thermal conversion of biomass through MAP. The RGIBBS reactor was modelled at optimized conditions from a previous study (550 ℃, 1 atm) (Makepa et al., 2023b) and the estimation of the product distribution is achieved through the minimization of Gibbs free energy. A constant flow of helium gas at 250 kmol/hr through the reactor was used to provide an inert atmosphere to facilitate the pyrolysis process.

6.3.2.3 Product recovery

The stream emanating from the PYROLY reactor is a combination of condensable and non-condensable vapours and entrained particles of ash and char. A high-volume cyclone operating at an efficiency of 0.9 was modelled to remove the entrained particles of ash and char from the process stream. To achieve high bio-oil quality and yields, it is important to rapidly condense the vapours immediately after they exit the PYROLY reactor. Secondary reactions that restricts the quantity and quality of the bio-oil collected are encouraged by prolonged residence times (Wright et al., 2010). To achieve quick condensation of pyrolysis vapours, the vapour fraction is condensed using a heat exchanger that operates in counter-flow. Bio-oil is produced by condensing the vapours in indirect contact heat exchangers, and it can be stored safely at ambient conditions before further processing. The major constituents of NCG are carbon monoxide, hydrogen and light hydrocarbons. These can be used in a combustion chamber to avail the heat required for the drying process.

6.3.2.4 Bio-oil transesterification

The bio-oil is transesterified in a REQUIL reactor to produce FAMEs (biodiesel). The bio-oil is reacted with excess methanol in the presence of 1 wt.% KOH catalyst, at 65 ℃ and 1 atm. Equations 6.1-6.5 were specified in Aspen Plus for the conversion of the fatty acids and carboxylic acids present in the bio-oil to biodiesel (Adeniyi et al. 2019). Glycerol was separated from the biodiesel as a by-product.

Oleic acid ($C_{18}H_{34}O_2$) + Methanol (CH_3OH) ↔ Methyl-Oleate ($C_{19}H_{36}O_2$) + water (H_2O) (6.1)

Palmitic acid ($C_{16}H_{32}O_2$) + Methanol (CH_3OH) ↔ Methyl-Palmitate ($C_{17}H_{34}O_2$) + water (H_2O) (6.2)

Linoleic acid ($C_{18}H_{32}O_2$) + Methanol (CH_3OH) ↔ Methyl-Linoleate ($C_{19}H_{34}O_2$) + water (H_2O) (6.3)

Acetic acid ($C_2H_4O_2$) + Methanol (CH_3OH) ↔ Methyl-Acetate ($C_3H_6O_2$) + water (H_2O) (6.4)

Formic acid (CH_2O_2) + Methanol (CH_3OH) ↔ Methyl-Formate ($C_2H_4O_2$) + water (H_2O) (6.5)

6.3.3 Cost estimation

The Aspen Process Economic Analyzer (APEA) was utilized in estimating the costs and size of equipment. The unit operations that were modelled in Aspen Plus were sent to APEA to approximate equipment procurement costs and conduct sizing measurements. The costs of the pyrolysis and esterification reactors were calculated using the scaling equation (Equation 6.6) as outlined by Shoaib Ahmed Khan et al. (2022).

$$C_1 = C_0 \cdot \left(\frac{S_1}{S_0}\right)^{0.6} \tag{6.6}$$

where C_1 represents the new calculated equipment cost, S_1 represents the size of the new equipment, C_o represents the base equipment cost and S_o represents the base equipment size. The equipment cost is updated to 2022 by employing the CEPCI by employing Equation 6.7.

$$New\ equipment\ cost = Base\ equipment\ cost \times \frac{2022\ cost\ index\ value}{Base\ year\ cost\ index\ value} \qquad (6.7)$$

CEPCI for 2022 is listed as 699.0 and for 2018 is 603.1 (Maxwell, 2022). Table 6.2 shows the assumptions made during the calculation of total operating cost. The assumptions employed in the discounted cash flow analysis are given in Table 6.3.

Table 6.2: Operating cost parameters

Material	
Biomass cost (US$/ton)	80
Helium (US$/ton)	12
Activated carbon (US$/ton)	2000
KOH catalyst (US$/ton)	2500
Methanol (US$/ton)	600
Utilities	
Electricity (US$/kWhr)	0.08
Cooling water (US$/m^3)	0.05

Table 6.3: Inputs for discounted cash flow analysis

Economic inputs	
Income Tax	40%
Revenue escalation	5%
Required rate of return	10%
Capital cost escalation	5%
Operating cost escalation	3%
Plant life	20 years

By summing up all the cost ratios, a Lang factor of 5.21 was attained, which represents the proportion of the TPI to the total procurement cost of equipment. This factor was utilized to determine the TPI. TCI was determined using Peters and Timmerhaus’s method as presented in Table 6.4 (Makepa et al., 2023a; Peters et al., 2003). Estimations derived using this methodology usually possess an accuracy of approximately 70% (Wright et al., 2010). The capital cost of biomass pyrolysis and bio-oil esterification is made up of direct and indirect costs, contingency and location factor. Regional labour, supervisor, and service costs are included in the cost model. TIC is approximated by 3.02 times the purchased cost of equipment. Installation cost includes electrical wiring, plumbing, structures, and other related costs. Indirect costs include contractor's fees, supervision and technical cost, legal fees and construction costs. The rate was calculated as 0.89 times the TPEC. In determining the MFSP of biodiesel for a required rate of return of 10% over 20 years, a modified DCFROR spreadsheet was utilized.

Table 6.4: Total project investment estimation method (Makepa et al., 2023a; Peters et al., 2003)

Parameter	**Percent of delivered equipment cost (%)**
TPEC	100
Purchased equipment installation	39
Instrumentation and controls	26
Piping	10
Electrical systems	31
Buildings (including services)	47
Yard improvements	12
Service facilities	55
TIEC	TPEC * 3.20
Engineering	32
Construction	34
Legal and contractors' fees	23
Contingency	15% of FCI
TIC	1.26 * TPEC
FCI	TIEC + TIC
Working capital (WC)	75
TCI	FCI + WC

6.3.4 Sensitivity analysis

The analysis of MFSP's sensitivity was conducted as there were several assumptions made in the model that caused uncertainties in the analysis. By conducting a sensitivity analysis, it was possible to ascertain the factors that exert the greatest influence on the MFSP. The process involved assessing the MFSP by modifying a single factor while keeping all other factors constant. In this evaluation, the factors that were examined included FCI, interest rate, income tax rate, biodiesel yield, annual operating cost, biomass cost, methanol cost, catalyst cost, activated carbon cost, electricity cost, and utility water costs. In this study, the variation range was ±25% of the base MFSP of biodiesel for the parameters evaluated, according to the most critical assumptions. The MFSP is assessed for the base case as well as for the low-end and high-end values of each parameter. The black bars depict how sensitive base MFSPs are to a 25% rise in the parameters, while the red bars portray how sensitive the base MFSPs are to a 25% decrease in the parameters. In general, the longer the bars, the more sensitive the base MFSPs are to parameter changes, and vice versa.

6.3.5 Uncertainty analysis

The findings of this research are based on a deterministic economic analysis that assumes precise knowledge of all the parameters. However, the costs and factors employed in the evaluation of the profitability of the chemical process are subject to significant volatility over the 20-year life of the project. Although the sensitivity analysis varied only a single factor at a time, in reality, numerous factors would vary simultaneously. Therefore, a Monte Carlo analysis was conducted on the biorefinery to assess the uncertainty of the process parameters. The triangular probability distribution was used with similar variations as those presumed in the MFSP sensitivity analysis. The analysis was carried out using Crystal Ball® software with 5000 trials, and the results were analyzed using Microsoft Excel® software.

6.4 Results and discussion

6.4.1 Process modelling results

The model processed 2000 dry MTPD of pine sawdust. The process modelling results showed that the pyrolysis section yielded 65.8 wt.% bio-oil, 8.9 wt.% biochar and 25.3 wt.% NCGs. The results are consistent with the process modelling results of previously published works (Dang et al., 2016; Hu et al., 2016; Makepa et al., 2023c). The bio-oil was further upgraded via esterification to produce biodiesel. The biodiesel product yield was 48 wt.% of the raw bio-oil. The final product yields of the process are presented in Table 6.5. The produced biofuel has several applications as a transportation fuel for diesel engines, boiler fuel for electricity generation in power plants through steam production, feedstock for chemical production and a potential sustainable aviation fuel (Chia et al., 2022; Qiu, Tao, et al., 2022). The process produced a by-product stream, also known as glycerol. Glycerol is a valuable chemical that can be used in a variety of applications, such as in the production of soaps, cosmetics and as a food additive. The glycerol produced during the esterification of pyrolysis bio-oil can be sold as a separate product, providing an additional source of revenue (Dhabhai et al., 2023).

Table 6.5: Process yields of the MAP of pine sawdust

Input	Output	Yield (MTPD)
Biomass	Bio-oil (65.8 wt.%)	1316.0
(2000 MTPD)	Biochar (8.9 wt.%)	178.0
	NCGs (25.3 wt.%)	506.0
Bio-oil	Biodiesel (48.0 wt.% of bio-oil)	631.7
(1316.0 MTPD)	By-products (52.0 wt.% of bio-oil)	684.3

6.4.2 Economic analysis

The TCI is illustrated in Figure 6.2. It is the sum of the TPEC, TIEC, TIC, WC and project contingency of $41.6 MM, $133.1 MM, $52.4 MM, $31.2 MM and $27.8 MM, respectively. The total purchased equipment costs for different areas are analyzed in the stacked bar chart in Figure 6.2. The installed equipment costs for the pyrolysis section are the major portion of the TIEC, contributing approximately 37.9% of the total, or $15.8 MM. The installed equipment costs for the biomass pretreatment section are also quite large, contributing 21.4% of the TPEC with a value of $8.9 MM. Pretreatment equipment costs are primarily driven by the inclusion of a dryer and the ball mill or biomass crusher. The bio-oil esterification section contributed 20.3% to the TPEC, with a value of $8.4 MM. This cost is driven by the employment of an esterification reactor which converts the bio-oil fraction to biodiesel and the final product separator which separates the biodiesel from glycerol. The pyrolysis product recovery section also contributed a significant amount to the TPEC. The cost was driven by the employment of condensate separators, heat exchangers and cyclone separators, contributing 17.1% to the TPEC with a value of $8.4 MM. The biodiesel storage facilities contributed 3.3% of the TPEC with a value of $1.4 MM.

The total annual operating costs are \$164.9 MM (see Figure 6.3). The cost of methanol is responsible for the greater part of the operating costs at \$80.7 MM annually, followed by biomass cost (\$46.7 MM), activated carbon (\$23.3 MM), and catalysts (\$9.6 MM). Utilities contributed \$4.5 MM to the annual operating cost with helium gas contributing the least with a value of \$0.1 MM. These results are similar to other techno-economic analyses (Carrasco et al., 2017; Dang et al., 2016; Wright et al., 2010), which find that feedstock and consumables costs comprise the vast majority of annual operating costs for fast pyrolysis facilities. To comply with the 10% required rate of return, a MFSP of \$2.31/litre of biodiesel was estimated from the DCFROR analysis. As with previous TEAs, product yields, fixed capital costs, biomass and other consumables costs have the greatest impacts on the MFSP (Carrasco et al., 2017; Li et al., 2015). A previous study estimated a MFSP of \$1.38/litre for biodiesel obtained from sugarcane lipids (Arora & Singh, 2020). The differences might be due to the complex thermochemical conversion of biomass, which requires expensive processing equipment. A study by Kedia et al. (2023) estimated a MFSP of biodiesel obtained from non-edible oils of \$2.15/litre, which was close to the MFSP estimated in this study.

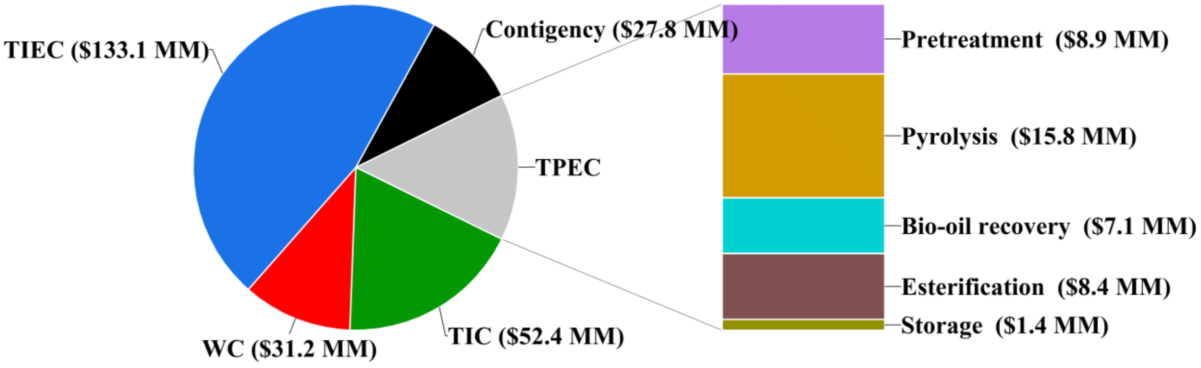


Figure 6.2: TCI for the production of biodiesel from pine sawdust

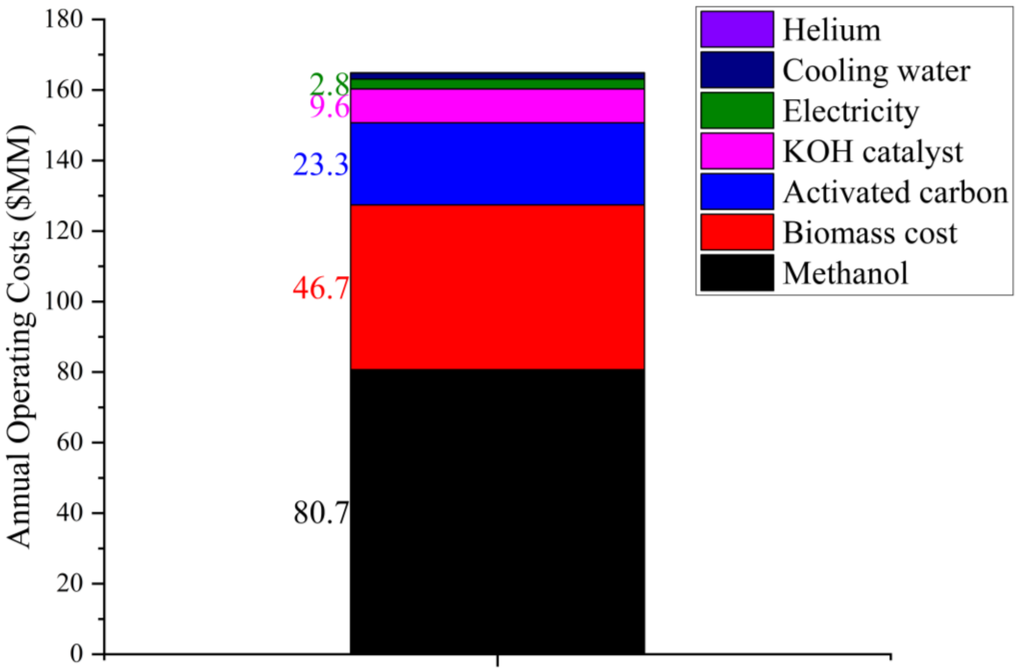


Figure 6.3: Total annual operating costs of biodiesel production from pine sawdust

6.4.3 Sensitivity analysis

Figure 6.4 presents the sensitivity analysis outcomes of biodiesel production from pine sawdust. The biodiesel yield has the highest sensitivity on the MFSP. A 25% increament in the yield of biodiesel resulted in a 20% decrease in the MFSP of biodiesel to $1.85/L. Conversely, a 25% decrease in the biodiesel yield resulted in a 20% increase in the MFSP to $2.77/L. Similar trends were observed in previous studies (Fivga & Dimitriou, 2018; Iglesias et al., 2021; Zhang, Brown, et al., 2013), which employed the fast pyrolysis technique for biofuel production. This implies that improving the process operating conditions to obtain more biodiesel can significantly reduce the MFSP. Another key parameter which affects the sensitivity of the MFSP is the annual operating cost. A 25% increament in the annual operating cost increases the biodiesel yield by 15% to $2.65/L, and reducing the annual operating costs reduces the biodiesel yield by 15% to $1.97/L. The process inputs which greatly affect the sensitivity of the MFSP are the costs of methanol, biomass and activated carbon. A 25% increase in the methanol, biomass and activated carbon increased the MFSP from $2.31/L (base case) to $2.48/L, $2.41/L and $2.36/L, respectively. Conversely, a 25% decrease in the methanol, biomass and activated carbon reduced the MFSP to $2.14/L, $2.21/L and $2.26/L, respectively. Among the process inputs, catalyst costs and electricity costs had the least sensitivity to the MFSP, and the effect of variation in the cost of utility water was negligible. The TCI also has a considerable effect on MFSP. The interest rate and the income tax rate also affected the sensitivity of the MFSP by a margin of 1.3%.

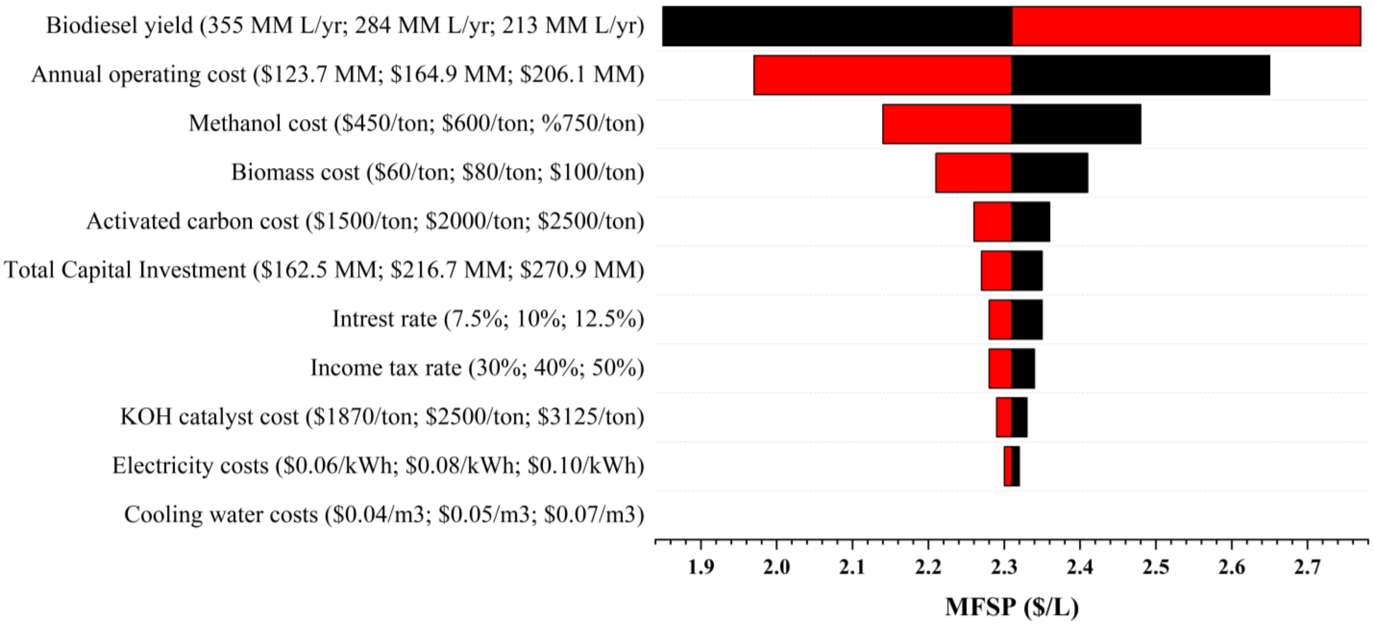


Figure 6.4: Sensitivity analysis of the MFSP of biodiesel produced from pine sawdust

6.4.4 Uncertainty analysis

To assess the uncertainty of the TEA results, a Monte Carlo analysis was carried out to determine the distribution of the MFSP. The sensitivity analysis indicated that the biodiesel yield, annual operating costs, methanol cost, biomass cost, activated carbon costs, and TCI have the most significant impact on the MFSP. Therefore, these six model parameters were regarded as fluctuating variables in the Monte Carlo analysis, with a varied range of ±25% as in the sensitivity analysis. During the simulation, 5000 random MFSPs were generated.

The probability distribution of MFSP for biodiesel is illustrated in Figure 6.5. An average MFSP for biodiesel of $2.49/L with a standard deviation of 0.74% was observed from 5000 runs. This means that the biodiesel needs to be sold at $2.49/L or higher to cover the production costs. This is an important metric for the profitability of the biorefinery and indicates the competitiveness of biodiesel in the market. The standard deviation of 0.74% indicates that the MFSP values have low variance, which means that the cost of biodiesel production is relatively consistent across the 5000 simulation runs. This suggests that the production process is stable and well-controlled and that the biorefinery can produce biodiesel with a consistent cost structure. Figure 6.6 presents the cumulative probability of the resultant MFSP, which ranged from $1.10 to $4.50/L with an 80% chance of falling within the range of $1.30 to $3.10/L. MFSP for the biorefinery has a 50% chance of being less than $3.21/L.

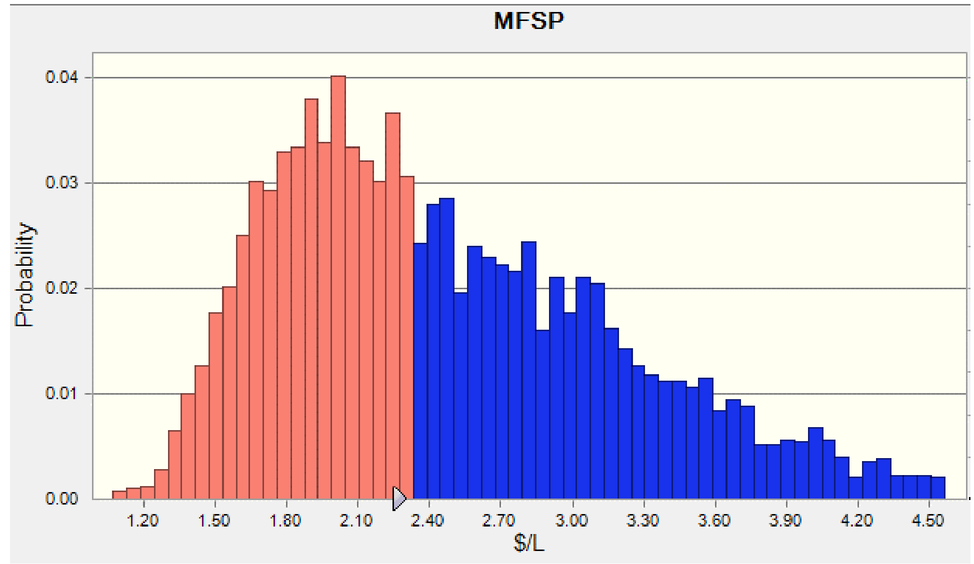


Figure 6.5: Probability distribution of MFSP for biodiesel

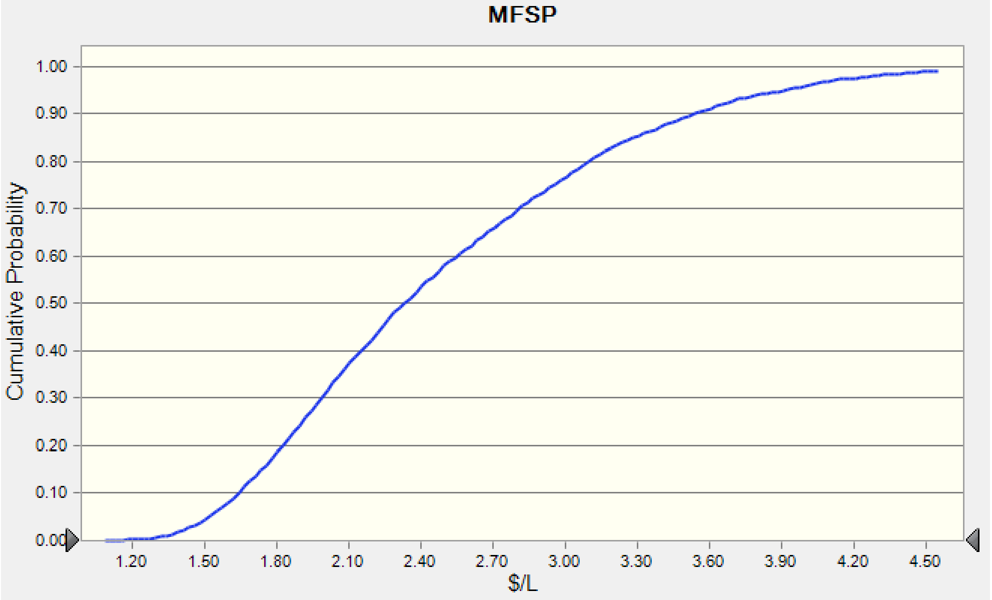


Figure 6.6: Cumulative probability of the MFSP of biodiesel

6.5 Conclusions

This study evaluated the TEA of MAP of pine sawdust with subsequent bio-oil esterification for biodiesel production. The findings of the process modelling revealed that the pyrolysis section yielded 65.8 wt.% bio-oil, 8.9 wt.% biochar, and 25.3 wt.% NCGs. The biodiesel product yield was 48 wt.% of the raw bio-oil, yielding 631.7 tonnes per day of biodiesel. The TCI was $216.7 MM, with the installed equipment costs for the pyrolysis section being the largest portion of the TIEC. The cost of methanol accounted for the majority of the operational costs, which came to a total of $164.9 MM per year. An estimated MFSP of $2.31/L of biodiesel was derived from the DCFROR study to meet the 10% required rate of return. The study also discovered that the two elements most strongly influencing the MFSP are the biodiesel output and annual operational costs. According to the Monte Carlo simulation, the average MFSP for biodiesel was $2.49/L, with a standard deviation of 0.74%. The cumulative probability of the resultant MFSP varied from $1.10 to $4.50/L, with an 80% possibility of lying within the range of $1.30 to $3.10/L. This work sheds important light on the techno-economic viability of pyrolyzing pine sawdust using a microwave to produce biodiesel. With an estimated MFSP that is comparable with traditional diesel fuel, the results point to the possibility of the method being commercially feasible. The outcomes also emphasize the significance of improving crucial process variables, such as biodiesel production and annual operational expenses, to enhance the operation's economic viability. Validating these findings and determining the process's scalability for commercial applications will require more study. However, this research makes a significant addition to the field of biofuels and renewable energy, and it may help guide future initiatives to create environmentally friendly and economically feasible fossil fuel substitutes.

CHAPTER SEVEN: LIFE-CYCLE ASSESSMENT

7.1 Chapter overview

Although biofuels are often presented as a renewable and eco-friendly substitute to fossil fuels, it is crucial to have a comprehensive understanding of the complete environmental consequences of biofuel production to make well-informed choices about their usage. This study evaluated the environmental impacts of producing biodiesel from MAP of pine sawdust using LCA. A cradle-to-gate system boundary approach encompassing pine cultivation, biomass pre-processing, pyrolysis, and biofuel synthesis via transesterification was used. The Ecoinvent v3.7 in openLCA v2.0 software was used to assess the environmental sustainability of the system. The ReCiPe 2016 (H) midpoint impact assessment methodology was used to analyze 18 environmental impact categories. The results showed that producing 1 kg of biofuel from MAP of pine sawdust had environmentally favourable impacts for most categories except global warming potential (1.18 kg CO_2 eq.), photochemical oxidant formation (0.71 kg NMVOC eq.), and human toxicity (2.46 kg 1,4-DCB eq.). Biomass production contributed significantly to global warming, freshwater ecotoxicity, human toxicity, and marine ecotoxicity. Pyrolysis contributed 33% of global warming potential due to NCGs emissions. Biofuel synthesis impacted human toxicity, photochemical oxidant formation, and terrestrial ecotoxicity, mainly due to methanol use. Implementing sustainable practices such as using organic fertilizers, optimization of transportation routes, implementing gas cleaning technologies and effective waste management practices can enhance the environmental performance of this biofuel production system.

This chapter is an original research manuscript submitted to Results In Engineering (Under review). The potential environmental impact of microwave assisted pyrolysis of pine sawdust was evaluated, fulfilling objective 5.

7.2 Introduction

The world has recently made significant progress towards achieving a circular economy as a sustainable way to replace fossil resources for energy generation and the production of chemicals and other materials. The bioeconomy has been envisioned as a sustainable technical pathway by biorefineries, which use biomass to create a variety of products, including chemicals, biofuels, energy, and heat (Makepa et al., 2023; Manhongo et al., 2021). Biomass is expected to play a significant role in lowering transportation-related CO_2 emissions. Furthermore, the use of biofuels in the transportation sector is expected to meet approximately 12% of the global transportation energy needs by 2030 (IEA, 2021).

The utilization of food crops for the production of biofuels has the potential to cause shortages resultantly driving food costs up. Furthermore, the production of some energy crops is associated with the use of a lot of pesticides and fertilizers which can potentially cause environmental pollution (Vienescu et al., 2018).

The timber processing industries in Zimbabwe produce approximately 40% of the raw logs as waste sawdust, with low utilization rates. Commercial sawmills have traditionally used wood chips and offcuts exclusively, in steam boilers used in the process of drying lumber in kilns, leaving huge amounts of sawdust to accumulate over time (Charis et al., 2019). Utilizing timber processing waste as a feedstock for biofuel production can help reduce waste and promote more sustainable use of resources. Furthermore, the use of timber processing waste for the production of biofuels can aid in lessening reliance on fossil fuels, enhance energy security, and can avoid competing with food crops for land and resources.

Biofuels obtained from non-food crops, such as timber processing waste, are often referred to as second-generation biofuels, and they are generally considered more sustainable and environmentally friendly (Vienescu et al., 2018). However, more complicated and energy-intensive conversion procedures are needed to produce second-generation biofuels. The presence of lignin and other recalcitrant components in the biomass matrix increases the energy required to initiate and sustain the pyrolysis process (Cheng et al., 2020). This is because lignin has high thermal stability and requires high temperatures to break down (Nawaz & Kumar, 2023). First-generation biofuels' large-scale feedstock production requires more fertile farmland, which reduces the amount of land available for growing crops for human consumption. This has serious financial, environmental, and political implications. Thus, it may be feasible to produce second-generation biofuels made from a variety of non-food products, including cellulosic biomass, inedible plant parts, straw, manure, used cooking oil, wood, and sawdust. But because of the expensive and cutting-edge equipment required for the production process, it is not economically feasible to produce ethanol from second-generation biomass feedstocks (Brennan & Owende, 2010). However, thermochemical conversion techniques for biofuel production can be employed.

Second-generation biofuels may be produced from waste biomass using a variety of thermochemical techniques. Pyrolysis, liquefaction, and gasification are examples of thermochemical conversion processes. A common technique for converting biomass into a composite combination of organic molecules, charcoal fractions, and gas is biomass pyrolysis. Fast pyrolysis is the thermal decomposition of carbonaceous materials under an inert environment at high temperatures (450-500 °C) (Makepa et al., 2022). An alternative to conventional heating commonly used during fast pyrolysis is the use of microwave radiation. MAP has been proven to be fast and energy-efficient as compared to conventional pyrolysis which utilizes external heating through electric or gas-fired furnaces or internal heating through the use of a fluidized bed reactor (Sharifvaghefi & Zheng, 2022). Current research reported that MAP technology is easy to use and control. MAP produces high-quality bio-oil that can be utilized as feedstock in the manufacture of biochemicals and biofuels sustainably, and the energy balances for the process are favourable (Makepa et al., 2023b; Mutsengerere et al., 2019).

Although bio-oil has qualities similar to those of petroleum-based diesel, it cannot be used directly as a fuel because of its instability, high acidity, and other undesirable characteristics (Sánchez-Borrego et al., 2021). Bio-oil transesterification is a potential technology for upgrading bio-oil into biodiesel, a useful fuel that may be blended with petroleum-based diesel or used as neat biodiesel as an alternative. During the transesterification process, FAMEs are produced by reacting the bio-oil with an alcohol, such as methanol (Elango et al., 2019). Although biodiesel produced from transesterification of bio-oil is a renewable source of energy, the environmental effects of its production and utilization needs to be assessed.

A LCA can be used to examine the environmental effects of producing transportation fuels through pyrolysis. LCAs permit comparison between fossil fuels and other biofuel production technologies. Numerous LCA studies have been conducted on fuels produced by pyrolysis of biomass and other thermochemical conversion techniques. The LCA of pyrolysis combined with hydrotreating was carried out by Iribarren et al. (2012). They concluded that the production of hydrogen from natural gas via steam reforming and the processing of feedstock using electricity had the biggest impacts. In a study on the pyrolysis with hydrotreating of poplar residues, Snowden-Swan & Male (2012) discovered that the emissions of carbon dioxide equivalent (CO_{2e}) were 32.5 gCO_{2e}/MJ. In a similar study, Peters et al. (2015) simulated the fast pyrolysis of hybrid popular by combining a pyrolysis plant and a biorefinery consisting of distillation, hydroprocessing and steam reforming sections. They discovered that the pyrolysis process and the biorefinery were the main sources of greenhouse gas (GHG) emissions, indicating that the environmental effect might be addressed by looking for ways to cut back on the use of energy. However, their findings stated that the production of biofuel from fast pyrolysis of biomass can reduce the greenhouse gas emissions by 54.5% as compared to conventional gasoline and diesel. Zhang et al. (2014) and Dang et al. (2014) looked into several hydrogen sources to improve pyrolysis oils. Their findings stated that the GHG emissions for traditional natural gas reforming were in the range of 30–40 gCO_{2e}/MJ. In contrast, the GHG emissions brought on by the usage of fossil fuels are around 94 CO_{2e}/MJ.

Most LCA studies on biofuels produced by pyrolysis have concentrated on taking pyrolysis with hydroprocessing as a bio-oil upgrading technique into account (Dang et al., 2014; Iribarren et al., 2012; Peters et al., 2015; Snowden-Swan & Male, 2012; Zhang et al., 2014). Recent literature has focused on the esterification of fast pyrolysis bio-oil (Lee et al., 2020; Mei et al., 2020), with no studies on the transesterification of bio-oil for biodiesel production. The main aim of this work is, however, to analyze the environmental effects of producing biodiesel from MAP of pine sawdust utilizing transesterification as a bio-oil upgrading technology, in order to make a more realistic comparisons to guide future research and development on obtaining transportation fuel from pyrolysis. The study's findings are intended to guide investment decisions about the choice of sustainable biomass utilization options.

7.3 Methodology

The LCA is a technique used to evaluate the environmental characteristics and possible environmental consequences related to a product, process, or service. The major aspects of the LCA include goal and scope, which identify the objective of the LCA and its expected outcomes, set the restrictions and expectations based on the objective definition. The LCI quantifies the materials, energy usage, and emissions produced in the process. The impact analysis evaluates the potential environmental consequences related to the system's inputs and outputs. The improvement analysis aids in the decision-making process by identifying the best option and finding solutions to minimize the environmental impacts.

7.3.1 Goal and scope definition

The accuracy and dependability of the outcomes of a LCA largely depends on the clarity and accuracy of the goal and scope of the study. This stage involves determining the objective, system boundaries, functional unit and assumptions. This research utilizes data obtained from Aspen Plus process simulation models and economic analyses to evaluate the environmental impacts of the entire life-cycle of biodiesel production technology that employs MAP. The analysis covers a comprehensive assessment of the impacts associated with different stages of biodiesel production, including raw material extraction, transportation, pyrolysis, biodiesel production, and end-of-life disposal. Additionally, this study explores the potential advantages and drawbacks of utilizing MAP technology for biodiesel production, such as its ability to decrease greenhouse gas emissions and reliance on fossil fuels, as well as its possible adverse consequences on local communities or ecosystems.

7.3.2 System boundaries and functional unit

The system boundary considered in this study includes four subsystems: biomass production, biomass pre-processing, pyrolysis of pine sawdust, and biofuel synthesis, enabling a cradle-to-gate environmental impact assessment. Figure 7.1 depicts the system boundaries for the production of biodiesel from MAP of pine sawdust. The pine wood cultivation and timber production stages are examined as a pre-assessment perspective of the pyrolysis system, and therefore, they are represented as a black box. Thus, only inputs and outputs are considered for assessing the first two stages (pine wood cultivation and timber production). In contrast, the pyrolysis system, which is the only stage represented in detail, is evaluated in a sequence of stages, including biomass pre-processing, biomass drying, pyrolysis, biochar recovery using a cyclone separator, gas cooling using a counter-flow heat exchanger, and separation of bio-oil and gases in a flash separator. The functional unit used as a reference for this research was 1 kg of biodiesel produced.

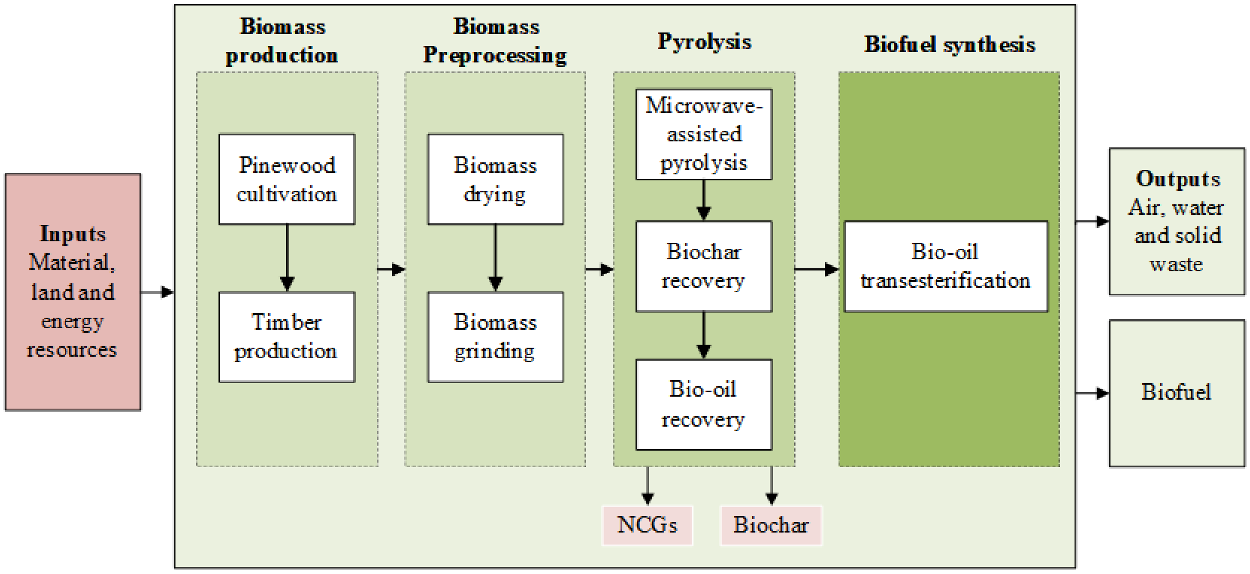


Figure 7.1: Life-cycle system boundaries for biodiesel production from MAP of pine sawdust

7.3.3 Impact assessment methodology

The openLCA 2.0 software was utilized to conduct the LCA in this research. This software is a comprehensive open-source tool for sustainability modelling and LCA developed by GreenDelta. It enables the modelling and analysis of the life-cycle of a product or service in a clear and methodical manner, adhering to the ISO 14040 series recommendations (Lopes Silva et al., 2019). The OpenLCA software also enables one to conduct LCA studies using a user-created database or one from its library.

The ReCiPe 2016 (H) midpoint impact categories were employed in this study to identify a wide range of impacts related to each of the previously mentioned subsections. In the midpoint phase, the data listed in the LCI is classified into impact categories based on shared cause-and-effect characteristics throughout the environmental mechanism chain. This impact assessment methodology has 18 impact categories which include: agricultural land occupation, global warming potential, fossil depletion, freshwater ecotoxicity, freshwater eutrophication, human toxicity, ionizing radiation, marine ecotoxicity, marine eutrophication, metal depletion, natural land transformation, ozone depletion, particulate matter formation, photochemical oxidant formation, terrestrial acidification, terrestrial ecotoxicity, urban land occupation and water depletion.

7.3.4 Life-cycle inventory analysis

The main input and output data for pine cultivation and timber production were obtained from a forestry and sawmilling company in Zimbabwe located in the Eastern Highlands. Aspen Plus® v11 software was employed in estimating the mass and energy balances related to the biomass pyrolysis and bio-oil transesterification system. Therefore, this simulation provided the necessary information to be used in the LCA for the estimation of the environmental impacts associated with emissions, resource consumption, and energy.

7.3.4.1 Feedstock cultivation, harvesting, and transportation

The timber sector in Zimbabwe is based on approximately 69,892 hectares of timber plantations, which consist of around 70% pine, 20% eucalyptus, and 10% wattle (Charis et al., 2019). Only 40-45% of round wood is recuperated, which leads to the production of a large amount of bulk waste. This waste is made up of approximately 50% sawdust and chips. The data in the inventory linked to pine growth relies on the expected pine yields and the supposed soil conditions. To satisfy the high demand for nitrogen, phosphorus, and potassium in pine cultivation, most timber plantations in Zimbabwe are treated with fertilizer. Forest plantations in Zimbabwe receive an annual application of 270 kg/acre of nitrogen, 6 kg/acre of phosphorus, and 25 kg/acre of potassium to supplement pine with nutrients. The energy necessary to produce 1 ton of timber ranges from 50-100 kWh. The electricity consumption in sawmills varies depending on several factors, such as the type and size of the sawmill, the type of sawing equipment utilized, the timber species being processed, and specific production processes such as log handling, debarking, sawing, and drying. Afterward, the raw feedstock would need to be transported to the pyrolysis processing plant from a collection point. The assumed transportation distance is within a 50 km radius. It is estimated that approximately 6 litres of diesel are required per ton of raw feedstock for this operation.

The LCA databases in OpenLCA are lacking in information regarding the precise crop inputs linked to fertilizers and other products. In this research, data on input products have been linked to other comparable products (containing N, K, and P) from the Ecoinvent v3.7 database. The application of phytosanitary products and fertilizers necessitates approximately 24.22 L/ha of diesel (Parascanu et al., 2018). The emissions associated with the application of fertilizers were taken into account as outputs to the environmental compartments of air and soil. As a result, the data on soil and air emissions employed in this research have been displayed in Table 7.1.

Table 7.1: LCA inventory data for the steps of biomass production and timber processing per kg of biodiesel produced

	Units	**Amount**
Inputs		
Ammonium nitrate	kg	2.25E+00
Potassium chloride	kg	1.90E-01
Ammonium phosphate	kg	5.00E-02
Diesel	L	3.20E-01
Outputs		
Pinewood timber	kg	1.05E+01
Pine sawdust	kg	3.16E+00
Wood waste	kg	4.21E+00
Emissions to air		
NO_x	kg	2.36E-04
SO_2	kg	3.60E-05
CO	kg	3.08E-03
PM	kg	1.12E-04
N_2O	kg	1.20E-05
CO_2	kg	1.18E+00
NH_3	kg	2.68E-02
NO	kg	3.20E-03
Cu	kg	1.60E-04
Dimethoate	kg	4.40E-03
Emissions to soil		
Al	kg	7.50E+01
Ca	kg	1.88E+03
Fe	kg	1.25E+02
K	kg	3.02E+01
Mg	kg	2.62E+01
Mn	kg	8.90E-01
Na	kg	1.63E+00
Sr	kg	1.52E+00

7.3.4.2 Biomass pre-processing

Before pyrolysis, the feedstock needs to undergo pre-processing, which entails the process of grinding and drying to reduce the size of particles and decrease the level of moisture. Smaller particle sizes are preferred for faster pyrolysis rates due to the greater surface area and shorter diffusion path lengths for heat and gases. The energy required for grinding and chopping is estimated to vary from 11-57 kWh/ton (Mani et al., 2004). In order to enhance the stability of reactor temperature and decrease the energy requirements for pyrolysis processing, it is necessary to reduce the moisture content of the feedstock to below 10% (Bridgwater & Peacocke, 2000). This is achieved by drying the feedstock before initiating the pyrolysis process.

7.3.4.3 Pyrolysis process

Assuming a temperature of 500 °C, the MAP plant is designed to process 2000 metric tons of pine sawdust per day. Generally, electricity is utilized as the energy input for a pyrolysis system, with power demands ranging between 140-487 kWh/ton of bio-oil produced (Vienescu et al., 2018). The yield of bio-oil from MAP of pine sawdust is 65 wt.% (Makepa et al., 2023b), although yields as high as 80% have been suggested (Bulushev & Ross, 2011). The LCI for this stage is presented in Table 7.2.

7.3.4.4 Transesterification

The process of transesterification can take place at various temperatures, between 25°C to 60°C, depending on the type of oil being utilized (Baadhe et al., 2014). The transesterification process is typically optimized with an ideal methanol-to-oil ratio of 3:1. However, comparable upgraded bio-oil yields (approximately 48 wt.%) have been observed using a methanol-to-oil ratio of 3:1 and a 1 wt% KOH catalyst. In this study, bio-oil derived from pine sawdust was utilized for biodiesel production. The transesterification of bio-oil under supercritical conditions (250-300°C) was not included in this study due to the possibility of altering the bio-oil composition (Vienescu et al., 2018). Assuming a bio-oil specific heat capacity of 2.435 kJ/kg, disregarding any heat losses, and considering an initial temperature of 30 °C and potential operating temperature ranges, the estimated energy requirement is anticipated to range between 0.027 to 0.095 kWh/kg. The LCI for this stage is presented in Table 7.2.

Table 7.2: LCA inventory data for the steps of pine sawdust pyrolysis and biofuel synthesis per kg of biodiesel produced

	Units	Amount
Inputs		
Pine sawdust	kg	3.16E+00
Activated carbon	kg	6.32E-02
Helium gas	kg	1.20E-02
Electricity	kWh	5.75E-01
KOH catalyst	kg	1.00E-02
Methanol	kg	3.00E+00
Outputs		
Biodiesel	kg	1.00E+00
Glycerol	kg	3.00E-01
Biochar	kg	8.60E-01
Emissions to air		
Hydrogen	kg	2.00E-03
Methane	kg	1.55E-02
Ethane	kg	4.15E-04
Carbon monoxide	kg	1.09E-01
Carbon dioxide	kg	1.62E-02
Water	kg	1.92E-02
Acetic acid	kg	9.23E-04
Propionic acid	kg	4.62E-04
Formic acid	kg	1.69E-03
Propyl benzoate	kg	1.54E-04
Toluene	kg	2.31E-03
Furfural	kg	6.15E-04
Benzene	kg	1.54E-03

7.4 Results and discussion

7.4.1 Environmental impact assessment

The environmental impact results provided in Table 3 were calculated for producing biodiesel from MAP of pine sawdust. The processes starting from pinewood cultivation until the final product being produced, are included in the environmental impact assessment of MAP of pine sawdust. The results show that the production of biodiesel from MAP of pine sawdust has a relatively low impact on most of the environmental impact categories studied.

The most significant impact is the global warming potential, with a value of 1.18 kg CO_{2eq}/kg of biodiesel produced. This indicates that the production of biodiesel results in the emission of greenhouse gases that contribute to climate change. This value is significantly lower than reported values in literature. (Vienescu et al., 2018) reported a GWP of 2.24 kg CO_{2eq}/ kg of synthetic biofuel obtained from hydrotreating and hydrocracking pyrolysis oil. Huang et al. (2022) reported GWPs in the range of 0.81-2.56 CO_{2eq}/kg of dried biomass for six different pyrolysis scenarios.

The production of biodiesel also has a significant impact on human toxicity, with a value of 2.46 kg 1,4-DCB eq. This impact category measures the potential for the production process to cause harm to human health. Foteinis et al. (2020) reported a human toxicity of 0.101 kg 1,4-DCB eq/kg of biodiesel produced from waste cooking oil. This shows that the transesterification process for biodiesel production does not cause harm to humans as the process does not involve the use of toxic chemicals. However, this shows that the biomass cultivation and pre-processing are responsible for the contribution to human toxicity, which justifies a higher value reported in this study. Therefore, the human toxicity for the MAP of pine sawdust is attributed to certain chemicals and processes used in the processing and treatment of pine wood that can potentially cause harm to humans. One such chemical is chromated copper arsenate, which is a common wood preservative used to protect against decay and insects. Chromated copper arsenate contains arsenic, which is a toxic chemical that can cause cancer and other health problems if ingested or inhaled (Marin Villegas & Zagury, 2023). Solvents and adhesives such as plywood and laminated veneer lumber that are used in the production of pine timber, contain formaldehyde, which is a known human carcinogen (Hussin et al., 2022).

In addition, the production of biodiesel has a moderate impact on photochemical oxidant formation, with a value of 0.71 kg NMVOC eq. This impact category measures the potential for the production process to contribute to the formation of smog and other air pollutants. Foteinis et al. (2020) also reported a photochemical oxidant formation of 1.66 kg NMVOC eq. Another study by Khang et al. (2017) concluded that the photochemical oxidant formation of biodiesel is significantly lower as compared to conventional diesel. The result indicates that the production of biodiesel from MAP of pine sawdust has a moderate impact on the formation of smog and other air pollutants.

A freshwater ecotoxicity, marine ecotoxicity, terrestrial acidification and terrestrial ecotoxicity of 0.011 kg 1,4-DCB eq., 0.0062 kg 1,4-DCB eq., 0.066 kg SO_2 eq. and 0.0005 kg 1,4-DCB eq., respectively, was estimated in this study. In a study by Foteinis et al. (2020), a freshwater ecotoxicity, marine ecotoxicity, terrestrial acidification and terrestrial ecotoxicity of 0.022 kg 1,4-DCB eq., 0.0023 kg 1,4-DCB eq., 0.0552 kg SO_2 eq. and 0.000315 kg 1,4-DCB eq., respectively, was estimated for biodiesel produced from waste cooking oil. One major contributor to these impact categories is the cultivation of pine wood. The use of fertilizers, pesticides and other chemicals can potentially lead to runoff and contamination of nearby water sources. Fertilizers and chemicals can also potentially lead to soil acidification which can negatively impact soil health and fertility. Additionally, the pyrolysis process typically requires large amounts of water for cooling, which can potentially lead to water scarcity in areas with limited water resources. Methanol, used in the transesterification process is highly toxic to aquatic life and can potentially cause harm to fish and other aquatic organisms if it enters water sources.

A marine eutrophication of 0.0025 kg N eq. was estimated in this study. Dufour & Iribarren (2012) estimated a marine eutrophication of 0.0012 kg PO_4^{3-} eq. for biodiesel derived from waste cooking oil. One of the major contributors to marine eutrophication is the cultivation of pine wood. As discussed earlier, the use of fertilizers can potentially lead to runoff and nutrient enrichment of nearby water sources, which can promote the growth of algae and other aquatic plants. This can lead to excessive algal blooms and oxygen depletion, which can affect marine ecosystems.

The results indicate that the production of biodiesel has a minimal impact on agricultural land occupation, fossil depletion, freshwater eutrophication, metal depletion, natural land transformation, ozone depletion, ionizing radiation, urban land occupation, and water depletion. The production of biodiesel from MAP of pine sawdust does not require any additional agricultural land since it uses pine sawdust waste from timber processing sawmills. This process does not emit any ionizing radiation or require the use of any metals, hence, contributing to a more favourable environmental impact of the overall process.

Table 7.3: LCA impact indicators for MAP of pine sawdust for biodiesel production

Impact category	**Reference unit**	**Result**
Agricultural land occupation	m^2a	0.00E+00
Global warming potential	kg CO_2 eq.	1.18E+00
Fossil depletion	kg oil eq.	0.00E+00
Freshwater ecotoxicity	kg 1,4-DCB eq.	1.11E-02
Freshwater eutrophication	kg P eq.	0.00E+00
Human toxicity	kg 1,4-DCB eq.	2.46E+00
Ionizing radiation	kg U235 eq.	0.00E+00
Marine ecotoxicity	kg 1,4-DCB eq.	6.26E-03
Marine eutrophication	kg N eq.	2.47E-03
Metal depletion	kg Fe eq.	0.00E+00
Natural land transformation	m^2	0.00E+00
Ozone depletion	kg CFC-11 eq.	0.00E+00
Particulate matter formation	kg PM10 eq.	8.58E-03
Photochemical oxidant formation	kg NMVOC	7.13E-01
Terrestrial acidification	kg SO_2 eq.	6.57E-02
Terrestrial ecotoxicity	kg 1,4-DCB eq.	4.88E-04
Urban land occupation	m^2a	0.00E+00
Water depletion	m^3	0.00E+00

7.4.2 Environmental impact of the production stages

Figure 7.2 shows the contribution of the production stages to each environmental impact category. Out of the 18 impact categories studied, the MAP of pine sawdust has a significant impact on global warming potential, Freshwater ecotoxicity, Human toxicity, Marine ecotoxicity, Marine eutrophication, Particulate matter formation, Photochemical oxidant formation, Terrestrial acidification and Terrestrial ecotoxicity. Figure 7.3 presents the contribution of each production stage to the environmental impact categories.

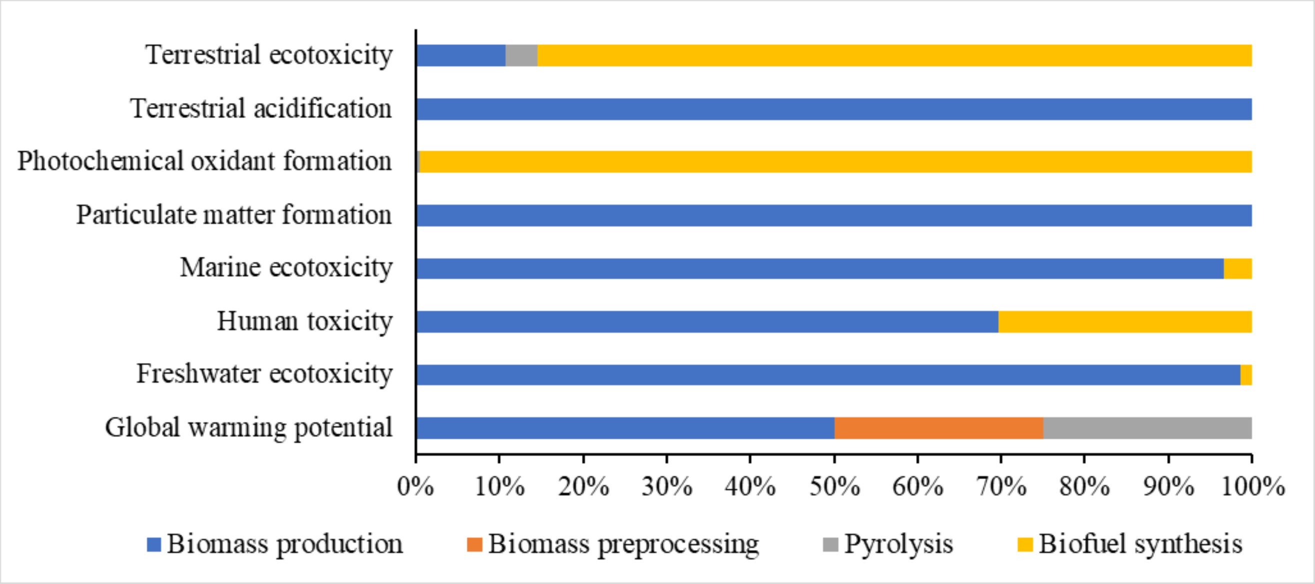
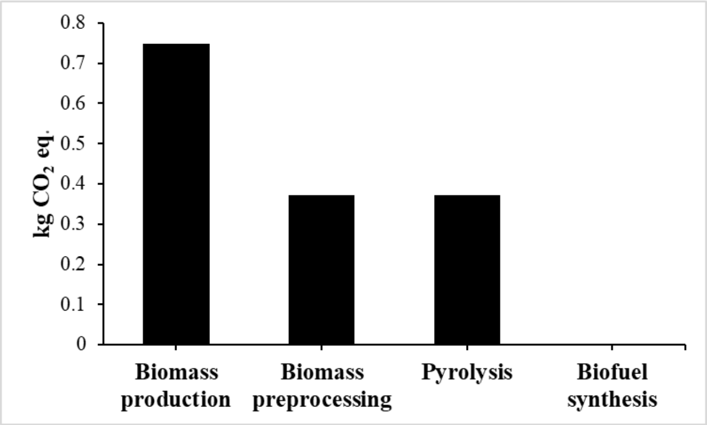
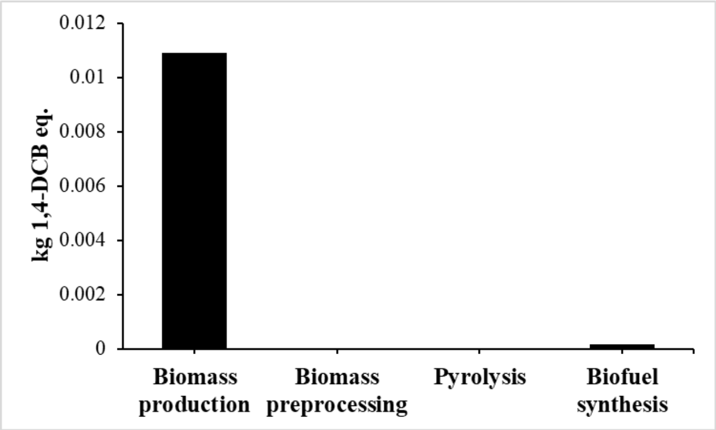


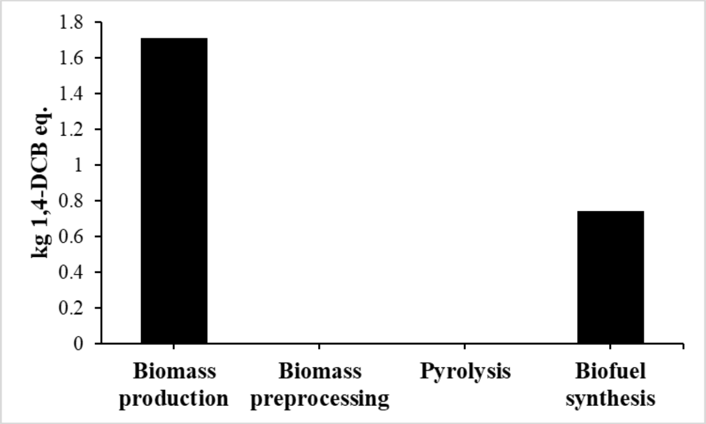
Figure 7.2: The contribution of the biodiesel production stages to the LCA impact categories


kg CO$_2$ eq.
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Biomass production
Biomass preprocessing
Pyrolysis
Biofuel synthesis

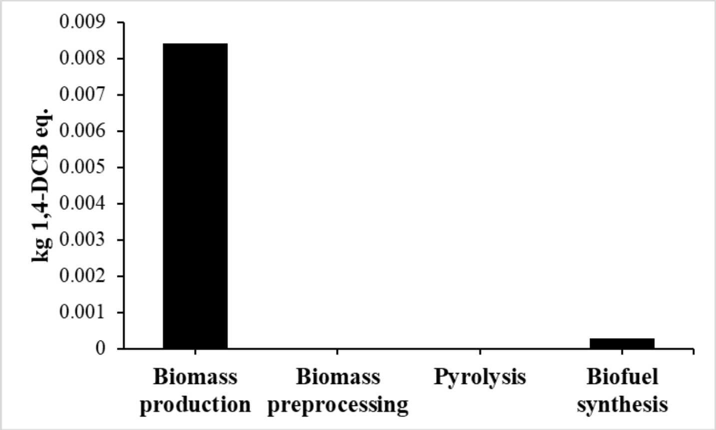
(a)


kg 1,4-DCB eq.
0.012
0.01
0.008
0.006
0.004
0.002
0
Biomass production
Biomass preprocessing
Pyrolysis
Biofuel synthesis

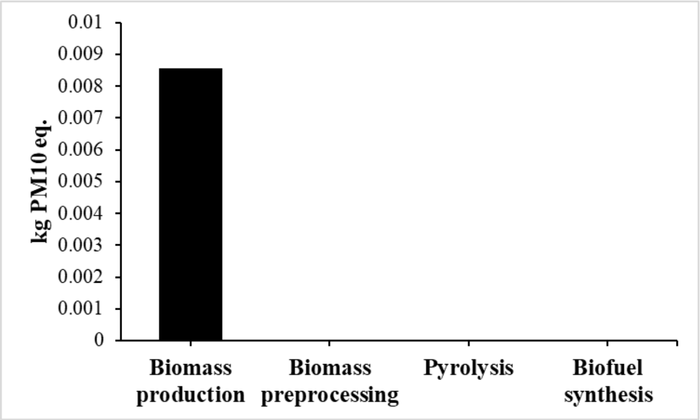
(b)


kg 1,4-DCB eq.
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Biomass production
Biomass preprocessing
Pyrolysis
Biofuel synthesis

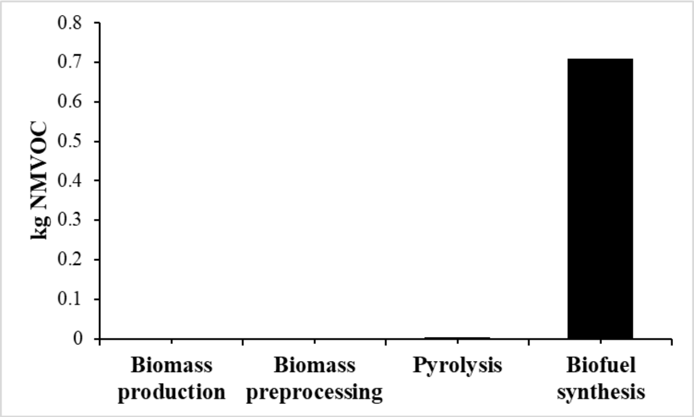
(c)


kg 1,4-DCB eq.
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Biomass production
Biomass preprocessing
Pyrolysis
Biofuel synthesis

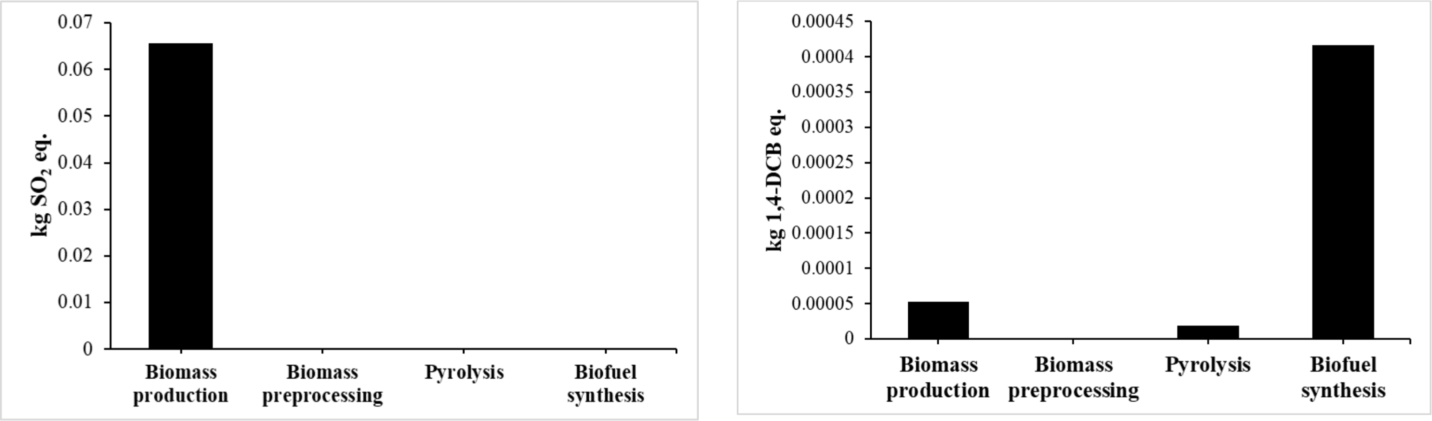
(d)


kg PM10 eq.
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
Biomass production
Biomass preprocessing
Pyrolysis
Biofuel synthesis

(e)


kg NMVOC
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Biomass production
Biomass preprocessing
Pyrolysis
Biofuel synthesis

(f)



(g) (h)

Figure 7.3: The contribution of each production stage to (a) Global warming potential, (b) freshwater ecotoxicity, (c) human toxicity, (d) marine ecotoxicity, (e) particulate matter formation, (f) photochemical oxidant formation, (g) terrestrial acidification, and (h) terrestrial ecotoxicity

7.4.2.1 Biomass production

The biomass production process has the highest environmental impact, contributing 100% of the terrestrial acidification and particulate matter formation evaluated in this study. Additionally, the biomass production process significantly contributed to global warming potential, freshwater ecotoxicity, human toxicity and marine ecotoxicity as shown in Figure 7.2.

The cultivation of pine trees for timber production can have both positive and negative environmental impacts. The cultivation of pine trees can help sequestrate carbon dioxide from the atmosphere (Henderson et al., 2020), at the same time providing feedstock for renewable energy production. However, the use of fertilizers, pesticides, and herbicides in pine cultivation can have negative impacts on the environment, such as water pollution, as fertilizers contain nutrients such as nitrogen and phosphorus that can leach into nearby water bodies and cause eutrophication, which can harm aquatic ecosystems and human health. When these chemicals leach into nearby water bodies, they contribute 0.0109 kg 1,4-DCB eq. to freshwater ecotoxicity (Figure 7.3(b)) and 0.0084 kg 1,4-DCB eq. to marine ecotoxicity (Figure 7.3(d)). The use of some fertilizers, such as ammonium-based fertilizers, can contribute to soil acidification, which can reduce soil fertility and hinder the growth of other plants (Guan et al., 2022). This has a contribution of 0.0657 kg SO_2 eq. to terrestrial acidification (Figure 7.3(g)) and 5.23E-05 kg 1,4-DCB eq. to terrestrial ecotoxicity (Figure 7.3(h)). The production and use of fertilizers also result in greenhouse gas emissions, including carbon dioxide, nitrous oxide, and methane, which can contribute to climate change with a global warming potential of 0.748 kg CO_2 eq., contributing approximately 63% of the overall global warming potential of the process. Pine cultivation can contribute to greenhouse gas emissions through the use of fossil fuels for machinery and transportation, as well as the release of soil carbon during land use change. The sawmilling process involves cutting, sawing and shaping raw logs into lumber. These operations generate wood chips and sawdust, which are small wood particles that can become airborne and contribute to particulate matter formation (0.0086 kg PM10 eq.) as illustrated in Figure 7.3(e).

To mitigate these negative impacts, it is important to apply fertilizers in a responsible and sustainable manner. This can include using slow-release fertilizers, reducing fertilizer application rates, and using organic fertilizers such as compost or manure. Additionally, sustainable forest management practices such as mixed-species plantations and agroforestry systems can help reduce the need for fertilizers and improve soil fertility.

7.4.2.2 Biomass pre-processing

The pre-processing of biomass prior to the pyrolysis process has the lowest environmental impact (Figure 7.2). The biomass pre-processing stage contributes 33% to the overall global warming potential of the process as illustrated in Figure 7.2. This impact is mainly attributed to the transportation of the pine sawdust from the source to the biorefinery site. Transporting sawdust over long distances can result in significant greenhouse gas emissions, particularly if fossil fuels are used for transportation. These emissions can contribute to climate change, with a global warming potential of 0.372 kg CO_2 eq./kg of biodiesel produced (Figure 7.3(a)). Transportation vehicles can emit air pollutants, such as nitrogen oxides and particulate matter, which can contribute to air pollution and negative impacts on air quality and human health. The grinding and drying process can require significant amounts of energy, which can contribute to greenhouse gas emissions and climate change. To mitigate these negative impacts, it is important to implement sustainable practices in the grinding and drying process. This can include using energy-efficient technologies, such as heat recovery systems. It is also important to implement sustainable transportation practices. This can include using fuel-efficient vehicles and optimizing transportation routes and reducing unnecessary transportation can help minimize energy consumption and environmental impacts.

7.4.2.3 Pyrolysis

The pyrolysis of pine sawdust produced three main products: bio-oil, biochar and NCGs. The bio-oil is used as feedstock to the transesterification process, while the NCGs are vented into the atmosphere. The NCGs are mainly comprised of hydrogen, methane, ethane, carbon monoxide and carbon dioxide. These gases contribute 33% of the overall global warming potential of the process as shown in Figure 7.2. The pyrolysis process has minimum impact on terrestrial ecotoxicity and photochemical oxidant formation. The constituents of the NCG released during pyrolysis can contribute to greenhouse gas emissions and climate change with a global warming potential of 0.373 kg CO_2 eq./kg of biodiesel produced (Figure 7.3(a)). Carbon monoxide and other NCG can contribute to air pollution and negative impacts on air quality. The pyrolysis stage contributes 1.87E-05 kg 1,4-DCB eq./kg of biodiesel produced to the overall terrestrial ecotoxicity (Figure 7.3(h)). Furthermore, NCG released during pyrolysis can emit unpleasant odors that can be disruptive to nearby communities.

To mitigate these negative impacts, it is important to capture and treat NCG generated during pyrolysis. This can include using gas cleaning technologies, such as scrubbers or filters, to remove pollutants from the gas stream. Additionally, using renewable energy sources or energy recovery technologies, such as co-generation or combined heat and power systems, to utilize the NCG can help minimize greenhouse gas emissions and reduce energy consumption. Finally, implementing appropriate odor control measures, such as biofilters or activated carbon filters, can help minimize odor emissions and reduce negative impacts on nearby communities.

7.4.2.4 Biofuel synthesis

The bio-oil from the pyrolysis process undergoes transesterification to produce biodiesel as the final product and glycerol as a waste product. The biofuel synthesis process has a significant impact on human toxicity, photochemical oxidant formation and terrestrial ecotoxicity. The production of methanol, which is the main input reagent in this process, releases various air pollutants, including carbon monoxide, nitrogen oxides, and sulphur oxides (Zang et al., 2021). This contributes 0.745 kg 1,4-DCB eq./kg of biodiesel produced to the overall human toxicity of the process (Figure 7.3(c)) and 0.709 kg NMVOC/kg of biodiesel produced to the overall photochemical oxidant formation (Figure 7.3(f)). Methanol production also generate wastewater that contains pollutants such as methanol, formaldehyde (Shamsul et al., 2014), and other organic compounds, which can contaminate water sources and harm aquatic ecosystems. Methanol is toxic and can have harmful effects on human health and the environment if it is not handled and disposed of properly. Glycerol, which is waste stream from the process can be released into wastewater during the biodiesel production process, leading to potential water pollution and harm to aquatic ecosystems. The disposal of excess glycerol can pose environmental challenges, as it can be difficult to dispose of safely and may require special treatment. These processes contribute 0.0001 kg 1,4-DCB eq. to freshwater ecotoxicity (Figure 7.3(b)), 0.0003 kg 1,4-DCB eq. to marine ecotoxicity (Figure 7.3(d)), and 0.0004 kg 1,4-DCB eq. to terrestrial ecotoxicity (Figure 7.3(h)). To mitigate these impacts, it is important to use sustainable and efficient production methods, manage waste carefully, and find new and innovative uses for glycerol to reduce the amount that needs to be disposed of.

7.4.3 Sources of uncertainty

The primary origins of uncertainty in this investigation are associated with the presumptions made regarding the feed composition and yields of the product during the process development phase. The quality and composition of pine sawdust can vary depending on factors such as the age of the tree, the location of the forest, and the harvesting method. This variability can affect the results of the LCA and introduce uncertainty. To estimate scale-up process conditions and yields, results from multiple literature sources for lab-scale experiments were employed on the assumption that the same performance would be attained. The real product quantities that may be produced at the simulated industrial scale, however, are illimitable, which has an influence on the environment.

The study made assumptions about certain aspects of the biodiesel production process, such as the disposal of waste and the impact of land use changes. Additionally, the study did not consider the end-of-life scenarios of the biodiesel or its co-products, such as the disposal or recycling of the products. These assumptions and omissions can affect the results of the LCA and introduce uncertainty.

7.5 Conclusions

The production of biodiesel from MAP of pine sawdust has a relatively low environmental impact compared to conventional transportation fuels. The most significant impacts are on global warming potential, human toxicity and photochemical oxidant formation. The biomass production stage has the highest environmental impact, contributing 100% of the terrestrial acidification and particulate matter formation. The pyrolysis stage contributes 33% of the overall global warming potential, mainly due to the release of NCG. The biofuel synthesis stage has a significant impact on human toxicity, photochemical oxidant formation and terrestrial ecotoxicity, mainly due to the use of methanol as a reagent.

To improve the sustainability of the biodiesel production process, it is important to implement sustainable practices at each stage of production. This includes using sustainable forest management practices, utilizing energy-efficient and renewable technologies, managing waste and emissions responsibly, and finding alternative uses for co-products to reduce waste. Implementing these practices can help minimize the environmental footprint of the biodiesel production process and reduce negative impacts on the environment, human health and communities.

While this study provides useful insights into the environmental impacts of producing biodiesel from MAP of pine sawdust, there are several sources of uncertainty due to assumptions made in the LCA. Additional research should focus on validating these assumptions and improving the accuracy of life-cycle inventories for second-generation biodiesel production processes. LCAs of the end-of-life scenarios for biodiesel and co-products can also provide a more holistic understanding of the environmental impacts of these production systems.

CHAPTER EIGHT: DISCUSSIONS, CONCLUSIONS AND RECOMMENDATIONS

8.1 Introduction and summary of objectives

The study investigated the economic feasibility and sustainability of producing biofuel from MAP of pine sawdust. The first and second objectives characterized the pine sawdust feedstock and thermochemically converted it to bio-oil via MAP process. The bio-oil was upgraded to biodiesel through a base-catalyzed transesterification process. A model of the MAP of pine sawdust was developed in Aspen Plus and the TEA of bio-oil production was performed (objective 3). Objective 4 evaluated the economic feasibility of converting pine sawdust to bio-oil and upgrading the bio-oil transesterification to produce biodiesel. Lastly, objective 5 evaluated the environmental sustainability of the MAP of pine sawdust for biodiesel production. The contribution of each production stage to the environmental impacts was analyzed.

8.2 Integration of research findings

Lignocellulosic biomass biorefinery technologies are still under research and development in many countries around the globe. Consequently, many studies have successfully converted lignocellulosic biomass to biofuels through various techniques. Pyrolysis of lignocellulosic biomass to biofuels has proven to be successful, however, the process is energy-intensive and the conversion efficiencies are low, owing to low heating rates. MAP of lignocellulosic biomass is a promising technology that can successfully convert biomass to bio-oil with high conversion efficiencies. As many studies have focused on the conventional pyrolysis of biomass, it is therefore crucial to evaluate the potential of MAP of pine sawdust for bio-oil production and evaluate the economic feasibility and environmental sustainability of the process.

8.2.1 The potential of pine sawdust as feedstock for biofuel production

The findings of the study suggests that pine sawdust can be a suitable feedstock for MAP process for the production of bio-oil, which can be further upgraded to biofuels. The proximate and ultimate analysis results for pine sawdust are presented in Table 4.1.

Pine sawdust has a high volatile matter (76.39 wt.%), which is desirable as it enhances bio-oil production and improves volatility and reactivity. A low ash content (2.08 wt.%) is desirable for thermal pyrolysis, as alkali metals found in ash can alter the composition of pyrolysis products. Pine sawdust has a high carbon content (51.6 wt.%) and low moisture, nitrogen and sulphur content, which implies that thermochemical conversion of pine sawdust is not likely to produce noxious NOx and SOx emissions to the environment. A high H/C molar ratio (1.20) of pine sawdust, implies that the resulting bio-oil will have a HHV and higher yield of liquid products, and an O/C ratio of 0.62 is considered optimal for producing high-quality bio-oil with moderate yields of biochar and syngas. The HHV of 20.23 MJ/kg, indicates that the resulting products have a high energy content and can be used as a source of renewable energy.

The MAP of pine sawdust resulted in higher bio-oil yields than biochar and NCGs yields. The bio-oil yield obtained in the study was 42.28 wt.%. The variance in yield with other studies reported in Table 4.2 could be due to differences in the chemical composition of the parent biomass. The weight fractions of the other products biochar and NCG were 36.11 wt.% and 21.61 wt.%, respectively. Co-feeding pine sawdust may aid in boosting the bio-oil yield. The pH of bio-oil was found to be low (2.87), indicating the presence of high concentrations of acidic organic compounds. The FTIR (Table 4.4) and GC-MS (Table 4.5) analysis results confirmed the presence of carboxylic acids, phenols and other oxygenated molecules and hydrocarbons. The breakdown of hemicellulose and lignin during the pyrolysis process is a significant contributor to the presence of acidic compounds in bio-oil. The oxidation of native alcohols and aldehydes to acids is a common trend observed during the ageing of bio-oil. Raw bio-oil has several undesirable properties due to its chemical composition, including being corrosive and thermally unstable. Upgrading methods are necessary to meet fuel requirements before application, as acids present in bio-oil are the principal cause of material corrosion during storage and application.

Bio-oil transesterification was carried out as an upgrading method to improve the properties of the bio-oil. The properties of bio-oil and biodiesel derived from bio-oil transesterification are presented in Table 4.3. The crude bio-oil obtained from pine sawdust had a high density, high flash point, high viscosity, high water content, and high ash content, making it unsuitable for direct use as a fuel. However, the bio-oil was upgraded via transesterification to produce biodiesel with a lower viscosity, lower water content, lower ash content, and lower TAN. The biodiesel also had a lower HHV than conventional fuels but higher than the HHV of crude bio-oil, wood, and straw. Drying and co-pyrolysis of pine sawdust with highly lignocellulose biomass can significantly increase the bio-oil yield and reduce its water content. Overall, bio-oil transesterification has been shown to improve the bio-oil properties by converting the organic acids and oxygenated compounds in bio-oil to methyl esters with a concentration of 510.05 mg/L. The properties of the biodiesel obtained were within the limits stipulated by the EN 14214 (a European standard that describes the quality requirements and test methods for biodiesel).

8.2.2 Process optimization of the MAP of pine sawdust

MAP of pine sawdust for bio-oil production was modelled in Aspen Plus based on the experimental results. To validate the model, the product distribution of the model was compared with experimental data from three sets of published works (Figure 5.3). The results showed that the model's predictions were consistent with the experimental results. The significance of the models was further demonstrated using ANOVA by the low p-values (less than 0.0001) and high F-values (74.94, 156.55, and 174.52, respectively) for the bio-oil, char, and NCGs yield regression models. The regression models that were developed for the product distribution of bio-oil, char, and NCGs exhibited R^2 values of 98.17%, 99.11%, and 99.20%, respectively. The high R^2 values suggest that the regression models accurately fit the experimental data and demonstrate a satisfactory level of precision for predicting the yield of bio-oil, char, and NCGs.

The product distribution at different pyrolysis temperatures and pressures was investigated. The results showed that the production of char was favoured at low pyrolysis temperatures, whereas the bio-oil product yield increased with increasing temperature up to around 500 °C, after which it began to fall (Figure 5.4). The decrease in bio-oil production was attributed to subsequent thermal cracking reactions between pyrolysis vapours and tar fragments to generate vapours, which enhanced the yield of NCGs. The formation of NCGs was observed to rise with increasing pyrolysis temperature, and at higher temperatures, both tar and char were transformed into lighter hydrocarbons like syngas. Comparable results were obtained in previous studies, indicating a consistent trend in the effect of temperature on the rapid pyrolysis of biomass feedstock in a fluidized bed reactor. The study also investigated the effect of reactor pressure on product distribution and found that it had no significant effect but indirectly affected the reactor's residence time due to its inverse relationship with the volumetric density of the vapour phase.

Three-dimensional (3D) response surface plots were employed to investigate the combined effects of reactor temperature and pressure on the production of bio-oil, char, and NCGs. The highest bio-oil yield was achieved at 550°C and atmospheric pressure. The findings suggest that reactor temperature is a crucial parameter affecting the conversion of biomass into bio-oil, while other parameters such as heating rate and residence time may also play significant roles.

8.2.3 Techno-economic analysis of bio-oil and biodiesel production

The techno-economic viability of the MAP process was analyzed in this study. The TCI was estimated to be $286.1 MM. The installed equipment costs for the pyrolysis section were found to be the major portion of the TIEC, contributing approximately 37.9% of the total. The total annual operating costs were estimated to be $164.9 MM, with the cost of methanol being the biggest contributor at $80.7 MM annually, followed by biomass cost, activated carbon, and catalysts.

The MSP of bio-oil was found to be $1.14/litre, while the MSP of biodiesel was estimated at $2.31/litre. The NPV of the bio-oil production process was estimated to be $2.08 billion over a 20-year plant life, while the NPV of the biodiesel production process was estimated to be $1.94 billion. The results indicate that the bio-oil production scenario may be more attractive from an economic standpoint. However, there are challenges with handling and long-term storage of bio-oil. Bio-oil is a highly viscous and corrosive liquid that requires special handling and storage facilities. Additionally, it has a relatively short shelf life due to its high water and oxygen content, which can lead to degradation and instability over time. On the other hand, biodiesel has a longer shelf life and is less prone to degradation, making it a more stable and transportable fuel. In addition to the challenges with handling and storing bio-oil, it is important to note that biodiesel is a finished product that can be used directly as fuel, while bio-oil requires further processing before it can be used as an energy source. Therefore, the decision to produce bio-oil or biodiesel depends on several factors, including the availability of suitable storage and handling facilities, market demand, and regulatory requirements.

The sensitivity analysis of biodiesel production from pine sawdust revealed that the biodiesel yield has the highest sensitivity on the MFSP. Increasing the yield of biodiesel by 25% resulted in a 20% decrease in the MFSP, while decreasing the yield by 25% resulted in a 20% increase in the MFSP. This finding suggests that improving the process operating conditions to obtain more biodiesel can significantly reduce the MFSP. The annual operating cost was identified as another key parameter that affects the sensitivity of the MFSP, with a 25% increase in annual operating cost increasing the biodiesel yield by 15% and a corresponding increase in the MFSP, while reducing the annual operating costs reduced the biodiesel yield by 15% and a corresponding decrease in the MFSP. The costs of methanol, biomass, and activated carbon were found to greatly affect the sensitivity of the MFSP, while catalyst costs and electricity costs had the least sensitivity. The TCI, interest rate, and income tax rate also affected the sensitivity of the MFSP, emphasizing the importance of considering these factors in the economic analysis of biodiesel production from pine sawdust. These findings highlight the need to optimize process operating conditions, minimize annual operating costs, and minimize the costs of key inputs such as methanol, biomass, and activated carbon, to reduce the MFSP of biodiesel and enhance the economic feasibility of the process.

8.2.4 Environmental implications

The environmental impact assessment of producing biodiesel from pine sawdust showed that the process has a relatively low impact on most environmental impact categories studied (Table 7.3). The most significant impact was found to be the global warming potential, with a value of 1.18 kg CO_{2eq}/kg of biodiesel produced. However, this value was significantly lower than reported values in literature, indicating that the production of biodiesel from pine sawdust has a lower impact on climate change. The production of biodiesel also had a significant impact on human toxicity, mainly attributed to the cultivation and pre-processing of pine wood, which can potentially cause harm to humans. The use of wood preservatives such as chromated copper arsenate and solvents and adhesives containing formaldehyde were identified as major contributors to human toxicity. The production of biodiesel had a moderate impact on photochemical oxidant formation but had minimal impact on other environmental impact categories such as agricultural land occupation, fossil depletion, and natural land transformation.

The study suggests that the use of pine sawdust waste from timber processing sawmills for biodiesel production can have a positive impact on reducing waste and mitigating climate change. However, the study also highlights the potential negative environmental impacts associated with the cultivation and pre-processing of pine wood, which should be considered in the overall assessment of the environmental impacts of biodiesel production from pine sawdust. Additionally, the use of methanol in the transesterification process was found to be highly toxic to aquatic life and can potentially cause harm to fish and other aquatic organisms if it enters water sources, emphasizing the need for proper handling and disposal of the chemical. However, the study provides valuable insights into the environmental impacts of biodiesel production from pine sawdust and highlights the importance of considering the entire production process, including the cultivation and pre-processing of the raw material, in assessing the overall environmental impact.

8.3 Challenges with the commercialization of MAP of biomass processing plants

MAP is a promising technology for the processing of biomass into valuable products such as biofuels, biochar, and chemicals. However, there are several challenges associated with the commercialization of MAP processing plants for biomass, including:

High capital costs: The initial capital investment required to build a MAP processing plant can be significant. The cost of the microwave equipment, reactors, and other components are much higher than traditional pyrolysis systems.

Limited scalability: MAP systems may be limited in terms of scalability. While the technology has shown promise at lab-scale, scaling up to commercial production is challenging due to the difficulty in uniformly heating and maintaining temperature across large volumes of biomass. The efficiency of the process may decrease as the size of the reactor increases, which could limit the size of the processing plant.

Energy consumption: MAP requires a significant amount of energy to heat the biomass and maintain the reaction temperature. While microwave pyrolysis can be energy-efficient compared to traditional pyrolysis, the process still requires significant energy input to generate the microwaves and maintain the reaction conditions, which can be a challenge in terms of cost and sustainability.

Regulatory challenges: The commercialization of new technologies is often subject to regulatory barriers, which can slow down or prevent the adoption of microwave pyrolysis technology.

8.4 Conclusion

The study demonstrated the potential of using pine sawdust, an abundant forestry waste, as a feedstock for producing biofuel via MAP. The properties of pine sawdust, such as high volatile matter content, low ash content, and suitable elemental composition, make it well-suited for thermochemical conversion. MAP of pine sawdust resulted in a bio-oil yield of 42.28 wt.%, which was upgraded via transesterification to biodiesel meeting fuel quality standards.

Process modelling and optimization in Aspen Plus showed temperature as the most influential parameter, with the highest bio-oil yield achieved at 550 °C. The TEA indicated the economic viability of bio-oil and biodiesel production from pine sawdust, with biodiesel production having a slightly better economic potential. The LCA revealed relatively low environmental impacts, though the global warming potential and human toxicity impacts need to be addressed.

While MAP shows promise for converting forestry waste to biofuels, challenges remain in terms of high capital costs, scalability limitations, high energy consumption, and regulatory barriers. Further research and development is needed to improve the commercial viability of MAP based biorefineries. In conclusion, the study demonstrated the potential of an integrated MAP process to convert low-value biomass waste into sustainable transportation fuels.

8.5 Recommendations for future research

The following are some potential areas for future research:

1. Development of cost-effective and scalable reactor designs: Research could focus on developing new reactor designs that can efficiently and cost-effectively process large volumes of biomass while maintaining uniform heating and temperature control. Research could also focus on improving the energy efficiency of microwave pyrolysis, such as by developing more efficient microwave generators or using waste heat from the process to generate electricity or heat.
2. Developing and optimizing downstream processing technologies: Research efforts could focus on investigating separation and purification methods to isolate specific bio-oil components with desired properties for biochemical, pharmaceutical and cosmetic applications. Focus could also be on developing cost-effective and scalable separation and purification technologies to achieve high product purity and yield, while addressing the technical challenges related to the highly oxygenated and acidic nature of bio-oil.
3. Evaluating the feasibility of integrating downstream separation and purification technologies with bio-oil production process, and identifying the optimal process configurations to maximize value and minimize environmental impact could be another potential area for future research.

4. Conducting life-cycle assessments and TEA to evaluate the environmental and economic sustainability of using bio-oil as a feedstock for biochemicals production, and comparing it with other renewable and non-renewable feedstocks.

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