THE SYNTHESIS OF ACTIVATED CARBON AND GRAPHENE OXIDE DERIVED FROM EMPTY FRUIT BUNCHES USING SLOW PYROLYSIS AS POTENTIAL ELECTRODE MATERIAL FOR SUPERCAPACITOR APPLICATION

AKINNAWO OLUMIDE OLUFEMI

UNIVERSITI SAINS MALAYSIA

2025

THE SYNTHESIS OF ACTIVATED CARBON AND GRAPHENE OXIDE DERIVED FROM EMPTY FRUIT BUNCHES USING SLOW PYROLYSIS AS POTENTIAL ELECTRODE MATERIAL FOR SUPERCAPACITOR APPLICATION

by

AKINNAWO OLUMIDE OLUFEMI

Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of philosophy

July 2025

ACKNOWLEDGEMENT

I would like to extend my profound gratitude to Dr. Nurhafizah Md Disa, my principal supervisor at Universiti Sains Malaysia (USM) during my PhD program. Dr. Nurhafizah's expertise, unwavering support, insightful guidance, and deep understanding have been invaluable throughout my academic journey. I express my sincere appreciation to my co-supervisor, Assoc. Prof. Dr. Nurhayati Binti Abdullah. Her expertise in biomass pyrolysis have not only shaped but also significantly enhanced my academic pursuits. My appreciation also goes to Dr. Mohammed Rabie Umar for his support and encouragement. I want to express my special appreciation to the Petroleum Technology Development Fund (PTDF), Nigeria, for awarding me a scholarship to USM. My sincere thanks also go to the Fundamental Research Grant Scheme (FRGS) and the Research University Grant (RUI) for providing financial support for my research project through the Postgraduate Incentive and Short-Term Grant. My heartfelt thanks are also directed to the Energy Studies Research Group (Isah Bakara, Amir Amzar, Hidayah, and Afza), as well as the staff and students at the School of Physics, notably, Associate Prof. Dr. Yam Fong Kwong, Ms Awanis Sirat, Mr Yushamdan Yusof, Mr Abdul Jamil Yusuf, Ms Mor Izzati, Associate Prof. Oluwaseun Adedokun and Samuel Obaseki for their unwavering support and assistance. I extend my gratitude to the management of United Oil Palm Industry Sdn. Bhd., Penang, Malaysia, for providing the Empty Fruit Bunch (EFB) samples crucial for my study. Lastly, I thank my wife and children for their endless support and understanding, which have been my most significant motivation and strength throughout this endeavour.

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF SYMBOLS

A	Pre-exponential factor
cm	Centimetre
cm^3/g	Cubic centimetre per gram
C_{sp}	Specific capacitance
E	Energy density
Ea	Activation energy
F/g	Farad per gram
I	Current
k	The rate constant of the reaction
m^2/g	Square metre per gram
MJ/kg	Megajoule per kilogram
mL	Millilitre
mL/min	Millilitres per minute
n	order of reaction
^oC	Degree Celsius
P	Power density
ppb	Parts per million
R	Universal molar gas constant
R^2	Coefficient of determination
T	Absolute temperature
t	Time
V	Voltage
w	mass of empty crucible

W/kg	Watt per kilogram
w_a	sample mass after volatilisation
w_b	sample mass before volatilisation
w_f	the final mass of the sample
Wh/kg	Watt-hour per kilogram
w_i	the initial mass of the sample
Wt. %	Weight percent
x	Conversion factor
β	Heating rate
Ω	Electrical resistance

LIST OF ABBREVIATIONS

AAEM	Alkali and Alkaline Earth Metal
AC	Activated Carbon
ASTM	American Society for Testing and Materials
CEC	Cation Exchange Capacity
CP	Conducting Polymer
CPE	Constant Phase Element
CV	Cyclic Voltammetry
CVD	Chemical Vapour Deposition
DTG	Differential Thermogravimetric
EDLC	Electric Double-Layer Capacitor
EDX	Energy Dispersive Spectroscopy
EFB	Empty Fruit Bunch
EIS	Electrical Impedance Spectroscopy
ESR	Equivalent Series Resistance
FC	Fixed Carbon
FTIR	Fourier Transform Infrared Spectroscopy
GO	Graphene Oxide
HHV	Higher Heating Value
ICPMS	Inductively Coupled Plasma Mass Spectrometry
KAS	Kissinger-Akahira-Sunose
LIB	Lithium Ion Battery
MC	Moisture Content
MF	Mesocarp Fibre
OFW	Ozawa-Flynn-Wall
OPF	Oil Palm Frond
OPT	Oil Palm Trunk
PANI	Polyaniline
pH	potential of Hydrogen
PKS	Palm Kernel Shell

POME	Palm Oil Mill Effluent
PPy	Polypyrrole
RGO	Reduced Graphene Oxide
SC	Supercapacitor
SERC	Science and Engineering Research Centre
TE	Troubling Element
TGA	Themogravimetric Analysis
UHR-SEM	Ultra-High-Resolution Scanning Electron Microscopy
UW	Unwashed
VM	Volatile Matter
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

SINTESIS KARBON TERAKTIF DAN GRAFIN OKSIDA YANG DIPEROLEH DARIPADA TANDAN BUAH KOSONG MENGGUNAKAN PIROLISIS PERLAHAN SEBAGAI BAHAN ELEKTROD BERPOTENSI UNTUK APLIKASI SUPERKAPASITOR

ABSTRAK

Kajian ini menyelidik kesan pra-perlakuan cucian air ke atas tandan buah kosong kelapa sawit (EFB) untuk sintesis karbon teraktif (AC) dan elektrod grafin oksida (GO) yang bertujuan untuk meningkatkan prestasi superkapasitor. Objektif utama adalah untuk menilai bagaimana pra-perlakuan cucian mempengaruhi sifat fizikokimia bioarang dan membandingkan prestasi elektro kimia AC dan elektrod GO yang diperoleh dari sumber biomassa yang sama. Metodologi yang digunakan melibatkan pendedahan EFB kepada pra-perlakuan cucian air, termasuk pengadukan dan merendam, diikuti dengan pirolisis perlahan pada 550 °C dalam atmosfera nitrogen untuk menghasilkan bioarang. Model Coats-Redfern digunakan untuk menilai kestabilan terma dan tenaga pengaktifan sampel yang telah dipra-perlakuan. Bioarang yang terhasil menjalani pengaktifan kimia menggunakan kalium hidroksida (KOH) pada nisbah impregnasi 1:3, dengan pengkarbonan pada 700 °C dan 800 °C untuk menghasilkan AC. GO telah disintesis daripada bioarang yang sama menggunakan kaedah Hummers yang diubah suai. Teknik pengkarakteran seperti fluoresensi sinar-X (XRF), spektrometri jisim plasma terinduksi (ICP-MS), sinaran X difraksi (XRD), spektroskopi inframerah Fourier-transform (FTIR), mikroskop elektron penskalan ultra tinggi resolusi (UHR-SEM), spektroskopi sinar-X pengedaran tenaga (EDX), dan analisis termogravimetrik (TGA-DTG) digunakan untuk

menilai bahan tersebut. Hasil menunjukkan bahawa rawatan perendaman secara signifikan mengurangkan kandungan abu sebanyak 67.08%, tahap kalium sebanyak 72%, dan tahap klorin sebanyak 76%. Pengurangan ini menyebabkan pemecahan struktur lignoselulosa yang dipertingkatkan dan meningkatkan kandungan karbon tetap, menghasilkan nilai haba yang lebih tinggi (HHV) sebanyak 25.4 MJ/kg selepas 72 jam perendaman. Walau bagaimanapun, rawatan awal juga mengurangkan hasil bioarang dari 35.5 wt.% kepada 30.4 wt.%. Analisis kinetik menggunakan model Coats-Redfern mendedahkan bahawa pirolisis EFB yang telah dirawat terlebih dahulu mengikuti mekanisme reaksi pelbagai langkah, dengan tenaga pengaktifan yang berkisar antara 31.77 hingga 43.67 kJ/mol. Penilaian elektrokimia menunjukkan bahawa elektroda berasaskan AC, terutamanya yang karbonisasi pada suhu 800 °C (AC2), menunjukkan prestasi yang lebih baik, yang dicirikan oleh kapasitans spesifik yang lebih tinggi dan rintangan siri yang lebih rendah, yang dikaitkan dengan kekosongan dan luas permukaan yang lebih baik. Sementara elektroda berasaskan GO menunjukkan metrik prestasi yang sedikit lebih rendah, kemasukan mereka adalah penting untuk menilai kebolehlaksanaan dan kelebihan perbandingan pelbagai bahan elektroda yang berasal dari sumber biojisim yang sama. Perbandingan menyeluruh ini menekankan potensi pra-perawatan pencucian dalam meningkatkan sifat bioarang dan menyokong pembangunan bahan elektroda yang cekap, yang berasal dari biojisim untuk aplikasi penyimpanan tenaga.

THE SYNTHESIS OF ACTIVATED CARBON AND GRAPHENE OXIDE DERIVED FROM EMPTY FRUIT BUNCHES USING SLOW PYROLYSIS AS POTENTIAL ELECTRODE MATERIAL FOR SUPERCAPACITOR APPLICATION

ABSTRACT

This study investigates the impact of water-washing pretreatment on oil palm empty fruit bunches (EFB) for the synthesis of activated carbon (AC) and graphene oxide (GO) electrodes aimed at enhancing supercapacitor performance. The primary objectives are to evaluate how washing pretreatment influences the physicochemical properties of biochar and to compare the electrochemical performance of AC and GO electrodes derived from the same biomass source. The methodology involved subjecting EFB to water-washing pretreatments, including stirring and soaking, followed by slow pyrolysis at 550 °C under a nitrogen atmosphere to produce biochar. The Coats-Redfern model was applied to evaluate the thermal stability and activation energy of the pretreated samples. The resulting biochar underwent chemical activation using potassium hydroxide (KOH) at impregnation ratios of 1:3, with calcination at 700 °C and 800 °C to produce AC. GO was synthesised from the same biochar using a modified Hummers' method. Characterisation techniques such as X-ray fluorescence (XRF), inductively coupled plasma mass spectrometry (ICP-MS), X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), ultra-high-resolution scanning electron microscopy (UHR-SEM), energy-dispersive X-ray spectroscopy (EDX), and thermogravimetric analysis (TGA-DTG) were employed to assess the materials. Results indicated that soaking

pretreatment significantly reduced ash content by 67.08%, potassium levels by 72%, and chlorine levels by 76%. These reductions led to an enhanced breakdown of the lignocellulosic structure and increased fixed carbon content, resulting in a higher heating value (HHV) of 25.4 MJ/kg after 72 hours of soaking. However, the pretreatment also reduced biochar yield from 35.5 wt.% to 30.4 wt.%. Kinetic analysis using the Coats-Redfern model revealed that the pyrolysis of pretreated EFB followed a multi-step reaction mechanism, with activation energies ranging from 31.77 to 43.67 kJ/mol. Electrochemical evaluations demonstrated that AC-based electrodes, particularly those carbonised at 800 °C (AC2), exhibited superior performance, characterised by higher specific capacitance and lower series resistance, attributed to their enhanced porosity and surface area. While GO-based electrodes showed slightly lower performance metrics, their inclusion was essential to assess the feasibility and comparative advantages of different electrode materials derived from the same biomass source. This comprehensive comparison underscores the potential of washing pretreatment in enhancing biochar properties and supports the development of efficient, biomass-derived electrode materials for energy storage applications.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Activated carbon (AC) and Graphene oxide (GO) are known for their extensive surface areas and favourable porosities. They are increasingly utilised as electrode materials in supercapacitors, significantly enhancing ionic movement between the electrode and the electrolyte. However, commercially available AC and GO involve costly processes and pose health risks due to releasing hazardous emissions [1].

In response to these challenges, this study explores an eco-friendly alternative by synthesising AC and GO from low-cost biomass waste using empty fruit bunches (EFBs), a byproduct of the palm oil industry, employing a slow pyrolysis method. This approach leverages the abundance, sustainability, and carbon neutrality of EFBs, thereby promoting biomass waste utilisation and mitigating environmental impact.

Using biomass as a carbon source significantly benefits the environment by reducing waste. GO derived from biomass share similarities with those produced from graphite; however, the inherent complexity of biomass leads to structurally distinct products. This complexity typically results in a graphene-like structure with inherent impurities [2].

Despite these structural differences, utilizing biomass waste offers substantial advantages. The process facilitates sustainable waste management by transforming agricultural and organic residues into high-value products, minimizing environmental impacts and maximizing resource efficiency. Moreover, the unique structural properties

of graphene-like materials from biomass could foster novel applications in electronics, filtration, and energy storage, thus broadening the scope of this innovative approach [2].

Malaysia's agricultural sector is a global leader in palm oil production, managing more than 5.74 million hectares of palm oil plantations and producing over 18 million tonnes of palm oil biomass annually [3]. This biomass includes palm kernel shells (PKS), oil palm fronds (OPF), mesocarp fibres (MF), empty fruit bunches (EFB), palm oil mill effluents (POME), and oil palm trunks (OPT), which can be used as energy resources and for generating value-added products. Most of this biomass waste is produced in over 450 oil palm mills and on the plantations themselves [3]. In particular, EFB has shown potential as a precursor for producing GO and reduced graphene oxide (rGO) based nanomaterials for supercapacitor applications, offering improved capacitive performance [4]. However, most of these waste materials are currently underutilized, commonly being used for recycling nutrients, preventing soil erosion, mulching, as boiler fuel at the mills, or being burned or discarded on plantations [3, 5]. Therefore, the thermochemical conversion of lignocellulosic EFB biomass presents a crucial opportunity for bioenergy generation, significantly contributing to environmental and economic sustainability. Additionally, the characteristics of the biomass feedstock used significantly influence the properties of the resulting biochar. These properties are vital in determining the biochar's suitability and effectiveness for specific applications. For instance, biochar derived from feedstocks with high carbon and lignin content has resulted in a final product with increased carbon content, enhancing its performance in targeted applications [6].

Farmers often discard fresh fruit bunches (FFBs) that are unsuitable for oil extraction—such as those that are rotten, underripe, or damaged—to maintain the quality of palm oil, contributing to significant waste in the palm oil industry [7]. Based on the

findings of Sagar et al. [8], fruit biomass losses largely result from improper handling practices, inadequate infrastructure, suboptimal storage conditions, and inefficient processing methods. These problems arise at different points in the supply chain, including during the harvesting, transportation, and marketing stages. Furthermore, regions that lack the resources to address these challenges tend to experience even higher levels of food loss. Such inefficiencies have economic and environmental implications, as the wasted biomass contributes to food insecurity and elevated greenhouse gas emissions from decomposition. Furthermore, converting lignocellulosic biomass, including agricultural and forestry waste, into carbon materials, such as AC and GO, has garnered attention as a sustainable alternative [9].

Pretreatment through washing is a straightforward, cost-effective, and energy-saving technique that successfully eliminates various troubling elements (TEs) from biomass, specifically soluble elements like potassium (K), sodium (Na), sulfur (S), and chlorine (Cl) [10, 11]. Such a method addresses common complications in thermal processing, such as sintering, fouling, slagging, and corrosion [11, 12]. Moreover, this pretreatment enhances the ash melting point, which in turn improves the quality of bio-oil and affects the generation of carbon monoxide and hydrogen during combustion, pyrolysis, and gasification processes [13–15].

Among the array of techniques available for the thermal conversion of biomass, notable methods include torrefaction, typically conducted at temperatures ranging from 200-320 °C [16, 17]; microwave-assisted pyrolysis, which utilizes electromagnetic radiation to generate heat without a fixed temperature range [18, 19]; slow pyrolysis, carried out at 300-550 °C [20–22]; fast pyrolysis, occurring at 400-600 °C with a rapid heating rate [3, 23]; gasification, typically performed at temperatures exceeding 700 °C

[24–26]; and hydrothermal treatment, conducted at 200-374°C under high pressure [27, 28]. Among these, slow pyrolysis has garnered considerable attention due to the exceptional quality of its end products, particularly biochar, which is promising for its environmental and agronomic benefits. Slow pyrolysis produces a substantial biochar yield at lower temperatures and extended residence times in a limited oxygen environment. This method enhances the biochar's carbon content and stability, making it ideal for long-term soil amendment applications that improve nutrient retention and carbon sequestration. Moreover, the process allows for precise control over the properties of biochar by adjusting process parameters, which can impact its porosity and surface area for specific applications such as water filtration as a catalyst carrier or for energy storage applications. Furthermore, slow pyrolysis generates valuable co-products like bio-oil and syngas, enhancing its economic value. Its energy efficiency and eco-friendly nature—producing fewer emissions such as nitrogen and sulfur oxides and requiring simpler, less costly technology—make slow pyrolysis a sustainable, cost-effective option for high-quality biochar production.

Biochar, a versatile product derived from the thermochemical conversion of biomass under low-oxygen conditions, has a wide range of practical applications [5]. It is crucial in enhancing soil quality, ecological cleanup, and greenhouse gas mitigation [29]. For instance, biochar can significantly improve the quality of contaminated soil, making it valuable for soil improvement and carbon sequestration in agriculture. Its high fixed carbon content and strong adsorption capabilities are crucial in adsorption and energy storage applications. Moreover, the large surface area of biochar is critical when used as a precursor for AC production. These practical applications highlight the significance of

biochar as a versatile and valuable resource in various environmental and agricultural settings.

Water-washing pretreatment can significantly influence the optimisation of EFB sourced from mills and plantations, facilitating sustainable biochar production. This processed biochar is ideal for developing AC and GO, both critical components in supercapacitor electrodes. Despite extensive research on EFBs from mills and industrial sources, there remains a notable gap in the literature regarding the viability of using plantation-sourced EFBs for slow pyrolysis to produce biochar. This study aims to address this gap by examining the effects of leaching—a crucial pretreatment method—on the properties of biomass and biochar from plantation and mill-sourced EFBs. The findings will offer new insights into biomass characteristics and possible uses, presenting a fresh perspective on the utilisation and valorisation of plantation-sourced biomass compared to mill-sourced counterparts. The research delves into the synthesis processes, characterises the resulting AC and GO, and assesses their effectiveness as electrode materials in supercapacitor applications. Ultimately, this study seeks to advance energy storage solutions and promote the sustainable use of EFB biomass wastes, enhancing biomass quality through water-washing pretreatment to facilitate the production of high-quality AC and GO supercapacitors.

1.2 Problem Statement

The palm oil industry generates significant amounts of biomass waste in the form of EFBs, often left to decompose on plantations or burned, contributing to environmental degradation. These practices contribute to environmental pollution and underutilisation of

a valuable lignocellulosic resource. Although EFBs have potential as precursors for carbon-based materials, their direct conversion without pretreatment typically yields biochar with low carbon content and poor structural properties.

While numerous studies have been conducted on converting biomass into AC, the combined use of water-washing pretreatment and kinetic modelling to improve and understand the thermal conversion of EFB—especially those sourced directly from plantations—remains underexplored. Furthermore, although AC and GO are promising electrode materials for supercapacitors, few comparative studies have assessed their electrochemical performance—such as surface area, capacitance, and thermal stability—when derived from the same biomass source.[4, 30].

These gaps limit the efficient valorisation of EFBs into high-performance, sustainable energy storage materials. Therefore, a deeper investigation into how pretreatment influences biochar quality, thermal degradation behaviour, and the resulting electrochemical performance of AC and GO electrodes is both timely and essential.

1.3 Research Questions

The research questions that are important to this study are as follows:

i. How does water-washing pretreatment affect the yield and quality of biomass and biochar produced from EFBs from palm oil mills and plantations?

   This question aims to evaluate the impact of the water-washing pretreatment process on the output and quality of biochar, providing insights into the effectiveness of this pretreatment method in enhancing the characteristics of biochar for further applications.

ii. What thermal degradation pathways are involved in the pyrolysis of pretreated EFB, and how can these be modelled using the Coats–Redfern method?

This question explores the suitability of pretreated EFB for biochar production and seeks to understand the kinetics of its thermal degradation. Understanding the kinetics of its thermal degradation is crucial for optimising the pyrolysis process and improving the efficiency of biochar production.

iii. How do the structural and chemical properties of AC and GO derived from pretreated EFB affect their suitability as electrode materials for supercapacitor applications?

This question focuses on characterizing the physical and chemical attributes of the final products (AC and GO) and examining how these properties influence their effectiveness and reliability as electrodes in supercapacitors.

The research questions thoroughly examine the study's primary objectives. These questions will ensure a comprehensive investigation into the effects of water-washing pretreatment on the production and application of biochar, AC and GO from EFBs in the context of energy storage technologies.

1.4 Research Objectives

The main objective of this research is to systematically evaluate the impact of water-washing pretreatment on the chemical properties of biochar derived from plantation-sourced EFBs and to assess the suitability of the resulting AC and GO as electrode materials for supercapacitor applications.

The specific objectives are:

i. To investigate the effects of water-washing pretreatment on the properties of biomass and biochar produced from EFBs from palm oil mills and plantations.

ii. To evaluate the thermal degradation behaviour of water-washing pretreated EFB through kinetic modelling using the Coats–Redfern method, with the aim of understanding decomposition mechanisms relevant to biochar synthesis.

iii. To characterise the structural, chemical, and electrochemical properties of the resulting AC and GO, including surface area, pore size distribution, functional groups, crystallinity, as well as performance metrics obtained through cyclic voltammetry and electrochemical impedance spectroscopy—parameters critical to their application as supercapacitor electrodes.

These objectives aim to close the current knowledge gap and contribute to the advancement of sustainable and efficient use of agricultural waste in energy storage technologies. Figure 1.1 shows a comprehensive process flowchart highlighting the steps for utilising EFB biomass through pretreatment, drying, and conversion into biochar and the subsequent use of biochar to synthesise AC and GO to fabricate supercapacitors.

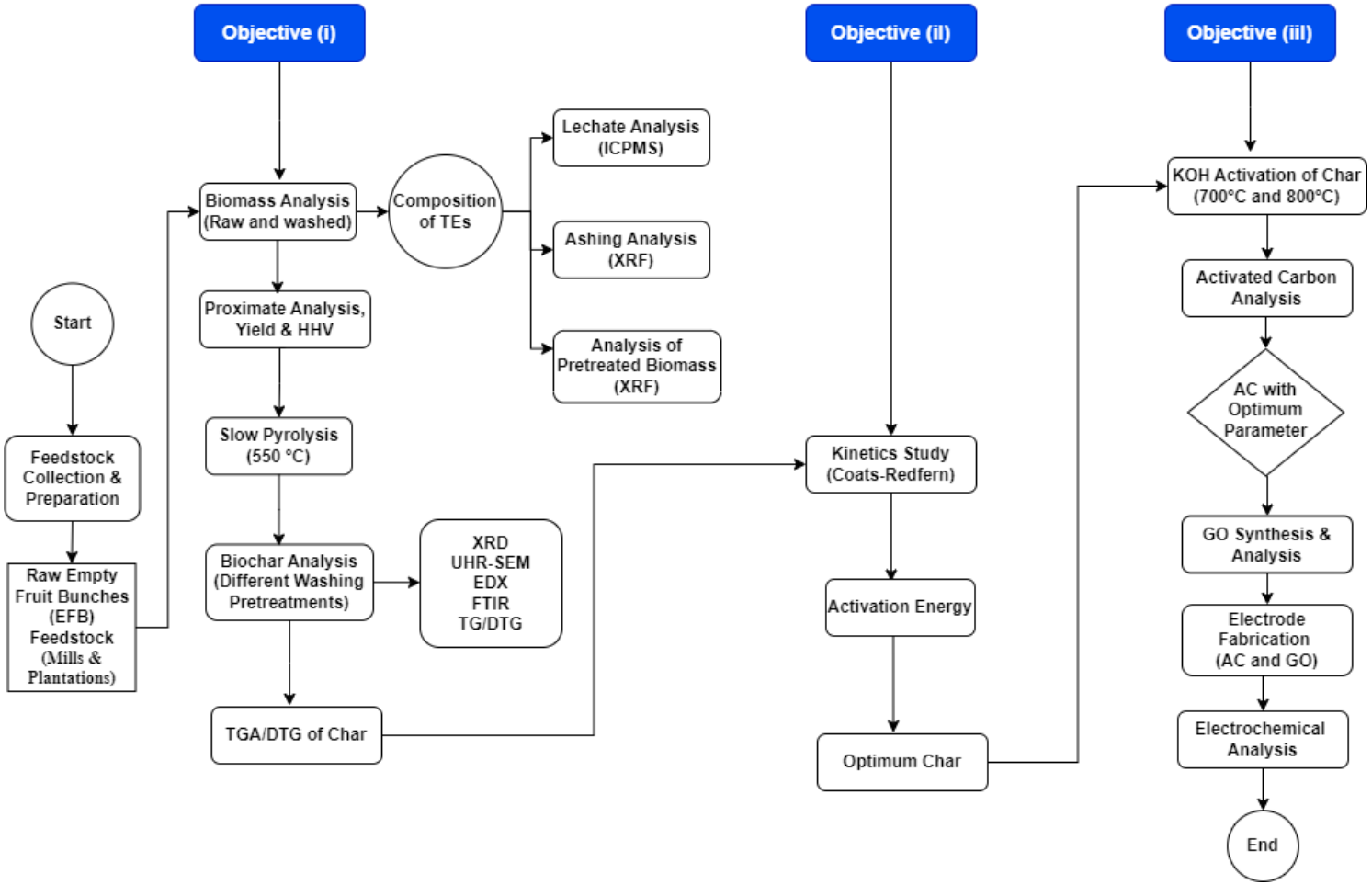

Figure 1.1 Process flow diagram for converting EFB biomass into electrode materials for supercapacitors

1.5 Scope of the Study

The scope of this research encompasses a thorough investigation of water-washing pretreatment effects on the properties of biomass and biochar derived from EFBs from palm oil mills and plantations. The research evaluates the effects of water washing on the chemical composition and ash removal in EFBs and its subsequent impact on the resulting biomass and biochar. The study then advances by utilising these pretreated EFBs to produce biochar, further processed into AC and GO for further analysis. Additionally, the study conducts a kinetic study using the Coats-Redfern method to understand the thermal degradation mechanism of the pretreated EFBs and to estimate the required activation energy for biochar production. The research also comprehensively characterises the structural and chemical properties of the resultant AC and GO, mainly focusing on attributes crucial to their functionality as supercapacitor electrodes, such as surface area, porosity, and electrical conductivity. Finally, the application evaluation segment assesses the synthesised AC and GO performance as electrode materials in supercapacitors, focusing on their capacitive properties and energy storage efficiency.

1.6 Limitations of the Study

The study has some limitations that narrow down the scope of its findings. Firstly, it assumes that EFBs have a relatively consistent chemical composition across different locations, potentially ignoring regional variations due to varying environmental conditions, harvesting techniques, and processing methods. The research specifically focuses on the impact of water-washing pretreatment, excluding other potential pretreatment methods that could also improve biochar quality, such as acid or alkali

treatments. Regarding analytical methods, the study mainly uses the Coats-Redfern method for kinetic analyses, which may not offer the precision achievable with more advanced real-time techniques like TGA-FTIR. Additionally, the entire research is conducted on a laboratory scale, which may not fully represent industrial-scale processing conditions, affecting the applicability of the results to larger-scale applications.

Furthermore, the study exclusively concentrates on AC and GO as electrode materials without considering other potential uses of biochar and its composites. Lastly, while the survey addresses the technical feasibility of using EFBs for biochar production, it should also include a thorough economic and life-cycle analysis to evaluate this approach's overall environmental impacts and financial benefits. These limitations are essential for defining the research boundaries and placing the findings in the broader context of biochar application in energy storage technologies.

1.7 Thesis Structure

This thesis is divided into five distinct chapters, each designed to systematically present the research conducted on the impact of water-washing pretreatment on the chemical properties of biochar derived from EFBs and the resultant AC and GO as electrode materials for supercapacitor applications. Here is a breakdown of each chapter:

Chapter 1: Introduction: This chapter explores AC and GO as electrode materials for supercapacitors, focusing on utilising low-cost EFBs. The chapter underscores Malaysia's substantial yet underutilised palm oil biomass and advocates for the valorisation of EFB into high-quality AC and GO. Additionally, it discusses the

advantages of water-washing pretreatment in improving biochar quality, which promotes environmental and economic sustainability.

Chapter 2: Literature Review: The second chapter delves into a detailed review of the existing literature related to supercapacitors, EFB biomass pretreatment, thermal conversion processes including slow pyrolysis and activation, and the methods employed in preparing GO. This chapter critically examines previous research, identifying gaps and how this study contributes to new knowledge and understanding in the field.

Chapter 3: Methodology: This chapter thoroughly describes the experimental procedures employed in the research. These procedures include preparing biochar through slow pyrolysis, producing activated carbon via two-step activation processes, synthesising GO, and fabricating electrode materials. Additionally, this chapter covers the techniques used to characterise the various energy products produced and details Hummer's method for converting activated EFB biochar into GO.

Chapter 4: Results and Discussion: The fourth chapter presents the core findings from the experiments conducted. These results include proximate analysis and calorific values of EFB feedstocks from mills and plantations, as well as results from the slow pyrolysis of EFB, the chemical activation of EFB biochar, and the synthesis and characterisation of AC and GO. The kinetic study of the biochar using the Coat-Redfern model is also discussed. The chapter concludes with a comparative analysis linking these findings to the theories and observations reviewed in Chapter 2.

Chapter 5: Conclusion and Recommendations: This final chapter compiles the entire study's findings, drawing conclusions about the impact and effectiveness of the materials and methods used. It also provides recommendations for future research, suggesting how these findings could be expanded upon or applied in practical or industrial

contexts to enhance the development of energy storage technologies and sustainable material processing.

Each chapter builds upon the information and analysis presented in the previous ones, ensuring a coherent and comprehensive exposition of the research. The thesis aims to address significant gaps in the current research landscape and offer practical recommendations that could lead to advancements in material science and energy technology.

CHAPTER 2

LITERATURE REVIEW

2.1 Biomass and Its Composition

Biomass is a rich source of organic carbon, comprising various materials categorized as woody biomass, energy crops, agricultural wastes, and domestic biomass resources, including municipal and solid wastes [25]. This diverse category of biomass draws energy from sunlight through photosynthesis and nutrient absorption from the soil. The thermochemical conversion of biomass into valuable products like biochar, bio-oil, and syngas represents a significant area of potential, particularly when considering agricultural residues such as rice husk, wheat straw, sugarcane bagasse, bamboo, mesocarp fibre from oil palms, empty fruit bunches, corn stover, coconut shells, and groundnut shells. The transformation of these residues into high-value products has garnered attention for its potential to foster socio-economic benefits and stimulate rural development.

Biomass comprises carbohydrates, lipids, proteins, and trace amounts of minerals, including phosphorus, calcium, nitrogen, sulfur, zirconium, and sodium. The three primary constituents in plant biomass are lignocellulosic components, extractives, and ash [24]. Figure 2.1 illustrates a schematic representation of biomass fractionation into extractives, lignocellulosic components, and ash.

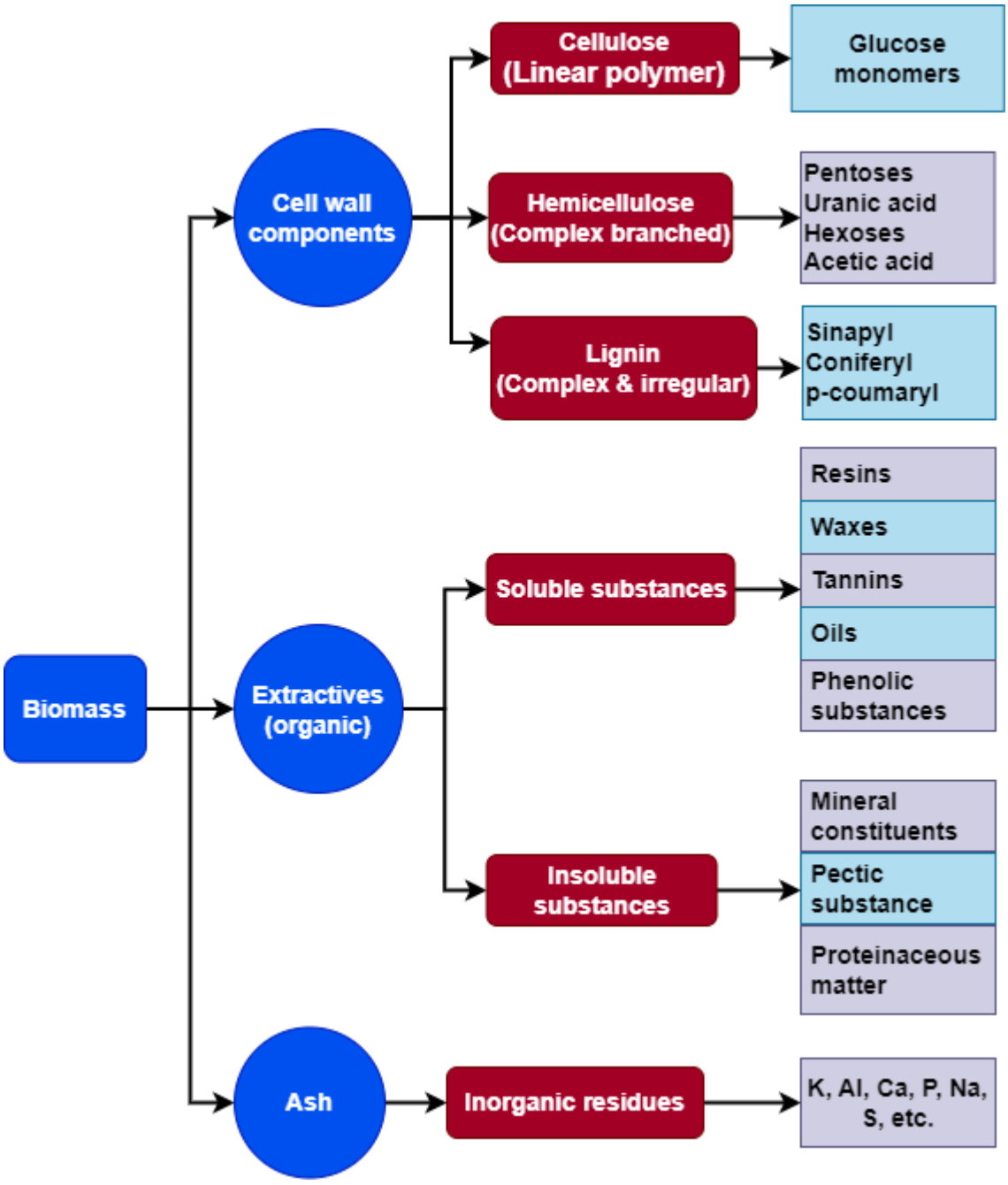

Figure 2.1 Showing a comprehensive breakdown of biomass composition and residual ash constituents

The lignocellulosic components of plants consist of holocellulose (55-90 %) and lignin (10-25 %) by weight. Holocellulose encompasses cellulose (40-60 %), featuring long-chain β-D-glucopyranose units linked through β-(1,4) glycosidic bonds, and hemicellulose (15-30%), which consists of a shorter, branched mix of various sugars [31, 32]. In the plant cell wall, cellulose molecules align with each other through hydrogen bonding, forming bundles known as microfibrils. Hemicellulose is generally less crystalline than cellulose, making it more easily hydrolysed. Lignin, on the other hand, has a significant molecular structure of cross-linked phenolic polymers that bind covalently with hemicellulose, contributing to the complexity of lignocellulosic biomass [33]. Lignin forms the outmost layer, next to which is the hemicellulose that binds with cellulose microfibrils to fortify and strengthen plant cell walls [34]. Hence, the rigidity of the cell wall makes it difficult to break down the lignocellulose structure.

Presently, various pretreatment processes are used for separating lignocellulosic components of biomass. Cellulose, a linear chain biopolymer, is the primary constituent of most woody biomass. It comprises solely units of anhydroglucose, as presented in Figure 2.6. Acid hydrolysis can extract it from biomass, which is insoluble in water and most organic solvents. Thermogravimetric analysis has provided insights into the thermal behaviour of cellulose, indicating that its degradation occurs within the temperature range of 240 °C to 350 °C [35]. This process results in the production of anhydrocellulose and levoglucosan. Anhydrocellulose is a cellulose derivative formed through water removal during thermal decomposition, while levoglucosan is a volatile compound derived from the

pyrolysis of glucose units within cellulose. Cellulose microfibers constitute the central backbone of lignocellulosic crystalline structure. They are held together by amorphous hemicellulose and lignin via hydrogen and covalent bonds, making the biomass recalcitrant [31].

Hemicellulose is an amorphous heteropolymer consisting of a diverse array of shorter-chain sugars, including d-glucose, d-galactose, d-xylose, d-arabinose, d-mannose, d-fucose, d-glucuronic acid, d-mannuronic acid, and d-galacturonic acid [36–38]. It plays a crucial role in reinforcing plant cell walls by connecting cellulose microfibrils and lignin, thereby providing strength and rigidity to plant cell walls [37]. During biomass conversion, the process breaks down hemicellulose alongside cellulose to produce valuable compounds such as ethylene glycol and sugar alcohols [39]. Additionally, hemicellulose exhibits lower strength and decomposes within the temperature range of 200 °C to 350 °C [36]. The hemicellulose components can be separated through alkali, acid or organosov hydrolysis to yield sugars subsequently convertible into biofuels [40]. However, these pretreatment processes are not without their environmental concerns [33]. Figure 2.2 illustrates biomass's primary constituents, emphasising cellulose, hemicellulose, and lignin molecular structures. The central image portrays the interwoven fibres of these three polymers, while the insets present detailed chemical structures of cellulose, various sugars in hemicellulose (including glucose, galactose, mannose, xylose, arabinose, and glucuronic acid), and lignin. These components significantly influence the characteristics and processing of biomass for diverse applications.

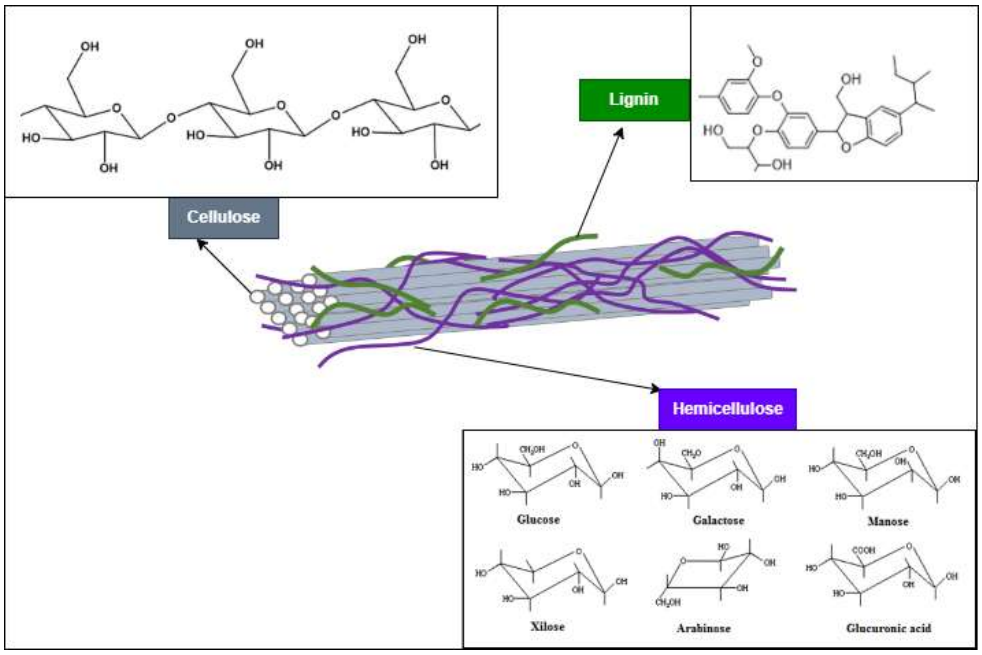

Figure 2.2 Lignocellulosic and molecular constituents of biomass

Lignin, a complex polyphenolic structure (non-carbohydrate), poses a significant challenge in the thermochemical conversion of biomass to bio-oil, biochar, and syngas due to its recalcitrant nature, with a higher decomposition temperature [14, 41]. Many techniques have been researched to extract lignin in biomass conversion [31, 42]. Among these, ionic liquids (ILs) are effective for removing lignin from different kinds of biomass [31]. Other methods, such as steam explosion, organosolv pretreatment using ethanol or methanol, and alkaline pretreatment with solutions like sodium hydroxide or ammonia, have also been used to break down lignin in biomass. These methods aim to disrupt the lignocellulosic structure of the biomass, making it easier to separate cellulose, hemicellulose, and lignin. The intricate structure poses a

challenge in utilizing lignocellulosic biomass as a viable biofuel source due to the recalcitrance of its cell walls, necessitating specialized techniques and technologies for efficient deconstruction and utilisation [43]. A comprehensive understanding of the lignocellulosic composition is crucial for evaluating suitability across diverse applications.

2.1.1 Oil Palm Wastes

Malaysia is preeminent as one of the largest oil palm producers globally, covering an expansive 5.9 million hectares [44] of plantation areas, contributing to 85% of the total output, a testament to its ideal tropical climates and plentiful rainfall. The oil palm industry has profoundly transformed the nation's economic and agricultural landscapes [45, 46]. The cultivation of these oil palm plantations leads to a substantial generation of biomass by-products. Notably, a mere 10% of the oil palm yield is utilized for palm oil production, leaving the vast remainder as agricultural waste—including oil palm empty fruit bunches (EFB), mesocarp fibres (MF), oil palm trunks (OPT), oil palm fronds (OPF), palm kernel shells (PKS), and palm oil mill effluents (POME). According to Chia et al. [47], one ton of fresh fruit bunch (FFB) can produce solid wastes, including 23 % EFB, 12 % MF, 5 % PKS and liquid waste such as 60 % POME. Palm oil has predominantly occupied a dominant position in the global vegetable oil market, surpassing the production of rapeseed and soybeans [48].

The Malaysian agricultural sector has traditionally managed agricultural waste through disposal or as a means of fertilisation for nutrient recycling and soil erosion

prevention [5]. However, the valorisation of oil palm waste, particularly for biochar production, has emerged as an imperative for sustainable bioenergy and environmental stewardship. The strategic utilisation of biomass not only counters the environmental impacts of fossil fuels but also serves as a renewable energy substitute [49]. EFBs present a cost-effective and abundantly available resource for bioenergy production and the derivation of value-added products via thermochemical conversion. Among the array of thermochemical conversion methodologies, pyrolysis is the most efficient and prevalent technique for yielding gas, bio-oil, and solid charcoal under oxygen-limited conditions [50].

Disposing of the considerable volumes of waste the oil palm industry generates represents a significant environmental challenge. Standard practices, such as the open burning of this waste, contribute to the emission of greenhouse gases, including methane and carbon dioxide, exacerbating climate change [46]. Additionally, depositing waste on oil palm fields can attract harmful insects due to the waste's high cellulose and sucrose content [51]. It is, therefore, imperative to channel biomass oil palm wastes toward energy production and innovate new energy generation methods from such waste streams to mitigate these environmental and ecological risks. Figure 2.3 depicts the flow diagram of an oil palm tree and its derivatives, showcasing the various components obtained from the oil palm tree. The process begins with the harvesting of fresh fruit bunches from the tree. These fruit bunches undergo processing to extract the oil palm kernel—further processing of the kernel results in the production of oil palm shell and mesocarp fibre. The empty fruit bunch (EFB),

remaining after kernel extraction, can be processed into a usable material. The oil palm frond is another byproduct of the oil palm tree.

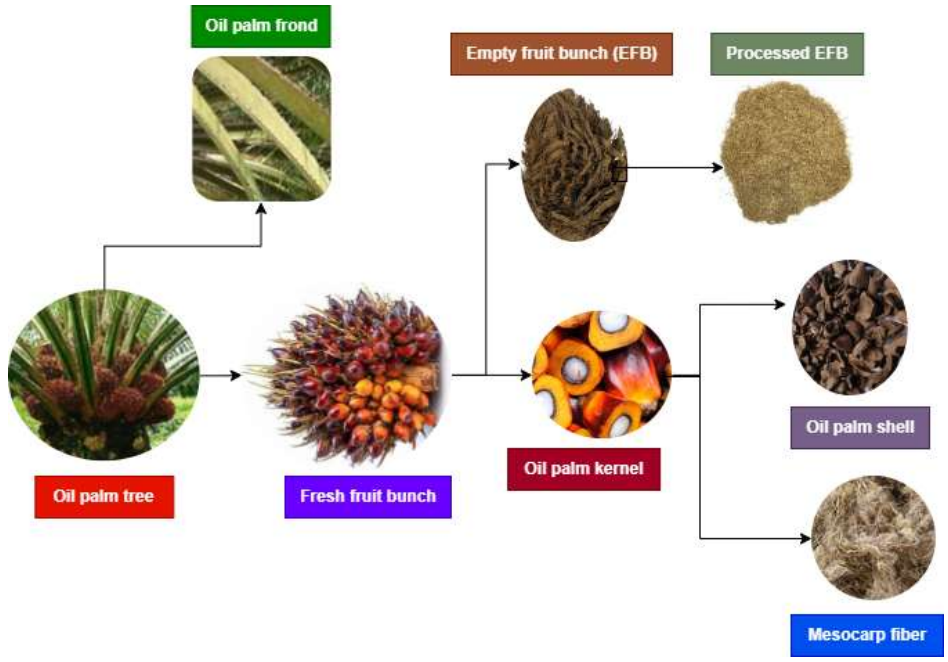

Figure 2.3 The waste produced from oil palm trees

The oil palm sector is at a critical juncture to adopt and invest in technologies that can mitigate the profound long-term impacts of waste on the environment and climate. Embracing these technologies would safeguard the environment and the health of human and animal populations and bolster regional economies. It creates opportunities for advancing conversion techniques that transform waste into biofuels, bio-based products, and biochemicals, thereby supporting a more sustainable and circular economy [52].

2.1.2 Oil Palm Biomass Conversion

The large volume of oil palm production in Malaysia generates humongous wastes such as oil palm empty fruit bunch (EFB), mesocarp fibre (MF), oil palm shell (OPS), oil palm frond (OPF) and palm oil mill effluent (POME). Oil palm biomass, primarily consisting of cellulose, hemicellulose, and lignin, stands out as a promising lignocellulosic feedstock due to its elevated cellulose (28-41 %), moderate hemicellulose (21-37 %) and lignin (18-23 %) content [53]. This composition renders it particularly conducive for biochemical processes such as fermentation, anaerobic digestion and esterification aimed at producing a diverse range of chemical products at a cost-effective rate [41, 53]. The intricate balance of these components holds a pivotal role in the selection of ideal lignocellulosic biomass, as a higher lignin content increases biomass recalcitrance, thereby influencing the overall cost of pre-treatment [53]. The favourable cellulose and hemicellulose composition in oil palm biomass underscores its potential as a valuable resource for sustainable and biochemical production.

Extractives in biomass are organic compounds that are not part of the plant cell wall's core structure. Solvents of varying strength can extract them. These extractives, comprising various substances—fats, waxes, resins, proteins, oils, simple sugars, starches, and compounds serving as a natural plant resistance—can amount to anything from 0 to 15 % of the weight of the biomass. They play pivotal roles in metabolism and energy storage and give resistance to microbial and insect attacks. Extracting these substances involves using solvents that can be polar, such as water and alcohol, or non-polar, such as hexane, to dissolve and remove the extractives. The