

**ASSESSMENT OF BIOCHAR PROPERTIES
DERIVED FROM TREATED AND UNTREATED
COCONUT FROND AS A POTENTIAL SOLID
FUEL**

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FUEL**

by

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LIST OF SYMBOLS

°C	Degree Celsius
A	Frequency factor
Al ₂ O ₃	Aluminium oxide
C	Carbon
CaO	Calcium oxide
CH ₄	Methane
CO	Carbon monoxide
CO ₂	Carbon dioxide
E _a	Activation energy
H	Hydrogen
H ₂ SO ₄	Sulphuric acid
HCl	Hydrochloric acid
k(T)	Rate constant
KOH	Potassium hydroxide
mf wt%	Moisture-free weight percent
MJ/kg	Megajoule per kilogram
N	Nitrogen
NO _x	Nitrogen oxides
n/a	Not available
O	Oxygen
R	Universal gas constant
S	Sulphur
SiO ₂	Silicon dioxide
SO ₂	Sulphur dioxide

T	Absolute temperature
wb%	Wet basis percent
wt%	Weight percent

LIST OF ABBREVIATIONS

AAEMs	Alkali and alkaline earth metals
AC	Ash content
ASTM	American Society for Testing and Materials
BWC	Bakau wood charcoal
CF	Coconut frond
CF-Br	Coconut frond briquette
CFB-Br	Coconut frond biochar briquette
CSC-Br	Coconut shell charcoal briquette
EC	Electrical conductivity
EFB	Empty fruit bunch
EJ	exajoule
FC	Fixed carbon
FWO	Flynn–Wall–Ozawa
HHV	Higher heating value
IEA	International Energy Agency
KAS	Kissinger–Akahira– Sunose
MC	Moisture content
NMR	Nuclear magnetic resonance
PKS	Palm kernel shell
PJ	petajoule
RM	Ringgit Malaysia
SNI	Indonesia National Standard
TCF-Br	Torrefied coconut frond briquette
TCFB-Br	Torrefied coconut frond biochar briquette

TG	Thermogravimetric
USM	Universiti Sains Malaysia
VM	Volatile matter
WCF-Br	Washed coconut frond briquette
WCFB-Br	Washed coconut frond biochar briquette
WTCF	Washed-torrefied coconut frond
WTCF-Br	Washed-torrefied coconut frond briquette
WTCFB-Br	Washed-torrefied coconut frond biochar briquette

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**PENILAIAN SIFAT – SIFAT BIOARANG YANG DIPEROLEH DARIPADA
PELEPAH KELAPA YANG DIRAWAT DAN TIDAK DIRAWAT SEBAGAI
BAHAN API PEPEJAL YANG BERPOTENSI**

ABSTRAK

Biojisim digunakan sebagai bahan mentah dalam proses pirolisis perlahan untuk mendapatkan bioarang, bahan karbon hitam dan berliang. Proses pra-rawatan biojisim adalah satu cara untuk meningkatkan kualiti biojisim dan sifat-sifat bioarang. Sifat bioarang sensitif terhadap perubahan sifat bahan mentah dan keadaan pirolisis. Penggunaan pelepah kelapa (CF) sebagai bahan mentah dalam proses pirolisis untuk menghasilkan bioarang adalah terhad berbanding dengan sisa kelapa yang lain. Kajian ini dijalankan dengan objektif untuk menilai sifat bioarang yang dihasilkan daripada pirolisis perlahan pelepah kelapa dan untuk mengkaji pengaruh pra-rawatan bahan mentah terhadap sifat bioarang CF. Penyelidikan ini juga bertujuan untuk menilai potensi bioarang CF dan bahan mentah CF sebagai bahan api pepejal dengan menilai sifat-sifat bio-briket CF. Hasil daripada rawatan pencucian menunjukkan bahawa masa rendaman selama 2 jam mengurangkan kandungan abu bahan mentah CF kepada 2.84 db wt% dan memanjangkan masa rendaman kepada 6 jam tidak menghasilkan pengurangan maksimum kandungan abu. Gabungan 2 jam cucian dan rawatan torefikasi pada 300°C meningkatkan kualiti bahan mentah CF dengan ketara. Rawatan cucian sebelum proses torefikasi menyumbang kepada pengurangan kandungan abu sampel yang ditorefikasi. Kejadian sedemikian menyumbang kepada peningkatan kandungan karbon tetap dan nilai pemanasan tinggi (HHV) bagi bahan mentah CF yang telah dibasuh dan ditorefikasi (WTCF), masing-masing sebanyak 49.49 db wt% dan 25.44 MJ/kg. Eksperimen pirolisis perlahan bagi bahan mentah CF yang tidak

dirawat telah dilakukan dengan suhu akhir yang berbeza, 400°C - 650°C. Kandungan abu, kandungan karbon tetap dan HHV bioarang CF meningkat dengan peningkatan suhu akhir, manakala peratusan hasil bioarang CF menunjukkan perubahan sebaliknya. 550°C ialah suhu optimum untuk pirolisis perlahan CF. Pada suhu ini, 30.64 wt% bioarang CF diperolehi, dan ia mengandungi 68.02 db wt% karbon tetap dan 26.49 MJ/kg HHV. Pra-rawatan bahan mentah CF sebelum eksperimen pirolisis perlahan menambahbaik sifat bioarang CF. Bioarang CF yang diperolehi daripada pirolisis perlahan bahan mentah WTCF pada 550°C mempamerkan kandungan karbon tetap tertinggi dan HHV masing-masing sebanyak 80.99 db wt% dan 29.71 MJ/kg. Analisis bio-briket menunjukkan bahawa briket bioarang CF mempunyai sifat bahan api yang lebih baik dengan bahan meruap yang lebih rendah, kandungan karbon yang lebih tinggi dan HHV yang lebih tinggi daripada briket bahan mentah CF. WTCFB-Br, briket bioarang yang diperolehi daripada bahan mentah WTCF, mempamerkan sifat terbaik antara bio-briket CF dengan karbon tetap tertinggi (66.30 db wt%), HHV (25.79 MJ/kg) dan kadar pembakaran terendah (0.253 g/min).

ASSESSMENT OF BIOCHAR PROPERTIES DERIVED FROM TREATED AND UNTREATED COCONUT FROND AS A POTENTIAL SOLID FUEL

ABSTRACT

Biomass is used as feedstock in the slow pyrolysis process to obtain biochar, a black and porous carbon substance. The pre-treatment process of biomass is a way to enhance biomass quality and biochar properties. The properties of biochar are sensitive to the change in feedstock properties and the pyrolysis conditions. The utilization of coconut frond (CF) as a feedstock in the pyrolysis process to produce biochar is limited compared to the other coconut residues. This study is performed with the objectives of evaluating the properties of biochar produced from slow pyrolysis of coconut frond and to study the influence of feedstock pre-treatment on the properties of CF biochar. This research also aims to assess the potential of CF biochar and CF feedstock as a solid fuel by evaluating the properties of CF bio-briquette. The results from washing treatment show that 2.0 hours of soaking time reduces the ash content of CF feedstock to 2.84 db wt% and extending the soaking time to 6 hours does not result in the maximum reduction of ash content. A combination of 2.0 hours of washing and torrefaction treatment at 300°C significantly enhances the quality of the CF feedstock. Washing treatment before the torrefaction process contributes to reducing the ash content of the torrefied sample. Such occurrence resulted in the higher fixed carbon content and high heating value (HHV) of washed-torrefied CF feedstock (WTCF), 49.49 db wt% and 25.44 MJ/kg, respectively. The slow pyrolysis experiment of untreated CF feedstock was performed at different terminal temperatures, 400°C - 650°C. The ash content, fixed carbon content and HHV of CF biochar increase with the increasing terminal temperature, while the yield percentage of CF biochar shows

the opposite trend. 550°C is the optimum temperature for the slow pyrolysis of CF. At this temperature, 30.64 wt% of CF biochar was obtained, and it contains 68.02 db wt% of fixed carbon and 26.49 MJ/kg of HHV. The pre-treatments of the CF feedstock before the slow pyrolysis experiment improve the properties of CF biochar. CF biochar derived from slow pyrolysis of WTTCF feedstock at 550°C exhibits the highest fixed carbon content and HHV of 80.99 db wt% and 29.71 MJ/kg, respectively. The analysis of bio-briquette indicates that CF-biochar briquettes have better fuel properties with the lower volatile matter, higher carbon content and higher HHV than CF-feedstock briquettes. WTTCFB-Br, the biochar briquette derived from WTTCF feedstock, exhibits the best properties among CF bio-briquettes with the highest fixed carbon (66.30 db wt%), HHV (25.79 MJ/kg) and lowest burning rate (0.253 g/min).

CHAPTER 1

INTRODUCTION

1.1 Research Overview

Interest in renewable energy and its resources is expanding globally due to the concern over environmental issues such as global warming and climate change, as well as the growing demand for energy, which leads to striving for an alternative form of energy. Such a concern is also due to the limitation and shortcomings of non-renewable energy resources and the increasing world population. According to projections by the United Nations, the population will reach 10 billion by 2060 (Gent et al., 2017). Additionally, decreasing fossil reserves, rising oil prices, concerns over the security of supply and environmental impacts since the 1990s have led to a global policy shift back towards using biomass as a local, renewable and low-carbon feedstock (Attard et al., 2015).

Renewable energy is energy derived from renewable resources. The resources such as biomass, flowing water, sunlight, wind and geothermal heat are naturally replenished. According to Clark and Deswarte (2015), an ideal renewable resource can be regenerated in a short amount of time or has an almost unlimited supply. Bioenergy refers to renewable energy derived from recently living biological material or biomass. It is a form of renewable energy because energy contained in biomass is the energy from the sun captured through the natural processes of photosynthesis (Williams et al., 2015). Solar energy is converted into chemical energy during photosynthesis and retained in the chemical bonds of biomass materials. Chemical energy is released when these chemical bonds are broken. The chemical energy then can be transformed into various chemicals, materials, biofuels, or forms of energy through different conversion technologies (Lam et al., 2015).

Biomass receives great attention worldwide as an alternative energy source. It has high potential in the bioenergy generation field because biomass resources are abundant, renewable and inexpensive, making it a suitable replacement for fossil fuel. According to Saratale et al. (2019), biomass supplies about 15% of the global energy demand. Additionally, according to a report by World Bioenergy Association (2019), about 55.6 EJ of biomass was used for energy purposes in 2017, where 86% of the use was in the form of primary solid biofuels such as fuelwood for cooking and heating, wood chips and wood pellets. Biomass is considered a carbon-neutral energy source because it absorbs carbon dioxide (CO₂) during its growth and releases it into the atmosphere during the combustion process, with a zero-net balance of CO₂ emissions (Perea-Moreno et al., 2019). Generally, biomass is available in various materials such as agriculture residues, wood wastes, household wastes and paper wastes.

Direct utilization of raw biomass for heat and power generation is not efficient due to the drawbacks of its physical and chemical properties. The high moisture content of biomass decreases the heating value, lowers the maximum combustion temperature and reduces the thermal efficiency of the biomass conversion (Liu & Han, 2015). Biomass also has a relatively low energy density which causes more biomass feedstocks required to supply the same amount of energy as a traditional hydrocarbon fuel (Irmak, 2019). In addition, the inherent properties of some biomass with high ash content, such as forest residues and agricultural biomass like wheat straw and barley straw (Zajac et al., 2018), lead to the agglomeration of the bed material inside the reactor and fouling problems in the combustion chamber (Wannapeera et al., 2011). To overcome these limitations and drawbacks, biomass pre-treatment and conversion of biomass into value-added products are necessary to enhance the quality and properties of biomass before its utilization as solid fuels.

The biomass pre-treatment process is a necessary way to enhance biomass quality. It is considered as an intermediate step, where the properties of biomass are modified chemically or physically before the conversion process into valuable products. This process also helps in improving the conversion efficiency of biomass feedstock. Besides, the high transportation costs and logistical challenges involved when using bulky biomass can be reduced via biomass pre-treatment, which produces a fuel or energy carrier with increased volumetric energy density. The biomass pre-treatment includes drying, sieving, leaching, washing or thermal treatment (Koppejan, 2019). Each of these pre-treatments has different effects on the biomass properties. Washing pre-treatment was conducted to reduce ash-related consequences such as slagging and fouling, which mainly occur during the thermal conversion process (Deng et al., 2019) and to enhance bio-oil properties (Abdullah et al., 2007). Reducing ash content in biomass composition also improved biochar properties, such as increment of heating values and fixed carbon in the biochar composition (Nikkhah et al., 2020; Shariff et al., 2014; F. Sulaiman et al., 2013). Meanwhile, thermal treatment such as the torrefaction process increases the energy density (Matali et al., 2016), grindability and hydrophobicity (D. Chen et al., 2015) of feedstock. Therefore, selecting suitable pre-treatment is essential in optimizing and enhancing the properties of biomass and the products derived from its conversion.

Biomass conversion via the thermochemical process is another way to enhance the properties of raw biomass. Different types of fuels, such as biochar and bio-oil, are obtained from thermochemical conversion methods such as pyrolysis, gasification, liquefaction and combustion (Demirbas, 2009; Gent et al., 2017). Pyrolysis of biomass is a promising and viable thermochemical method to produce energy from biomass. The pyrolysis parameters such as temperature, heating rate and residence time

influence the physicochemical properties of pyrolysis products (Yorgun & Yıldız, 2015). The selection of optimum parameters is essential to obtain the products with the best features and properties according to their specific application.

Biochar is one of the products from the thermochemical process of biomass. It is a carbon-rich product produced from the thermal decomposition of organic materials under limited or absence of oxygen supply at relatively low temperatures, approximately below 700°C (Lehmann & Joseph, 2009). Biochar production using various types of feedstocks attracted attention among researchers since the type of feedstocks greatly influences the feasibility of biochar production, especially for large-scale production. Agricultural wastes or residual lignocellulosic biomass have the potential as sustainable precursors for biochar production because these wastes are rich in carbon composition, abundant and renewable feedstock (Rangabhashiyam & Balasubramanian, 2019).

Biochar is usually associated with carbon sequestration and soil fertility. Nevertheless, numerous studies were reported on the potential and utilization of biochar in other applications such as solid fuel (Liu et al., 2013; Yang et al., 2017), carbon filler for polypropylene composites (Elnour et al., 2019), adsorbent (Lam et al., 2018; F. Li et al., 2016) and energy storage material (Caguiat et al., 2018; Liu et al., 2019).

Briquettes are usually used for heat and power generation in domestic and industrial applications. The briquettes also substitute conventional fuels such as diesel, coal, lignite and firewood (M. K. Sharma et al., 2015). The properties and quality of the briquette rely on the raw material and briquetting process. The properties of the material used to produce briquette usually affect the desired qualities of briquette as fuel, such as heating value, ash content and ease of ignition. Meanwhile, the

briquetting parameters determine the stability and durability of the briquette, which are usually measured by its compressive strength, impact resistance, density and moisture absorption (Kpalo et al., 2020b). Various materials have been used to produce briquettes, which can be classified into three main groups: biomass, torrefied biomass, and biochar. The briquette produced from these materials is also known as bio-briquette.

Coconut palm is one of the main industrial crops in Malaysia after oil palm, rubber and paddy. The demand for coconut products has increased over the past decade due to the rise in awareness of the health benefits from the fruit, such as virgin coconut oil (Yun, 2019). The coconut production in Malaysia amounted to 517,589 tons with 83,250 hectares of total planted area in 2017 (Kementerian Pertanian dan Industri Makanan, 2019). It increased to 560,984 tons with 84,942 hectares of plantation area in 2020 (Unit Perangkaan Pertanian, 2021). Coconut fruit has been used in various industries, mainly in the food industry. The production process in the coconut industry and the harvesting process in coconut plantations generate numerous residues such as coconut shells, coconut husk and coconut frond. According to Inayat et al. (2018), 166,000 tons of coconut husk, 735,000 tons of coconut shell, 103,000 tons of coconut frond and 22,000 tons of coconut empty bunches are obtained as a by-product from the coconut industry.

Coconut frond (CF) is one of the residues obtained from the coconut plantation. It is generated abundantly throughout the year by natural pruning and silvicultural practice. The use of CF as material and feedstock in previous studies is limited compared to oil palm wastes and other coconut residues such as coconut husk and coconut shell. Usually, the residues generated from the mill gained more attention for biofuel studies than those generated in the plantation. Previous works reported the

utilization of coconut fronds as feedstock for pyrolysis to produce biochar as an adsorbent (Njoku et al., 2014; Pohs et al., 2019) and soil enhancers (Gopal et al., 2020). However, no studies reported the production of coconut fronds as potential solid fuel and the evaluation of pre-treatment of CF feedstock before the pyrolysis process. For these reasons, the novelty of this research is to assess and present detailed information regarding the properties of CF biochar derived from treated and untreated feedstock via a slow pyrolysis experiment and its potential as solid fuel.

The finding of this study will contribute to a better understanding of bioenergy-related properties and fuel characteristics of biochar derived from raw and treated coconut fronds. This study will also focus on evaluating and explaining the potential of coconut fronds as a viable and practicable feedstock associated with solid fuel application for bioenergy production.

1.2 Problem Statements and Research Motivations

The abundance of agricultural wastes or biomass generated from the coconut palm industry due to the increment of production every year led to the concern for managing and disposing of these wastes in proper ways. The high-rate waste generation with limited biomass utilization, such as coconut frond (CF), can be avoided by using feedstocks to produce biochar in the slow pyrolysis process.

The quality of raw feedstock could be not suitable for direct utilization as solid fuel. High ash content, low heating values and low energy density are among the drawbacks of raw biomass, restraining its potential as a solid fuel. Additionally, the products obtained from pyrolysis of low-quality biomass (high ash content, high oxygen content and low carbon content) exhibit relatively poor quality. Therefore, a

study of pre-treatments of feedstock before the slow pyrolysis experiment is essential to enhance the properties of biomass and biochar.

The type and composition of feedstocks and the operating parameters, such as pyrolysis temperature, influence the yield and properties of biochar. Previous studies have reported the characterization of biochar derived from coconut wastes under different conditions (Gonzaga et al., 2018; Pituya et al., 2017; Suman & Gautam, 2017). However, the evaluation of the properties of CF biochar, especially for solid fuel applications, is limited. Hence, further studies should be conducted due to insufficient and incomplete information on biochar characteristics produced from CF feedstock.

1.3 Research Objectives

The objectives of this study are:

- i. To evaluate the properties of biochar produced from slow pyrolysis of coconut frond.
- ii. To study the influence of feedstock pre-treatment on the properties of CF biochar.
- iii. To assess the potential of CF biochar and CF feedstock as a solid fuel by evaluating the fuel properties of CF bio-briquette.

1.4 Hypothesis

This study was performed to test the following hypothesis:

- i. Coconut frond is suitable to be used as feedstock to produce biochar in the slow pyrolysis process.
- ii. Slow pyrolysis temperature significantly influences the yield percentage and properties of CF biochar.

- iii. Pre-treatments of CF feedstock significantly improve the properties of biochar.
- iv. The bio-briquette produced from treated CF biochar has a higher potential to be used as solid fuel.

1.5 Scope and Limitations of Study

This research focuses on the utilization of coconut frond (CF) as feedstock in laboratory-scale slow pyrolysis experiments and the properties of CF biochar derived from the slow pyrolysis process. This work also covers the pre-treatment of CF feedstock before the slow pyrolysis experiment. Three types of pre-treatments performed in this research are torrefaction, washing and a combination of washing and torrefaction.

For the slow pyrolysis experiment of raw CF feedstock, the terminal temperature of the pyrolysis process is varied, while other parameters, such as heating rate and residence time, are fixed. This study investigates the influence of temperature on the CF biochar yield and its properties. The slow pyrolysis experiments are also performed on the treated CF feedstocks.

This research evaluates the properties of biochar derived from untreated CF feedstock at various slow pyrolysis temperatures and treated CF feedstock at a fixed slow pyrolysis temperature. Meanwhile, this study does not evaluate and investigate the properties of other slow pyrolysis products such as bio-oil and gas.

This study also evaluates the potential of CF biochar derived from untreated and treated feedstock as solid fuel by the briquetting process. The briquetting parameters are fixed, and the properties of the briquettes derived from raw CF and CF biochar are investigated.

In this study, all the measurements were repeated at least two times, and the presented data were not statistically treated.

1.6 Thesis Outline

This thesis is divided into five chapters, as listed below:

Chapter 1 presents a brief introduction of this research work. This chapter presents and introduces the current situation of renewable energy and the principal of the research topics such as biomass, biochar and bio-briquette. This chapter also presents the problem statement, research objectives and scope of the study for this research.

Chapter 2 describes and reviews the utilization of biomass in the pyrolysis process, the pre-treatment of biomass and the properties of biochar from the previous works. The information on coconut wastes and the application of biochar for briquetting are also presented in this chapter.

Chapter 3 presents the flow of this research work, detail of materials, related analysis and experimental methods of this research. This chapter elaborates the methods of the preliminary analysis, slow pyrolysis experiment, pre-treatment of feedstock, analysis of biochar, briquetting process and analysis of briquette.

Chapter 4 presents and discusses the data and results of the preliminary analysis, slow pyrolysis experiment, pre-treatment of feedstock and analysis of biochar. The results of the briquette analysis are also included in this chapter.

Chapter 5 summarizes and concludes the findings and significant contributions of this research. This chapter also presents the recommendations for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides an overview of biomass and its utilization as a renewable energy resource. The background and review of the coconut production and residues from the industry are presented to evaluate the abundance of the coconut biomass and its potential as feedstock for the pyrolysis process. Then, this chapter reviews the details and findings of related studies such as feedstock pre-treatment, slow pyrolysis and biochar production from the relevant literature. This chapter also covers the review of briquette production from biomass and biochar (bio-briquette) under different parameters.

2.2 Biomass

Biomass is a natural and renewable carbon resource that is known to be used as a substitute for fossil fuels. It is one of the most promising renewable energy sources with high potential to alleviate the global energy crisis and mitigate the effects of global warming and pollution (Tripathi et al., 2016). Biomass refers to the biological material derived from living or recently living organisms (Khan et al., 2009) that stored energy via the photosynthesis process. During this process, the chlorophyll pigments in the plants use the sunlight to convert carbon dioxide, CO₂ and water into carbohydrates. The energy from the sunlight is being stored within the chemical bonds of the carbohydrates formed and can be extracted via an appropriate process such as combustion or pyrolysis of biomass.

Generally, biomass is classified according to its origin, function and final products. The categorization based on types of biomasses existing in nature (according to ecology or type of vegetation) is the most used classification dividing biomass into different groups, as presented in Table 2.1.

Table 2.1 Classification of biomass, adopted from Tursi (2019)

Biomass groups	Varieties and species
Wood and woody biomass	Coniferous or deciduous; Angiospermous or gymnospermous; Stems, branches, foliage, bark, chips, lumps, pellets, briquettes, sawdust, sawmill and others from various wood species.
Herbaceous and agricultural biomass	Grasses and flowers (alfalfa, Arundo, bamboo, bana, brassica, cane, Cynara, miscanthus, switchgrass, timothy, others); straws (barley, bean, flax, corn, mint, oat, rape, rice, rye, sesame, sunflower, wheat, others); other residues (fruit, shells, husks, hulls, pits, pips, grains, seeds, coir, stalks, cobs, kernels, bagasse, food, fodder, pulps, cakes, etc.
Aquatic biomass	Marine or freshwater algae; macroalgae (blue, green, blue-green, brown, red) or microalgae; seaweed, kelp, lake weed, water hyacinth, etc.
Animal and human waste biomass	Bones, meat-bone meal; various manure, etc.

Wood and woody biomass are the main source of biomass which are usually a by-product or residue of forestry operations and forest industry. Wood biomass is used directly as fuelwood or charcoal to fulfil daily energy needs for heating and cooking, specifically in developing countries (IEA Bioenergy, 2003). Herbaceous and agricultural biomasses are the next biomass source covering a wide range of crops. Herbaceous biomass is usually derived from plants that have non-woody stems. Meanwhile, crop residues are usually obtained in various forms, such as shells, pulps and stalks. Aquatic biomass includes macroalgae, microalgae and emerging plants which grow partially submerged in marshes and swamps.

2.2.1 Structure and Composition of Biomass

Biomass consists of a complex mixture of organic materials. Figure 2.1 shows the composition of plant biomass.

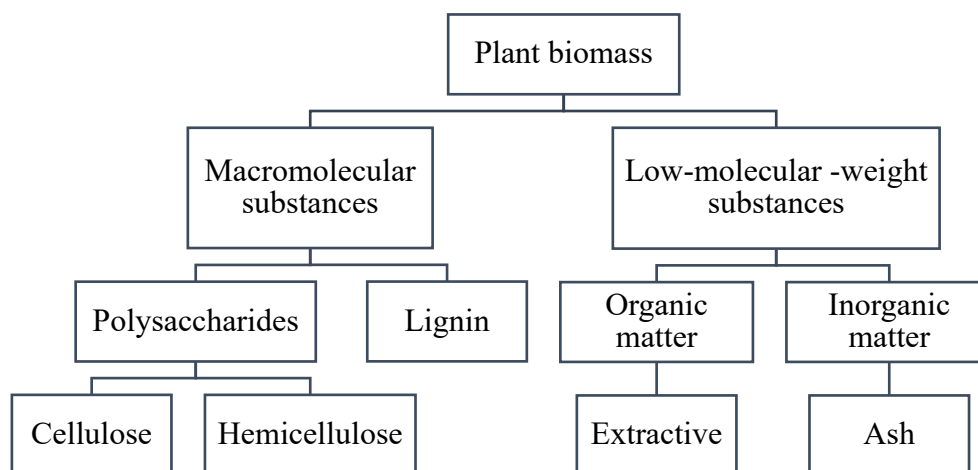


Figure 2.1 General components of biomass, adopted from Mohan et al. (2006)

Biomass mainly comprises three lignocellulosic components: cellulose, hemicellulose and lignin. Cellulose is the primary structural component in the lignocellulosic biomass. The chemical formula for cellulose is $(C_6H_{10}O_5)_n$. It is a linear and remarkable pure organic polymer that consists solely of units of anhydroglucose held together by $\beta(1\rightarrow4)$ linkages. Cellulose is insoluble in water and most organic solvents. The degradation occurs around 240°C to 350°C to produce anhydrocellulose and levoglucosan (Mohan et al., 2006). Meanwhile, Yang et al. (2007) reported that the decomposition of cellulose mainly occurred around $315\text{-}400^\circ\text{C}$. Cellulose also has high strength due to the crystalline structure of thousands of units made of many glucose molecules (Basu, 2010). Figure 2.2 shows the structure of cellulose.

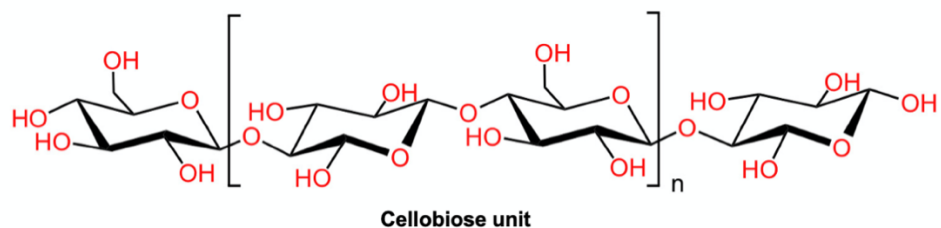


Figure 2.2 The primary structure of cellulose, adopted from Li et al. (2013)

The cellulose molecules in the plant cell wall are interconnected by another molecule called hemicelluloses. It is also known as polyose. The formula for hemicellulose is $(C_5H_8O_4)_n$. It is a mixture of various polymerized monosaccharides such as glucose, mannose, galactose, xylose, arabinose, 4-O- methyl glucuronic acid and galacturonic acid residues (Mohan et al., 2006). Hemicellulose is a branched polymer and consists of shorter chains. It has an amorphous structure. Due to its structure, hemicellulose is more soluble and labile, which is more susceptible to chemical degradation than cellulose (Bajpai, 2018). Usually, it degrades at a lower temperature than cellulose degradation, around 200°C - 260°C and tends to yield more gases (volatiles) and less tar than cellulose (Basu, 2010, Tiwari and Mishra, 2011).

Figure 2.3 shows the main components of the hemicellulose.

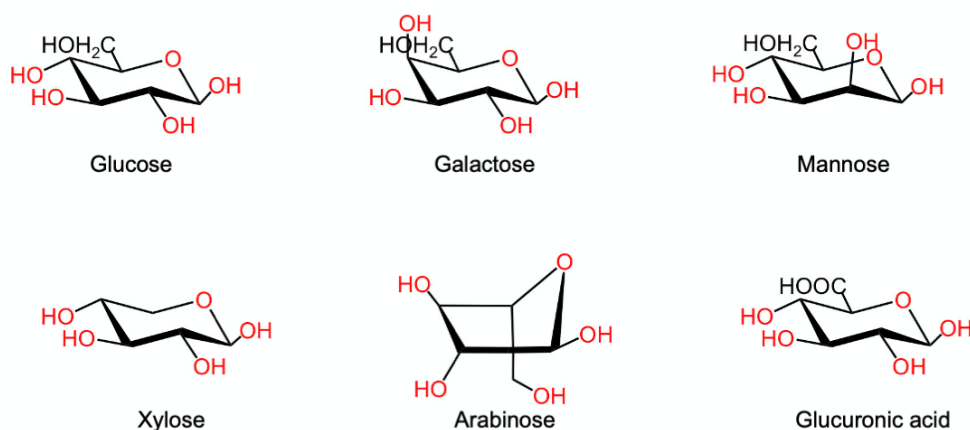


Figure 2.3 Main monomers of hemicellulose, adopted from Li et al. (2013)

Lignin is the other main component in plant biomass. It is a complex polymer consisting of hydro phenylpropane units. It functions as the main binder or cementing agent for the agglomeration of cellulose fibre components. Lignin decomposes when heated in the temperature range of 280°C to 500°C (Tiwari and Mishra, 2011). According to Yang et al. (2007), lignin degradation also happened slowly for a temperature range of 150-900°C. Lignin is the most thermally resistant component compared to cellulose and hemicelluloses due to its complex chemical composition. According to Mohan et al. (2006), lignin pyrolysis produces more residual char than the pyrolysis of cellulose. Figure 2.4 illustrates the structural units of lignin.

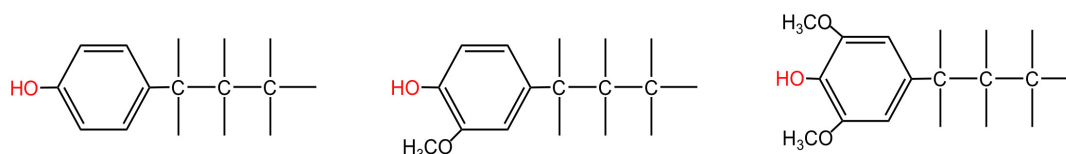


Figure 2.4 Structural units of lignin, adopted from Basu (2010)

The percentage of cellulose, hemicelluloses and lignin in biomass composition varies according to the type of biomass. Determining these components is essential for a better understanding of the thermal conversion of lignocellulosic biomass. Table 2.2 presents the percentage of cellulose, hemicelluloses and lignin of various types of biomasses from previous studies.

Table 2.2 shows that the proportions of lignocellulosic components are present in different proportions for different types of biomasses. The percentage of lignocellulosic components affects the distribution of pyrolysis process products. Cellulose and hemicellulose components are responsible for the formation of volatile products, while lignin leads to the formation of char (A. Sharma et al., 2015).

Table 2.2 Lignocellulosic and extractive components of various types of biomasses

Biomass	Hemicellulose (%)	Cellulose (%)	Lignin (%)	Extractive (%)	References
Coconut shell	27.70	25.20	46.00	1.00	(Anuchi et al., 2022)
Palm kernel shell	23.30	20.70	49.50	6.50	(Abdullah et al., 2017a)
Oil palm empty fruit bunch	36.29	43.31	20.40	n/a	(Abdullah et al., 2017b)
Wood (<i>Abies religiosa</i>)	12.37	54.81	24.68	8.13	(Musule et al., 2016)
Coconut coir	17.73	26.72	41.19	14.36	(Sangian et al., 2015)
Beech wood	31.20	45.30	21.90	1.60	(Demirbas, 2004a)
Tea waste	19.90	30.20	40.00	9.90	

Extractives are the substances that exist in the biomass tissues which function as intermediates in metabolism, as energy reserves and as a defence against microbial and insect attacks (Mohan et al., 2006). Protein, oil, simple sugar, fat, waxes, starches and resin are the example of the extractive consists in biomass composition. These extractives can be extracted by specific treatment with the polar or non-polar solvents and recovered by evaporation of the solution.

Ash is the inorganic mineral component of biomass. The ash in biomass consists of various proportions of elements such as phosphorus, potassium, calcium, sulfur, copper, ferum, manganese, zinc, nickel, chromium, lead and arsenic (Zajac et al., 2018). Generally, the ash components are concentrated in three parts within the plant cells. Some of the minerals are bound loosely in the biomass structure and some are held more tightly. The hollow lumen of the cell is one of the parts where ash is loosely held. The ash that is incorporated into the hollow lumen is easily removed. Ash is also bonded to the cell wall material and chemically bonded to hemicellulose. The

minerals concentrated in these parts are very hard to eliminate. Stronger solvents like acid or assertive techniques are required to remove the ash (Hague, 1998). The percentage of ash content also varies for different types of biomasses. Table 2.3 presents the values of ash content of various biomass from previous studies.

Table 2.3 Ash content of various types of biomasses

Biomass	Ash content (%)	Basis	References
Sunflower seed hulls	2.10	Dry	(Casoni et al., 2019)
Sago frond	4.32	Dry	(Rampli et al., 2018)
Sago bark	4.60	Dry	
Rice straw	14.00	-	(Yang et al., 2017)
Chinese fir wood	0.08	-	
Coconut fiber	8.05	Dry	(Liu & Han, 2015)
Pine wood	1.40	Dry	
Rhodes grass	14.70	-	(Jouiad et al., 2015)
Date palm frond	2.90	-	
Oil palm frond	1.30	Dry	(Guangul et al., 2011)
Rice husk	13.2	Dry	

Table 2.3 shows that wood biomass such as pine wood and fir wood have lower ash content than other biomass types. Meanwhile, agricultural biomass from grasses and straws varieties have been reported to contain higher ash content compared to other variety of biomass such as fronds and seed hulls.

Variation of ash in biomass compositions is attributable to the different concentrations of ash-forming elements such as potassium silicates, calcium carbonates and other metals (Yang et al., 2017). The amount of ash content in biomass also depends on other factors such as sampling point, harvesting time and harvest conditions (Zajac et al., 2018). The presence of ash in biomass compositions is not favoured because it negatively influences the calorific value of the biomass (Islam et al., 2019; Vankat et al., 2010). High ash in biomass is also associated with problems

during biomass combustion. The agglomeration of the residues resulted in reduced heat transfer (Madanayake et al., 2017), unnecessary downtime and a reduced process efficiency (Yang et al., 2017).

The ash content also influenced the behaviour of biomass during the thermochemical conversion of biomass. Shariff et al. (2014) reported that biomass samples with higher ash contents were degraded at lower temperatures. Such an observation occurred due to the presence of ash, which contains minerals that trigger the catalytic reactions during the thermal degradation of the lignocellulosic components. Hence, it resulted in the decomposition of hemicellulose and cellulose at a lower temperature. The catalytic effect of ash content also influenced the distribution and properties of products from the pyrolysis of biomass. Abdullah et al. (2007) reported that reducing ash content to less than 3 mf wt% led to the production of homogeneous liquid and an increment of liquid yield up to 72%.

Biomass also consists of chemical compositions such as carbon, hydrogen, nitrogen, sulphur and oxygen. The proportion of these elements in the biomass composition is a function of biomass species, geographical location and growing conditions of the plants. For the utilization of biomass as an energy source, the evaluation of C, H and O elements is necessary as these elements control the fuel property of the biomass. These three constituents are the main contributors to the energy content of biomass and are usually used to predict the heating value of the biomass (Tripathi et al., 2016). Meanwhile, biomass contains fewer N and S components compared to fossil fuel (Liu et al., 2013), making it environment friendly as it can reduce greenhouse gas emissions. Table 2.4 presents the percentage of C, H, N, S and O content of various biomasses from previous studies.

Table 2.4 Percentages of elemental components (carbon, hydrogen, nitrogen, sulphur and oxygen) of various biomasses

Biomass	C (%)	H (%)	N (%)	S (%)	O (%)	References
Coconut husk	49.90	5.40	0.40	-	44.30	(Anuchi et al., 2022)
Coconut shell	39.22	4.46	0.22	-	56.10	(Sarkar & Wang, 2020)
Oil palm frond	42.60	5.71	0.42	0.29	51.00	(Inayat et al., 2018)
Palm kernel shell	48.91	5.81	0.85	0.12	44.31	(Abdullah et al., 2017b)
Rice husk	38.60	4.98	1.40	0.03	54.99	(Lim et al., 2016)
Poplar wood sawdust	48.36	5.93	0.52	0.12	43.94	(Chen et al., 2016)
Corn cob	43.81	6.54	0.77	0.69	48.19	(Shariff et al., 2016)
Apricot kernel shell	47.33	6.37	0.37	-	45.93	(Demiral & Kul, 2014)
Rubber wood sawdust	53.4	6.7	3.1	0.0	36.8	(Ghani et al., 2013)

Table 2.4 shows that carbon and oxygen are the main elemental component in biomass composition. C content in woody biomass is higher compared to herbaceous biomass. C and H components in biomass become oxidized during the combustion process via exothermic reactions, which will form carbon dioxide (CO₂) and water and therefore influence the calorific value of the biomass (Oberberger & Thek, 2004). On the other hand, the percentages of both N and S contents are lower than C, H and O components.

2.2.2 Potential and Utilization of Biomass

The number of agricultural wastes has been rising rapidly in recent years. About 140 billion tons of biomass from global agricultural wastes are generated annually (Tripathi et al., 2019). It increased significantly as Werther et al. (2000) reported that only 3 billion tons of agricultural residues were generated globally. An abundance of biomass, such as agricultural wastes, leads to disposal problems.

Disposal of biomass by open burning, landfilling and composting is considered an impractical practice due to various environmental issues such as the possible discharge of toxic compounds from open burning activity, emission of methane as greenhouse gases from landfilling and poor air quality resulting from the odour released during composting (Lam et al., 2018). Using biomass as a renewable energy source is a promising way to solve waste disposal problems.

The utilization of biomass as a source of energy receives worldwide attention due to the great benefits it provides. Moreover, rapid economic growth in developing countries, high dependence on global and local transportation, pollution issues, depletion of sources, and endangered national security of energy importing countries have raised the awareness of the need for non-fossil based renewable energy sources (Medic et al., 2012). Biomass utilization as a source of energy contributes to the reduction of fossil fuel consumption and greenhouse gas emissions. Biomass has been identified as the only renewable energy source that can be converted into three distinct forms of products: solid, liquid and gaseous fuel (Tripathi et al., 2016). In terms of economy, the utilization of biomass promotes the conversion of agricultural wastes into value-added products such as bioproducts and bioenergy (Duque-Acevedo et al., 2020). The valorization of biomass resources by the farmers also plays a role in promoting local economic development, particularly in rural areas.

Lignocellulosic biomass is a potential renewable energy source to produce biofuel. Biomass energy currently provides almost 14% of the world's primary energy (Yang et al., 2017). In general, biomass is utilized for power and heat generation via the burning process, digestion process to produce gas-like fuels such as methane and hydrogen and thermochemical conversion processes such as pyrolysis and

gasification. Biomass such as oil palm wastes has been used as the boiler fuel for fresh fruit bunches processing activity in the mill (Mahlia et al., 2001).

Malaysia is blessed with abundant and fertile agricultural land. The agriculture sector in Malaysia contributed 7.1% (RM 101.5 billion) to the Gross Domestic Product (GDP) in 2019 (Mahidin, 2020). The abundance of residues derived from the agricultural sectors provides a significant portion to the utilization of biomass. According to the National Biomass Strategy 2020 blueprint, the annual production of biomass is projected up to 80 million tons by 2020 (Yun, 2020). The biggest contributor of biomass from agricultural residues in Malaysia comes from the palm oil industry, which accounted for about 77% of the total agricultural residues in Peninsular Malaysia (Hamzah et al., 2019). It is followed by the timber industry and other industries such as rice, coconut and sugar (Moni et al., 2016). The agricultural wastes can be categorized into plantation-based and mill-based biomass. Common biomass generated at the plantation includes oil palm frond, oil palm leaflet, coconut frond and oil palm trunk. Meanwhile, mill-based biomass is usually obtained from the processing process of the crop. For example, oil palm empty fruit bunches, palm mesocarp fiber and palm kernel shell are the by-products from the extraction of palm oil at the processing mills, coconut flesh waste and coconut shell from coconut milk production and rice husk from the production of rice.

Moni et al. (2016) also estimated the potential energy of selected Malaysian biomass after taking account of the actual production amount based on the residue to product ratio and the accessibility and recoverability factors. The study reported that around 23.1 million tons of unused dry biomass residues were generated, with a total potential energy of 408.8 PJ as shown in Table 2.5. This data shows the potential of

unused biomass in Malaysia, and it is crucial to utilize these residues rather than left unprocessed in the plantation and mill.

Table 2.5 Annual availability and total potential energy of selected biomass in Malaysia (Moni et al., 2016)

Residue	Representative calorific value (MJ/kg)	Annual availability (ton db)	Total potential energy (PJ)
Oil palm frond	17.59	11,370,989	200.02
Palm mesocarp fiber	17.81	3,110,014	55.39
Empty fruit bunch	18.44	2,186,729	40.32
Palm kernel shell	18.64	1,943,759	36.23
Oil palm trunk	17.31	110,970	1.92
Wood	18.48	4,093,380	69.88
Rice husk	16.87	214,132	3.61
Coconut frond	15.33	10,791	0.17
Coconut shell	20.64	60,697	1.25
Sugarcane bagasse	17.33	420	0.01
Total		23,101,881	408.8

2.2.3 Problems Associated with Utilization of Biomass as Fuels

Despite the availability and increasing attention of biomass as a renewable source to reduce the dependency on fossil fuels, there are some disadvantages and several properties that limit its utilization as biofuels.

In general, biomass contains higher oxygen and lower carbon content compared to fossil fuels such as coal (Khan et al., 2009). The higher oxygen content in biomass composition decreases its heating value. Therefore, the oxygen composition in biomass must be reduced to obtain fuels that can be comparable with fossil fuels.

In natural conditions, the moisture content of biomass varies tremendously according to the type of biomass, ranging from less than 15% in cereals straw to more than 90% as in algae biomass (Sánchez et al., 2019). In the utilization of biomass as

fuel, high moisture content limits the potential of biomass. The high moisture in biomass fuels can cause ignition and combustion problems (Demirbas, 2004a). The fuels with high moisture content cannot burn easily. Additionally, a high moisture content also reduces the effectiveness of the biomass conversion process. Irmak (2019) suggested that the moisture content of biomass should be less than 20% to maximize the heating value of the fuel produced.

Meanwhile, in terms of biological degradation, the high moisture content in biomass leads to mould formation and loss of organic content, which consequently reduces the yield of the fuel derived from the biomass. Previous studies (Khalib et al., 2010; Taib, 2019) reported that biomass is usually dried until the moisture content achieves less than 10% before the storage and conversion process.

Biomass relatively has low energy densities compared to other conventional fuels such as coal or fuel oil (Krigstin et al., 2012). Therefore, much larger volumes of biomass are required to supply a similar amount of energy. Although the amount of biomass is abundant, this issue leads to logistical problems and inconveniences in terms of increased traffic and large storage facilities. The energy density of biomass could be elevated via palletization or briquetting process, and thermochemical conversion technology such as torrefaction and pyrolysis.

2.3 Coconut Palm

Coconut palm, *Cocos nucifera* is one of the members of the family Areaceae (palm family). The coconut palms are categorized as tropical plants, which will bear fruit all year around. They are grown for different purposes in various parts of the world. Coconut is most widely cultivated in the tropics area such as India, Indonesia,

Philippines, Malaysia, South Sea Island in the Pacific, Central and South Americas and East Africa (A.Ross, 2005; Batugal et al., 2009).

The coconut palm grows up to 25 m high. In general, the coconut tree will start fruiting at an age 5-7 years, reach full bearing after 10-12 years, achieve maturity at about 15 years and will live up to 60 – 100 years in the wild state and 50-70 years under cultivation (Bassam, 2010). Coconut plants can be categorized into two distinct groups, tall and dwarf. The details of these two groups of coconut are summarized in Table 2.6 below.

Table 2.6 Details of Tall and Dwarf varieties (DebMandal & Mandal, 2011)

	Tall	Dwarf
Growth rate	Slow	Fast
Fruit	6-10 years after planting	4-5 years after planting
Life Span / Ripe age	80 – 120 years	Shorter
Pollination	Cross-pollinated	Self-pollinated
Nuts	Mature in 12 months after pollination	Yellow, red, green and orange

The coconut palm mainly consists of trunk, leaves and fruits. The coconut trunk has a diameter of 30 to 40 centimetres. Coconut is a monocotyledon plant. Therefore, it has no branches but carries crown leaves at the top of the stem, which is about 70 to 100 feet above the ground. Usually, the leaves are referred to as fronds. In general, these fronds are 10 to 20 feet long (Lucas, 1982). Coconut fruit is a fibrous drupe, and it consists of three layers; exocarp, mesocarp and endocarp. The exocarp is the outer part of the fruit, which is tough and hard. Usually, the colours of the exocarp are different according to the age or type of the coconut. The colours of the exocarp would be green, yellow, orange, red, brown or greyish brown. The second layer is the mesocarp consisting of fibrous layers, also known as a husk. Endocarp is the hard, stony and dark brown shell with three germination pores (stoma) or “eyes”.

These “eyes” are visible on the shell if the husk is removed. In terms of percentages, the fruit consists of 4 parts, 35% of husk, 12% of shell, 28% of meat and 25 % of water (Oyedepo et al., 2015). Coconut is usually consumed as oil (55%), fresh (37%), desiccated (5%) and a small number of other products such as husk products and kernel products (Smith et al., 2009).

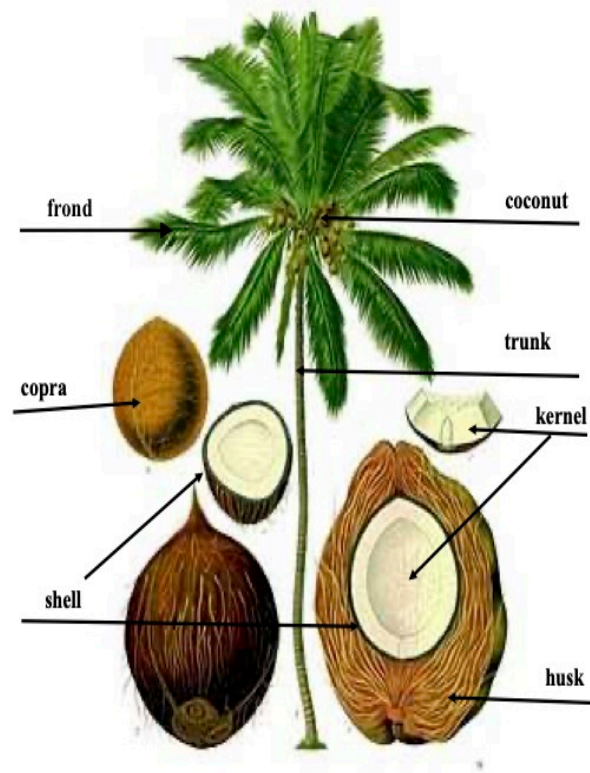


Figure 2.5 The Coconut Palm (Schöpke, 2004)

The coconut palm is grown in more than 93 countries. Asia is the main production area which accounts for 84% of global output and relatively stable yields, which are around 5 tons of nuts per hectare (Bassam, 2010). Meanwhile, the European Union and the United States are the leading importers. The world’s production of coconut is concentrated in the Asian region. Indonesia, the Philippines and India are the Asian countries that are listed as global coconut leaders, which cover about 9.262 million hectares of plantation area and contribute to 70% of the global coconut