THE MIXTURE OF BIO-OIL AND BIOCHAR PRODUCED FROM SLOW PYROLYSIS OF OIL PALM WASTES FOR BRIQUETTES PRODUCTION AND COMBUSTION AS SOLID FUELS

AMINU ALIYU SAFANA

UNIVERSITI SAINS MALAYSIA
2018

THE MIXTURE OF BIO-OIL AND BIOCHAR PRODUCED FROM SLOW PYROLYSIS OF OIL PALM WASTES FOR BRIQUETTES PRODUCTION AND COMBUSTION AS SOLID FUELS

by

AMINU ALIYU SAFANA

**Thesis submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy**

April 2018

Dedication

This work is dedicated to the

PROPHET MUHAMMAD ﷺ BIN ABDULLAH BIN ABDUL MUTTALIB,

HIS FAMILY AND COMPANIONS.

ACKNOWLEDGEMENT

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

A	Pre-exponential or frequency factor
cP	centipoise
C_p	specific heat capacity
E	Apparent activation energy
k	Rate constant of reaction
$kJkg^{-1}K^{-1}$	kilojoule per kilogram per kelvin
$kJmin^{-1}$	kilojoule per minute
$kJmol^{-1}$	kilojoule per mole
Q_{in}	Heat inside the furnace
Q_F	Heat supply by the furnace
R^2	Correlation coefficient
wt%	Weight percentage
N	Newton
ml	millilitre
M_i	Initial weight of sample
M_c	Mass of empty crucibles
M_f	Final weight of sample
MW	Megawatt
Js^{-1}	Joule per second
α	Conversion factor
β	Heating rate
V	Volume
μm	Micrometer

db   Dry basis

daf   Dry ash-free basis

R Gas constant

LIST OF ABBREVIATION

ASTM	American Society for Testing and Materials Standard
COMBr	Commercial briquettes
CO	Carbon monoxide
CO$_2$	Carbon dioxide
CHNOS	Carbon, Hydrogen, Nitrogen, Oxygen and Sulphur
CR	Combustion rate
DP	Degree of polymerization
DTG	Derivative Thermogravimetric
EFB	Empty fruit bunches
EBBr-R	Biomass briquette formed from raw EFB
EBBr-T$_{200}$	Biomass briquette formed from torrefied EFB at 200 ºC
EBBr-T$_{250}$	Biomass briquette formed from torrefied EFB at 250 ºC
EBBr-T$_{300}$	Biomass briquette formed from torrefied EFB at 300 ºC
ECBr$_{400}$	Charcoal briquette formed from EFB biochar at 400 ºC
ECBr$_{700}$	Charcoal briquette formed from EFB biochar at 700 ºC
FBBr-R	Biomass briquette formed from raw fibre
FBBr-T$_{200}$	Biomass briquette formed from torrefied fibre at 200 ºC
FBBr-T$_{250}$	Biomass briquette formed from torrefied fibre at 250 ºC
FBBr-T$_{300}$	Biomass briquette formed from torrefied fibre at 300 ºC
FCBr$_{400}$	Charcoal briquette formed from fibre biochar at 400 ºC
FCBr$_{700}$	Charcoal briquette formed from fibre biochar at 700 ºC
FC	Fixed carbon
GHG	Greenhouse Gas

HHV	Higher Heating Value (MJkg^{-1})
KBr	Potassium bromide
KCL	Potassium chloride
LHV	Lower Heating Value (MJkg^{-1})
M	Moisture
MF	Mesocarp Fibre
NO$_x$	Nitrogen oxide
PKS	Palm Kernel Shell
PBBr-R	Biomass briquette formed from raw PKS
PBBr-T$_{200}$	Biomass briquette formed from torrefied PKS at 200 ºC
PBBr-T$_{250}$	Biomass briquette formed from torrefied PKS at 300 ºC
PBBr-T$_{300}$	Biomass briquette formed from torrefied PKS at 300 ºC
PCBr$_{400}$	Charcoal briquette formed from PKS biochar at 400 ºC
PCBr$_{700}$	Charcoal briquette formed from PKS biochar at 700 ºC
RES	Renewable energy sources
SO$_x$	Sulphur Oxide
TGA	Thermogravimetric Analysis
VM	Volatile Matter

CAMPURAN BIO-MINYAK DAN BIO-ARANG TERHASIL DARI PIROLISIS LAMBAT SISA-SISA SAWIT UNTUK PENGELUARAN BRIKET DAN PEMBAKARAN SEBAGAI BAHAN API PEPEJAL

ABSTRAK

Malaysia menjana sejumlah besar sampah pertanian, terutamanya dari industri sisa kelapa sawit. Sisa-sisa ini akan terus membawa masalah pembuangan sisa pertanian di Malaysia sehingga langkah-langkah perlu diambil untuk meningkatkan aplikasi mereka. Tujuan utama kajian ini adalah untuk meningkatkan penggunaan sisa-sisa ini untuk pembentukan briket sebagai sumber panas. Dalam kajian ini, kesan penyemburan untuk menaikkan nilai pemanasan lebih tinggi (HHV) tandan buah kosong (EFB), gentian mesocarp (MF) dan tempurung sawit (PKS) telah disiasat. Pengeluaran biojisim tahan lama dan kualitatif dan briket arang dari sampel mentah dan produk tertorefaksi (briket biojisim), dan bioarang dan bio-minyak (briket arang) yangdiperolehi dari pirolisis diselidiki. Selain itu, sifat-sifat pembakaran dan haba yang dikeluarkan semasa pembakaran briket arang dan arang batu bitumen Malaysia telah disiasat dan dibandingkan. Kadar suhu, pemanasan dan masa tindak balas berubah-ubah menjadi 200, 250 dan 300 ^{o}C, 5, 10 dan 20 ^{o}Cmin^{-1}, dan 15, 30 dan 45 minit untuk torefaksi, dan 300-700 ^{o}C, 5, 10 dan 20 ^{o}Cmin^{-1}, dan 30, 60 dan 120 minit untuk pirolisis. Kelikatan bio-minyak bertambah baik dengan penambahan kanji dan digunakan sebagai pengikat bagi briket arang. Hasil kajian menunjukkan bahawa pemusnahan telah menaikkan HHV EFB, MF dan PKS kepada nilai maksimum 20.96, 22.76 dan 22.81 MJkg^{-1} pada suhu torefaksi 300 ^{o}C dari nilai awal 16.90, 19.06 dan 19.50 MJkg^{-1}. Telah didapati bahawa kesan suhu pada torefaksi dan pirolisis lebih besar daripada kadar pemanasan dan masa reaksi. Bagi semua sampel pirolisis, hasil

bioarang maksimum, hasil bio-minyak, dan hasil gas diperolehi pada suhu pirolisis 300 $^{\circ}$C, 500 $^{\circ}$C, dan 700 $^{\circ}$C. Parameter briket yang disiasat termasuk tekanan, pengikat, saiz zarah dan kaedah pengeringan. Hasil keseluruhannya mendedahkan bahawa pengaruh tekanan lebih tinggi daripada parameter lain. Parameter terbaik untuk briket tahan lama dan stabil ialah tekanan 400 kgcm^{-2}, saiz zarah 300 μm, pengikat (B3) dan kaedah pengeringan semula jadi (D2). Telah didapati bahawa bio-minyak sahaja (B1) tidak dapat berfungsi sebagai pengikat untuk briket. Briket biojisim yang terbentuk dalam kajian ini di bawah parameter terbaik yang menggambarkan keperluan piawai 90% untuk briket biojisim. Briket biojisim buatan tangan menunjukkan profil pembakaran yang lebih baik daripada briket biojisim mesin. Semua briket arang yang dihasilkan mempunyai HHV antara 26.65 MJkg^{-1} hingga 31.11 MJkg^{-1} yang lebih tinggi daripada arang batu bitumen Malaysia dan briket komersil (COMBr) yang masing-masing mempunyai 26.21 dan 25.71 MJkg^{-1}. Walau bagaimanapun, briket arang EFBr400, FCBr400 dan PCBr400 telah menunjukkan profil pembakaran yang lebih baik dan menunjukkan sifat yang serupa dengan arang batu. Pelepasan haba maksimum dan minimum 0.06 W dan 0.04 W diperoleh daripada pembakaran ECBr400 dan FCBr400 masing-masing. Walau bagaimanapun, arang batu sub-bitumen Malaysia dan PCBr400 juga telah melepaskan haba yang ketara sebanyak 0.05 W dan 0.05 W. Diasaskan bahawa setiap tan mentah (kering kering) EFB, MF, dan PKS, terdapat 0.20, 0.21 dan 0.23 tan briket arang yang bersamaan dengan 1.90 MW, 2.05 MW dan 2.41 MW haba.

THE MIXTURE OF BIO-OIL AND BIOCHAR PRODUCED FROM SLOW PYROLYSIS OF OIL PALM WASTES FOR BRIQUETTES PRODUCTION AND COMBUSTION AS SOLID FUELS

ABSTRACT

Malaysia generates an enormous amount of agricultural wastes, especially from the oil palm wastes industries. These wastes will continue to bring about the agricultural wastes disposal problem in Malaysia until necessary measures are taken to upgrade their applications. The primary aim of this study is to upgrade the application of these wastes for briquettes formation as a source of heat. In this study, the effect of torrefaction to upgrade higher heating value (HHV) of empty fruit bunches (EFB), mesocarp fibre (MF) and palm kernel shell (PKS) was investigated. The production of durable and qualitative biomass and charcoal briquettes from raw samples and torrefied products (biomass briquettes), and biochar and bio-oil (charcoal briquettes) obtained from pyrolysis were investigated. In addition, the combustion properties and heat released during the combustion of charcoal briquettes and Malaysian sub-bituminous coal were investigated and compared. The temperatures, heating rates and reaction time were varied to be 200, 250 and 300 $^{\circ}$C, 5, 10 and 20 $^{\circ}$Cmin^{-1}, and 15, 30 and 45 min for torrefaction, and 300-700 $^{\circ}$C, 5, 10 and 20 $^{\circ}$Cmin^{-1}, and 30, 60 and 120 min for pyrolysis, respectively. The viscosity of the bio-oil was improved by the addition of starch and used as a binder for the charcoal briquettes. The results revealed that torrefaction had upgraded the HHV of EFB, MF and PKS to a maximum value of 20.96, 22.76 and 22.81 MJkg^{-1} at torrefaction temperature of 300 $^{\circ}$C from an initial value of 16.90, 19.06 and 19.50 MJkg^{-1}, respectively. It was discovered that the effect of temperature on torrefaction and pyrolysis is greater than

that of heating rate and reaction time. For all the samples pyrolyzed, the maximum biochar yield, bio-oil yield, and gas yield were obtained at a pyrolysis temperature of 300 °C, 500 °C, and 700 °C, respectively. Briquetting parameters investigated include pressure, binder, particle size and drying method. The overall result revealed that the influence of pressure was greater than other parameters. The best parameters for durable and stable briquettes were the pressure of 400 $kgcm^{-2}$, the particle size of 300 μm, binder (B3) and drying method of natural drying (D2). It was found that bio-oil alone (B1) could not serve as a binder for briquettes. The biomass briquettes formed in this study under the best parameters portrayed 90 % standard requirement for biomass briquettes. The handmade biomass briquettes have shown better combustion profiles than the machine biomass briquettes. All the charcoal briquettes produced had HHV between 26.65 $MJkg^{-1}$ to 31.11 $MJkg^{-1}$ higher than Malaysian sub-bituminous coal and commercial briquette (COMBr) which have 26.21 and 25.71 $MJkg^{-1}$, respectively. However, charcoal briquettes $EFBr_{400}$, $FCBr_{400}$ and $PCBr_{400}$ have shown better combustion profiles and showed similar properties with coal. The maximum and minimum heat release of 0.06 W and 0.04 W were obtained from the combustion of $ECBr_{400}$ and $FCBr_{400}$ respectively. Though, Malaysian sub-bituminous coal and $PCBr_{400}$ have also released an outstanding heat of 0.05 W and 0.05 W, respectively. It was established that in each tonne of raw (dry basis) of EFB, MF, and PKS, there is 0.20, 0.21 and 0.23 tonnes of charcoal briquettes which corresponds to 1.90 MW, 2.05 MW and 2.41 MW of heat respectively.

CHAPTER 1

INTRODUCTION

1.1   Background of the Study

International Energy Agency (IEA) in its new policy scenario stated that the world energy demand is anticipated to persistently rise yearly to about 1.2 % from 2008 to 2035, with 70 % of the demand imminent from the developing countries. However, the majority (87%) of this energy demand will be obtained mainly from fossil fuels. The rise of the entire global energy demand is associated with the increase in the world population and global economic growth [1, 2]. Furthermore, the energy uses in the main cities of developing countries is related to stages of greenhouse-gas (GHG) emissions and are anticipated to increase [3]. Global warming has been one of the fundamental environmental problems for many decades. However, the quantity of CO_2 in the atmosphere will persistently increase, except key modifications are made in the manner fossil fuels are utilised in the energy production [4, 5]. Fossil fuels still control the world's energy market value of about 1.5 trillion United States Dollars (USD). For example, the World Energy Council (WEC) estimated in 2007 that recoverable coal mineral deposits would be about 850 billion tonnes in 2006 [6].

As at 2010, the coal generation in Malaysia is derived majorly from six mines in Sarawak. There are about 1724 million tonnes of coal resources of which 274 million tonnes are identified, 347 million tonnes indicated and the balance of 1102 million tonnes as inferred [2]. Presently, community and political sensitivities to environmental problems and energy security have focused on the promotion of non-fossil fuel energy sources instead of fossil fuels. Renewable energy sources such as small hydropower, solar, wind, geothermal and biomass have presently contributed 14% of total world

energy consumption, of which 62 % is biomass [7]. Bioenergy and other chemicals can be derived from the converted biofuels product of biomass such as solid, liquid and gaseous. It is acknowledged that the burning of biofuels does not add to the greenhouse effect because of the CO_2 neutral conversion due to the renewability of biomass. The emphasis on bioenergy as a substitute for fossil energy has expanded colossally lately in light of an abnormal weather change as a result of fossil powers ignition. Along these lines, extensive investigations have been completed globally to improve biomass use for energy generation [8].

Internationally, Malaysia is known as the second-biggest manufacturer and the most significant oil palm exporter of about 17.7 million tonnes. It manufactured 41.3 % portion of the total world oil palm in 2008 [1, 9]. However, this resulted in the production of large quantity of biomass from oil palm industries. It has been declared that in the year 2012 there were profitable oil palm wastes (dry weight) of about 83 million tonnes in Malaysia. Moreover, it will eventually ascend to 100 million tonnes in few years to come (2020). In 2009, the oil palm wastes rendered in Malaysia were 7.0 million tonnes of EFB, 11.6 million tonnes of PKS and MF, 44.8 million tonnes of fronds and 13.9 million tonnes of trunks. However, the potential utility of these wastes is assumed to limited [10]. Between the oil palm biomass, mesocarp fibre contains a high calorific value in comparison with palm shell and EFB [11]. The basic structures of biomass lignocelluloses components can be written as $(C_6H_{10}O_5)m$, $(C_5H_8O_4)m$ and $[C_9H_{10}O_3 \cdot (OCH_3)_{0.9-1.7}]m$ for cellulose, hemicellulose, and lignin respectively, where m is a degree of polymerization [12]. These oil palm residues contain various chemical composition and high heating value of about 18-19 $MJkg^{-1}$. They are better complement and ingredients for fuels in the form of pellets and briquettes [13]. For instance, in 1 kg of palm oil, about 4 kg of dry biomass is generated [14]. It is, therefore, accepted that

they could be transformed into other forms of useful energy resources. Fibre and shells are utilised as fuel in the palm oil mill to power the processing plants [9].

The combustion properties of biomass can be improved through thermochemical and biological methods. These methods include torrefaction, pyrolysis, gasification, anaerobic digestion, fermentation, and so forth. Thermochemical are usually favoured more than biological methods, because of their advantages such as short reaction time and high conversion effectiveness [15]. Among the thermochemical methods, pyrolysis conversion process is one of the prominent methods through which biomass is converted into three major by-products namely; solid char, bio-oil and gases [16, 17]. The advantage of pyrolysis is that it yields quantitative and qualitative products.

Briquetting is predominantly used for compacting of biomass During the briquetting processes; biomass underwent compression at a specified pressure and temperature. In this case, cellular structures within the material release lignin, which binds individual particles into a compact unit briquette. However, briquetting can be used for compacting of compounded plastic waste or municipal waste. The briquette physical property and quality control of briquettes rely on factors, such as density, moisture content, and compressive strengths [18].

This research study is intended to use biomass sources from oil palm wastes because of their large quantity. In this study, the production of bio-briquettes from the mixture of biochar and bio-oil made from slow pyrolysis of oil palm wastes for coal replacement application will be conducted and investigated. Moreover, the factors that determine the quality of briquettes will be thoroughly studied and reported.

1.2   Problem Statement

Malaysia generates an enormous amount of agricultural wastes, especially from the oil palm wastes industries. In 2012, about 83 million tonnes of the dry weight of oil palm wastes were generated. Additionally, it has been projected that the oil palm wastes will increase to 100 million tonnes in the year 2020 [10]. These wastes will continue to bring about the agricultural wastes disposal problem in Malaysia until necessary measures are taken to upgrade their applications. Lack of assessing good and modern cooking fuels and government policies have led to deforestation in rural communities of developing countries, and this activity is linked to climate change because it advances the rate of CO_2 discharge to the atmosphere [19].

1.3   Scope of the Research

This research work is restricted to the slow pyrolysis of EFB, MF and PKS at an operational temperature ranging from 300-700 ^{o}C, a heating rate of 5, 10 and 20 ^{o}Cmin^{-1} and at a reaction time of 30, 60 and 120 min. However, pre-treatment of EFB, MF, and PKS via torrefaction was also investigated. It is also limited to the use of biochar and bio-oil. Furthermore, other factors that affect the briquettes during preparation and production apart from binder, pressure, type of biomass, drying and particle size have not been investigated in this work. However, energy content, thermal stability, compressive strength, shatter resistance, moisture and water resistance of bio-briquettes are studied. The research work is also limited to the application of bio-oil as a binder for briquettes production. Other applications of bio-oil and biochar have not been covered in this research.

1.4   Potential of Briquettes

Biomass densification is one of the important methods of utilization of biomass. Briquettes and pellets are the conventional densification processes. Densified biomass has the following characteristics and advantages such as higher bulk density, high durability as well as stable and small size products that are portable [20-22].

Briquettes are household and industrial fuels, produced through densification of biomass waste. However, with current energy demand, energy scarcity, global warming, and inconsistency of prices of fossil fuels, local consumers, and industries, especially in developing countries, are seriously searching for an alternative, affordable, and sustainable fuels. Briquettes from biomass sources could, therefore, be an option because of the following features. It can be used for domestic cooking and water heating, burning creative methods such as tobacco curing, fruits, tea drying and poultry rearing, firing ceramics and clay wares such as improved cooking stoves, pottery, and bricks, fuel for gasifiers to generate electricity and power boilers for steam [23].

1.5   Research Objectives

This research aims to upgrade the application of EFB, MF, and PKS as a source of heat. The primary objectives include.

1. To upgrade the heating value of EFB, MF, and PKS via torrefaction pre-treatment.

2. To produce durable and qualitative biomass and charcoal briquettes from raw samples and torrefied products (biomass briquettes), and biochar and bio-oil (charcoal briquettes) obtained from pyrolysis.

3. To compare the heat release during the combustion of charcoal briquettes and Malaysian sub-bituminous coal under the same condition.

1.6   Structure of the Thesis

The thesis is arranged into the following chapters:

Chapter 1 − Introduction: This chapter contained the general introduction of the research field, statement of the problem and objectives.

Chapter 2 − Literature review: This chapter encompassed the concepts of the relevant research on renewable energy sources, biomass, pyrolysis and its products, briquettes among others by exploring the relevant literature.

Chapter 3 − Experimental methodology: Chapter 3 illustrated the detail preliminary preparations, methodology and different kinds of equipment used in the research.

Chapter 4 − Result and discussion: This chapter presented the research findings and discussion.

Chapter 5 − Conclusion and recommendation: Chapter 5 summarised the significant contributions of the study and recommendations for future research.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction

Recently, there is an increasing number of literature related to renewable energy research as a result of continued research interests. Indeed, the number of publications on renewable energy has grown exponentially in recent years from a yearly output of less 300 records before 2009 to more than a thousand annually in the past three years (Fig. 2.1 (a)). In fact, before the year 2000, less than a total of 600 publications can be counted in the Web of Science database. Moreover, the number of publications on renewable energy appearing annually in the Scopus database in the past two years exceeds 10,000 each year (Fig. 2.1 (b)).
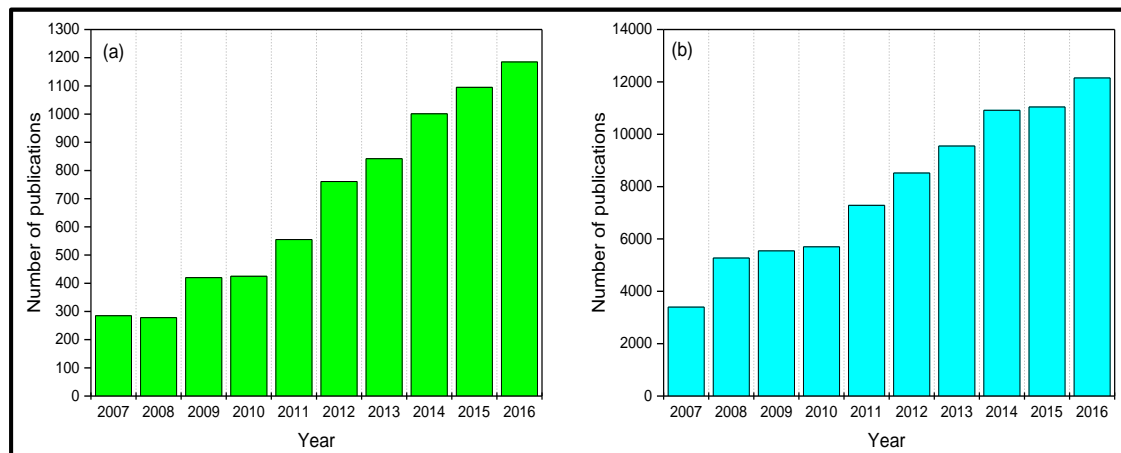
Figure 2. 1: Publication trends in Renewable energy research (2007-2016)
Sources: (a) Thomson Reuters Web of Science (b) Scopus. Assessed on June 2017.

2.2   Renewable Energy Sources

Renewable energy is the energy sources that do not varnish. These types of energy sources have been in use since the beginning of human civilisation. They are plentifully because they exist naturally in our environment [24]. There are three sources of energy and these include; fossil fuels, renewable and nuclear power sources.

However, among these energy sources, renewable energy is the only source that can be used to generate energy repeatedly. They can also be used easily to provide the domestic energy demand for local communities. Table 2.1 presents the global renewable energy scenario as predicted by the year 2040. Sun is the largest source of all energies. Renewable energy sources (RES) have advantages for the alleviation of greenhouse gas emission, minimising global warming by replacing conventional energy sources and reducing disposal of a lot of wastes. Renewable energy sources such as biomass, hydropower, geothermal, solar, the wind and marine energies provide about 14 % of the total world energy demand. The percentage is predicted to improve extensively to about 30 to 80 % by 2100 [25].

Table 2.1: Global renewable energy scenario by 2040 [25].

Decades	2001	2010	2020	2030	2040
Total consumption (million tonnes oil equivalent)	10,038	10,549	11,425	12,352	13,310
Biomass	1080	1313	1791	2483	3271
Large hydro	22.70	266	309	341	358
Geothermal	43.20	86	186	333	493
Small hydro	9.50	19	49	106	189
Wind	4.70	44	266	542	688
Solar thermal	4.10	15	66	244	480
Photovoltaic	0.10	2.00	24	221	784
Solar thermal electricity	0.10	0.40	3.00	16	68
Marine(tidal/wave/ocean)	0.05	0.10	0.40	3.00	20
Total RES	1365.5	1745.5	2964.4	4289	6351
Contribution of RES in (%)	13.60	16.60	23.60	34.70	47.70

2.2.1 Biomass Energy

Currently, available renewable energy sources include solar, wind, geothermal, hydroelectric and biomass energies. Among these renewable energies, biomass is the largest and an essential one that has been employed in both developed and developing countries. Biomass is formed when carbon dioxide and solar energy (sunlight) with water are mixed via photosynthesis. However, burning of biomass results in the release of carbon dioxide into the atmosphere accompanied by the conversion of stored

chemical energy in the biomass into thermal energy [26]. Biomass supplies a clean, renewable energy source that could considerably improve our environment, economy and energy security by reducing the burning of fossil fuels, emission of greenhouse gasses (GHG) and environmental pollution [27].

Biomass can be used to generate heat and power for industry and domestic purposes. This particular value over wind power and solar energy via photovoltaic cells makes biomass a significant pillar in the energy contribution today and in the future. Biomass such as wood, energy crops, forest and agricultural residue, industrial and municipal wastes could be the prominent alternatives to coal [27, 28]. Moreover, according to statistics from the IEA, biomass contributed about 10 % of primary global energy demand in the year 2005. Biomass can be converted into gas and liquid fuels (bio-oil, biodiesel, and bioethanol) through gasification and pyrolysis, transesterification and fermentation respectively [12].

2.2.2   Components of Biomass

Biomass is a lignocellulosic material obtained from living organic substances such as wood and agricultural wastes. However, non-lignocellulosic substances, like an animal and municipal solid wastes (MSW) are also regarded as biomass. The three major constituents of biomass [15, 29] are cellulose, hemicellulose, and lignin. It also contains water extractives and ash [29]. The constituents are highly associated and chemically bonded by noncovalent forces. They are cross-linked collectively, thus bearing composition and firmness of the plant [15].

Cellulose is a homopolymer of D-glucose subunits connected by β-1,4 glycosidic links making extended chains. Cellulose is insoluble in water under normal condition. However, it can be hydrolysed in sub-critical water roughly at 180 °C and

about 300–400 °C in normal circumstances. The hydrophobicity of cellulose is considered moderate, and it has a calorific value between 17 – 18 MJkg^{-1}. Apparently, cellulose is known to be used for the production of paper, textiles, biofuels, chromatography, binding/composite materials. The molecular formula for cellulose can be written as $(C_6H_{10}O_5)_n$, where n is a degree of polymerisation [15]. The polymer molecules in cellulose are bonded by strong hydrogen bonds which make it crystalline. However, these hydrogen bonds could be altered by some pre-treatments which minimise the degree of polymerisation (DP), or the number of glucose repeat units. The chemical structure of cellulose polymer molecules are the same and have no side chains. However, the percentage of cellulose may vary in different biomass type. For instance, wood contains cellulose ranging from 38 – 55 %, grasses from 20 – 35 %, switchgrass about 40 % and rice hulls provide 36 % [29].

Hemicellulose is a heteropolymer compound made up of Xylose, Mannose, Glucose, and Galactose. B-(1→4)-glycosidic or α-(1→2)-bonded 4-0-methyl glucoronic acids connects the major component in hemicellulose (xylan). It could also combine with an acetyl group. The thermal stability of hemicelluloses is comparatively simple, because of the amorphous shape. The hydrolysis of hemicellulose is about 160 °C and about 200 – 300 °C beneath normal circumstances. The calorific value of hemicellulose is between 17 – 18 MJkg^{-1} and the hydrophobicity is short. The molecular formula for hemicellulose can be written as $C_5H_{10}O_5$. Some of the functions of hemicellulose include the formation of animal feed, food packaging, healthcare and bio-refinery production [15]. The hemicellulose amorphous polymer chains have small branches and contain many monosaccharide units. The non-crystalline nature of hemicellulose allows it to dissolve in water and makes it more reactive than cellulose. However, the degree of polymerisation ranges from 50 – 200 °C [29].

Lignin is a heteropolymer made up of p-coumaryl, coniferyl and sinapyl alcohol (phenyl-propane monomers groups). The lignin polymer is joined by many points of phenyl-propane monomers making large molecular structures. Lignin is considered more thermally steady compound in wood and greatly unsolvable in water. The hydrolysis of lignin in water commences about 600 °C in ambient conditions. The calorific value (23.3 – 26.6 MJkg^{-1}) and hydrophobicity of lignin are higher compared to cellulose and hemicellulose. It is known to be used in the production of adhesive compounds and bioenergy [15]. The basic structure of lignin can be written as [C$_9$H$_{10}$O$_3$ $\cdot$ (OCH$_3$)$_{0.9-1.7}$]m, where *m* is a degree of polymerisation [12].

The extractive content in biomass is described as the organic materials with low molecular weight and are soluble in inert solvents. The extractives comprise of terpenes, high oil and the fatty acids, esters, and triglycerides, which contribute to paper mill pitch problems. Resin (combination of the following components: terpenes, lignans and other aromatics), fats, waxes, fatty acids and alcohols, terpentines, tannins, and flavonoids are categorised as extractives [30]. Extractives as a proportion of combustible organic constituents affect the heat content of fuel material. For example, the heating value of a free extractive plant was found to be lower than those with extractive contents which signify the possibility of a positive role of extractives towards the improvement of high heating value (HHV) [31].

2.2.3 Oil Palm Biomass in Malaysia

Oil palm is the most important product that has changed the situation of the agricultural sector and economy in Malaysia. Palm oil has made significant and continued development in the worldwide market in the past few decades. It is projected that in the period 2016 – 2020, the standard yearly production of palm oil in Malaysia

will achieve 15.4 million tonnes. Lignocellulosic biomass which is produced from the oil palm industries incorporate oil palm trunks (OPT), oil palm fronds (OPF), empty fruit bunches (EFB) and palm pressed fibres (PPF), palm shells, and palm oil mill effluent (POME). The occurrence of these oil palm wastes has created a significant disposal crisis, but the primary objectives of waste management in Malaysia are to limit and reuse the waste and recuperate the energy. This principally applies to agro-industrial wastes, for example, palm oil residues as applied to municipal waste. One of the significant advantages of oil palm wastes is that the palm oil mill is independent in energy, utilising PPF, EFB, and shell as fuel to generate steam in waste fuel boilers for handling, and power-generation with steam turbines [32].

The oil extraction rate is just around 10% of the palm oil production with the larger part 90% remaining as biomass. For instance, in 1 kg of palm oil about 4 kg of dry biomass is generated [14, 33]. The oil palm wastes generated from palm oil industry in Malaysia is among the most excellent biomass residues. After being lignocellulosic biomass, they also show non-edible characteristic which makes them attractive globally [34]. Malaysia produced around 9.9 million tonnes of palm oil wastes as a fundamental of biomass sources including EFB, shell, and fibre, which continues to expand at 5 % yearly [36]. However, the proportions of agricultural residues generated from oil palm include mesocarp fibre (13.5 %), palm kernel shell (5.5 %) and empty fruit bunch (22 %). Figure 2.2 shows the distribution of oil palm biomass wastes. Palm shell and palm fibre were utilised as fuel to power the steam boilers, whereas empty fruit bunch is used for mulching in the plantation area [34].

Figure 2. 2: Product and waste distribution from oil palm tree.
Source: JFE project, 2016: http://jfe-project.blogspot.my/2010/04/utilization-biomass-oil-palm.html

2.3   Briquettes Generation

Briquetting is a process of compressing materials into a small portable size with a diameter ranging from 30 to 100 mm and of any length depending on the technology applied, which could either be screw or piston compression [35]. The briquetting process is perhaps regarded as a way to improve the application of low-grade wastes materials. Briquetting is mainly used for compacting of biomass (sawdust, wood shavings, bark, straw, cotton, paper). However, it was reported that briquettes could also be generated from none biomass sources such as plastic, many types of milled paper wastes and other combustible wastes [18]. Municipal solid waste (MSW), industrial waste and sludge are used to produce fuel briquettes in some countries [36]. It is well-known and believed that biomass residues could be utilised as a replacement to fuel for combustion at coal-fired power plants [37].

2.3.1 Densification Processes

Densification (briquettes or pellets) is described as a suitable technology that has improved the application of biomass waste such as wood and agricultural residues for domestic and industrial fuels [38]. However, briquettes differ from pellets in term of size. The size in length varies from 5 to 30 mm and 50 to 400 mm for pellets and briquettes, respectively [39]. The briquettes produced from the densification of biomass are portable because of their consistent sizes and shape which make it less problematic in handling, in storage and lesser cost in transformation [38]. It was reported that the densification of biomass is believed to improve the bulk density of biomass to about $600 - 800$ kgm^{-3} from $40 - 200$ kgm^{-3} [40]. Testing the strength and durability of bonding in densified products is recommended. The compressive resistance, impact resistance, and water resistance are for testing strength, whereas abrasion resistance for durability [40]. Densification process is divided into two categories [39].

a. Continuous or semi-continuous extrusion process. This process is usually related to the higher scale industrial manufacture. It involves densification at high-pressure.

b. Discontinuous process. In this process, one briquette is made from each mould per single press. In this study, the discontinuous process will be applied for the briquette production because it is commonly used in the laboratory and small-scale business.

2.3.2 Briquettes and its Advantages

The mechanical benefits of briquetting include improvement of bulk density and energy contents per volume of material, low-cost and easy transportation due to the increase of cohesive forces in the densified material, conversion of composite material into a homogeneous product and improving the standard amount of energy of

combustion for material [39]. Briquettes contain a greater energy content and density, and low moisture content than the raw materials. Though, factors such as ash and moisture content, volatile matter, density, and heating value should be managed and controlled effectively to obtain better biomass briquettes for fuel application [38]. Adapa et al. [41] reported that the bulk density of densified biomass could be increased from an initial of $40 - 200$ kgm^{-3} to a final density of $600 - 1200$ kgm^{-3}.

Asamoah et al. [36] revealed that high quality, productive fuel briquette relies on lesser moisture content, volatile matter and ash content with advanced fixed carbon content. The raw materials and the briquettes should fulfill the summarised requirements listed in Table 2.2 [36] to guarantee the required biomass briquette for fuel application.

Table 2.2: Characteristics of good biomass briquettes [36].

Properties	Unit	Requirement
Proximate analysis		
Moisture content	wt,%	6-14
Ash content	wt%	Less than 4% to avoid slagging
Particle size	mm	1-10 mm with 10-20% powdery
Fixed carbon	wt,%	9-25
Volatile matter	wt,%	50-90
Calorific value	MJ/kg	10-35
Elemental analysis		
Carbon	wt,%	40-55
Hydrogen	wt,%	5-8
Oxygen	wt,%	35-48
Nitrogen	wt,%	0-1
Sulfur	wt,%	0-2
Chloride	wt,%	0-1

2.3.3 Oil Palm Biomass Briquettes

The production of briquettes from oil palm wastes is not new; there have been many studies conducted on densification of oil palm wastes and biochar derived from it [42-44]. Ugwu and Agba [20] produced and characterized briquettes from carbonized palm kernel shell (biochar) using cassava starch as a binder [20]. Bazargan et al. [21]

investigated the effects of water content, compaction pressure, feed particle size, compaction retention time, and the use of starch as a binder on the briquettes/pellets made from the biochar residue obtained from the gasification of palm kernel shell [21]. These researchers used biochar acquired from carbonization and gasification of palm kernel shell, respectively; water and starch were used as a binder for the briquettes production. Lam et al. [13] investigated the effect of steam explosion pretreatment on the physical and mechanical properties of pellets made from empty fruit bunch and palm kernel shell, and comparison to that of softwood Douglas-fir (DF) [13]. However, the densification of biochar and bio-oil as a binder has not yet been reported. Therefore, the addition of bio-oil in the proper distribution to biochar is a process requiring active physical forces that bond solid particles together. This study is intended to use the slow pyrolysis products (biochar and bio-oil) however, the addition of starch additives became necessary to upgrade the viscosity of bio-oil. In our previous researchers [45, 46] the production of briquettes from the mixture of biochar and bio-oil derived from slow pyrolysis of PKS and MF were reported. In this research, the briquettes produced from raw and torrefied EFB, MF and PKS and their pyrolysis products will be compared with Malaysian sub-bituminous coal and commercial wood briquette for replacement purposes. This could be one the proper method to minimize the agricultural disposal problem in Malaysia, over-dependence on coal for heat generation and deforestation in local communities of West Africa countries (Nigeria).

2.4   Process of Briquettes Production and Operational Parameters

This segment canvasses the processes, pre-treatment and operational parameters (factors) controlling the quality of fuel briquettes. Physical properties such as a binder, moisture content, particle size and compressing forces (pressure) are among the factors that influence the quality of briquettes regarding durability and resistivity during

transportation [40]. However, a briquette quality significantly depends on the drying process [47].

2.4.1 Pre-treatment of Biomass by Heating or Drying

Preheating of raw materials preceding the briquette making process is frequently important to defeat the difficulties of truncated density, low heating value, high moisture content and low fixed carbon content of the feedstock. It is additionally important to maintain a strategy to avoid hardship transportation, poor grindability, soot formation and hygroscopic nature. Moreover, preheating has the upside of decreasing the bacterial checks [36, 48]. Sugarcane bagasse, banana rachis, rice husk, palm oil fibre, sawdust, coffee waste were preheated via torrefaction between $200 - 300\ ^{\circ}\text{C}$ for 30 minutes and the heating value increased by 5 % to 1 5% [49].

2.4.2 Briquettes Binders

The use of adhesive is necessary for any material that cannot solely bind itself under pressure to make strong briquettes. Adhesive materials increase the bonding force and other durable properties of the briquettes. The quantity of binder to be applied relies on the nature of the binding features of the material, binding agent and briquettes machine [36]. Biological binders for example molasses, starch, waste paper, and sawdust are known to increase the value (quality) of densified products. Starch is commonly used as a binder [40]. Suboil, lignin, fibres, glycerine, pitch, paper, starch, molasses, and plastics have the good binding capacity [21, 50]. Chaney [39] showed that the relaxed density, durability and sheer strength of the briquette depend on the amount of binder applied. The higher the amount of binder, the stronger is the briquette. However, the binders are divided into combustible binders such as natural resins, tar,

animal manure, fish waste, algae and starch and non-combustible binders which include clay, mud, and cement. It is recommended that the binder should not be toxic for the safety of the producers [39]. It is important to note that in this study Sago starch will be used as an additive to enhance the viscosity of the bio-oil as previously reported [45, 46].

2.4.3 The Effect of Compaction Pressure

The pressure applied during the densification process forced the particle to facilitate different binding mechanisms. High pressure helps the densification. The pressure in the range of 100 – 150 MPa or more is recommended. However, there are various densification apparatus and feedstock that cannot withstand a higher amount of pressure [40]. It was reported that the bonding caused by the molecules diffusion between the particles and the formation of the solid bridge is highly efficient at higher pressures. Therefore, denser and durable products could be achieved at high pressures because of better bonding. Besides, higher pressures are known to diminish sample porosity [21, 37].

2.4.4 The Importance of Water or Moisture Content

During the briquetting process, water serves as grease and binding agent as well. It assists with the building of van der Waals' forces via improving the area of contact between the particles. When water-dissolvable compounds such as starch, sugar, soda ash, sodium phosphate, potassium salt, and calcium chloride are available in the briquette feed, water helps the briquetting process [40]. However, there is a decrease in briquette density and stability if the moisture content is very high. Furthermore, high moisture content makes the materials to relax highly on the die which does not allow obtaining coherent briquette [39]. Moisture contents in the range of 13 to 18 % were

found to facilitate the compaction. However, the influence of moisture content of the briquettes can be handled by controlling the machine and the mixture ratio effectively [37]. The optimal moisture content depends on nature and type of material. Nevertheless, a moisture content ranging from 10 to 15 % is suggested. In application, the range is between 6 % and 23 % [51, 52].

2.4.5 Drying and Storage Processes

The drying process of briquettes is energy and time demanding. However, a briquette quality significantly depends on the drying process. Drying is a method of moisture or water elimination from a solid material through mechanical, thermal or natural methods under atmospheric conditions. Natural drying is recommended for less dense briquettes, and it is considered more economical [47]. A drying period of 7 days is considered acceptable for any binder to reach its full efficiency. The shatter and compressive strengths of briquettes increase with drying from 1 to 7 days for binders such as guar gum, wheat starch, and lignosulfonate [53]. After drying, briquettes could be stored at room temperature (20 °C) and left to cool for 24 hours before use. Storage at higher temperatures can make briquettes too dry and consequently hard to ignite, while low temperature would make the briquettes soft and not durable burning [36].

2.4.6 Particle Size Adjustment

For proper and sustainable briquettes to be produced, the particle size of the material is required to be adjusted. For qualitative densified briquettes, the particle size is recommended to be between 1 to 10 mm [38]. Biochar was ground and sieved into three different sizes of 300, 700 and 3000 μm before densification, respectively. The briquettes produced using smaller particle make the surface of the briquettes smooth. However, as the particle size increase over 300 μm the tensile crushing strength

decrease. When particle sizes are too fine, it may result in jamming within the equipment and adversely affect the production. In a situation, whereby the particle sizes are different (powder and larger), it leads to a high value of tensile strength [21], because larger particles help in mechanical interlocking, while powder particle increases the number of contact points. The recommended particle size of biomass for charcoal-based and non-carbonised briquettes ranged below 6 mm [21, 36, 40].

2.5   Quality Parameters

Charcoal briquettes express indisputable qualities, such as low smoke emission, in comparison to non-carbonised briquettes. In addition, they possess low ash content, non-sparkling characteristics, and long-lasting fire, which cannot be quench by termites. Marketing of charcoal briquettes is easy as users are familiar with this type of briquette because its colour and features resemble conventional charcoal [36]. The unfavourableness is that it may be very hard to start a fire than non-carbonised briquettes [40]. The briquettes qualities regarding durability, strength, and density differ with the raw materials used and production parameters. For durable briquettes, the crushing strength, impact resistance index and water resistance should be at least 375 kNm^{-2}, 50 and 90 %, respectively [54].

2.5.1   Compressive Strength

Compressive strength or hardness of the material is the maximum crushing load a densified material can resist before failure or crack. It is usually tested using diametric compression test as described in other work [40]. According to the recent research, the quality of a densified cylindrical product is often measured via crushing which could either be conducted parallel or perpendicular to the cylindrical axis. The strength of the

material is, of course, higher in cylindrical direction. The strength of the material in the cylindrical axis direction is known as compressive strength while strength perpendicular to the cylindrical axis direction is identified as tensile strength as shown in Figure 2.3 [21].
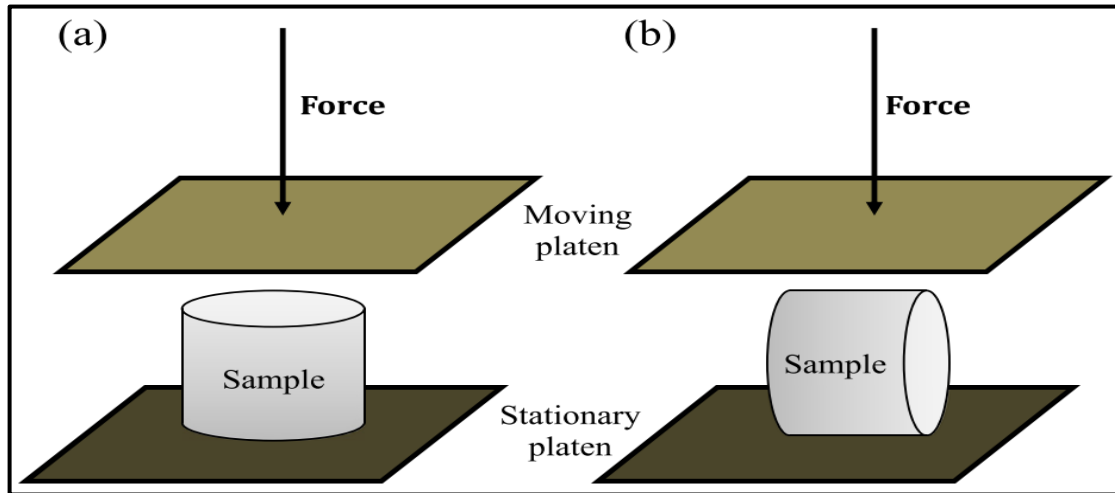

Figure 2. 3: Strength of cylindrical material (a) compressive strength and (b) tensile strength [21].

The briquettes are made from water hyacinth and plantain peel as a binder in the ratio of 10, 20, 30, 40 and 50 % by weight, respectively. It was found that compressive strength is extensively affected by the binder ratio. Thus, compressive strength is described as a means of determining the capacity of briquettes to resist mechanical stability [55].

2.5.2 Shatter Index/Resistance

The durability test is a measure of the degree of the briquettes to resist damaging forces such as compression, impact, and shear in the course of handling and transportation. The impact forces cause the briquette to shatter, e.g., during emptying and dumping of the briquettes. The shatter index is done by dropping the briquettes four times from a height of 1.85 m onto a metal surface. Briquettes can also be dropped ten

times from a height of 1 to 2 m onto a concrete surface. The weight of the briquette retained is then recorded [36, 40].

2.5.3 Density

Density is recognised as one of the fundamental factors in briquetting because it defines the quantity of mass per unit volume. The density of densified materials depends on binder and densification machine used. It has a significant influence on the compressive strength of material [38]. It was discovered that the density of pellet derived from barley straw, corn stover and switch grass is notably influenced by particle size, moisture content and compressive force [56]. However, the density and durability of the biomass pellets and briquettes are independent of each other [57].

2.5.4 Water Resistance

Sensitive measures are recommended to avoid short time contact with either rain or high humidity environment during transportation and storage as it may significantly affect the quality of densified products [40]. The briquetting pressure influenced the water resistance. It was reported that during the water resistance test of briquettes made from pulping reject and spruce sawdust under 300 MPa with a moisture content of 10 %, the briquettes begin to collapse at about 50 and 70 min, respectively [37]. The moisture content of briquettes affects the calorific value of briquettes sample, as the moisture content raised the calorific value of briquettes reduced [37, 56].

2.5.5 Effect of Briquettes on Environmental Sanitation

The use of various sorts of waste for briquettes generation has note-worthy enhanced waste administration. Residential waste, other wastes from schools, faecal sludge, and agricultural waste can be converted into briquettes. Most urban

communities in sub-Saharan Africa confront the test of waste administration. Gathering wastes from urban communities by ladies, youth and organisations for manufacturing briquettes helps to clean the environment. The administration of waste through briquette generation bolsters a perfect and healthy society. Briquettes could add to relieving the adverse effects of fuelwood. Concentrates at the provincial level show that as much as 66 % of the fuelwood utilised for cooking overall originates from non-forest sources, for example, agricultural land and roadsides [36].

2.5.6 Briquettes Market

The chance to use agricultural wastes and the natural divisions of MSW more efficiently with a potential diminishment in pollution levels has stimulated the enthusiasm of developing and developed nations in briquetting. The market portions for briquettes can be separated into residential, institutional and industrial use, and for export. The larger part of briquette organisations in developing nations supply briquettes to a local/nearby market and just a couple of briquette organisations are export-oriented [36]. The most open markets for briquettes delivered from non-carbonised waste are energy concentrated enterprises which utilise fuelwood for their operations, for example, block making, concrete processing plants, and other comparative businesses. Different markets for non-carbonised briquettes are institutional kitchens, for instance, restaurants, schools, and hospitals. Charcoal briquettes are for the most part focused on the family use and institutional kitchens in rural and urban territories. In spite of the fact that briquettes are normal in casual settlements in East Africa, comprehensively, there is still a low appropriation of briquettes in developing nations which is halfway because of lack of awareness, and the accessibility of less expensive firewood to numerous clients [59]. An investigation

directed by the Energy and Environment Partnership in Southern and Eastern Africa on the briquette business in East Africa contended that the substitution of conventional cooking fuels is one reason for the small achievements of the briquette business [60].

2.6   Solid Fuel Combustion

The combustion process of solid fuel is categorised into four sub-processes namely; moisture removal (evaporation), volatile release/char creation, hydrocarbon volatile (gases phase), and char particles combustion consecutively. However, moisture content, volatile matter, fixed carbon and ash content have significant influence during the combustion process. Other factors such as airflow rate, fuel particle size, type of reactor, and duration of combustion also have a significant effect on solid fuel combustion. There are three stages of combustion: ignition stage, a primary combustion stage, and final char-burning-only stage. When the fuel is very wet, and the primary airflow is higher, the rate of char-burnt is greater. For highly wet fuel the char can completely be burned in the primary stage in respective of the low level of air flow [61]. Constituents such as nitrogen and ash are very significant to consider in biomass combustion. Nitrogen is a source of NO_x, and ash is a source of potassium chloride (KCl) which results in particulate emissions [62].

The quantity of burnt briquette (solid fuel) and burning time can be used to calculate the combustion rate. Moreover, the combustion rate can be used to determine the heat release during combustion, as shown in the equation 2.1 and 2.2 [35]. The combustion characteristics of Malaysian oil palm biomass such as palm kernel shell (PKS), palm mesocarp fibre (PMF) and empty fruit bunch (EFB) and sub-bituminous coal (Mukah Balingian (MB)) was studied. The burning profile of the samples was shown in Table 2.3 [11].

24