PHYSICOCHEMICAL PROPERTIES CHANGES ON PALM OIL WASTE TORREFACTION: EFFECT OF TEMPERATURE AND RESIDENCE TIME

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Thesis submitted in partial fulfilment of the requirements
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Signature :
Name of main supervisor : SURIYATI BINTI SALEH
Position : SENIOR LECTURER
Date : 10 JANUARY 2017

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DEDICATION

I dedicate my dissertation work to my supervisor, my family members and my friends for all your care, support and trust on me. A special appreciation to my supportive supervisor, Dr Suriyati Bt Saleh who gives a lot of guidance and shared knowledge to me.

An exclusive gratitude toward my parents, Thor Lian Soon and Koh Koon Hyim who give different extent of supports and nursing with love and their dedicated for success in my life.

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ABSTRACT

As a second largest palm oil exporter, utilization of palm oil biomass in Malaysia as the main renewable energy source is encouraged. To make the palm oil biomass more competitive with conventional energy source like coal, torrefaction pre-treatment was applied on the palm oil wastes which were palm kernel shell (PKS) and palm mesocrap fiber (PMF). The palm oil biomass were torrefied in a torrefaction reactor at different final temperatures of 240 ℃, 270 ℃, 300 ℃, and 330 ℃ with different residence time of 30 min and 60 min in an inert condition. The change of the properties of the torrefied biomass include physical appearance, morphology structure, CHNS mass fraction, higher heating value (HHV), proximate analysis, and mass and energy yield. The physical appearance of torrefied biomass showed darken colour with higher torrefaction temperature. In term of morphological structure, SEM image revealed that severe torrefaction had more severe impact on the surface structure of PKS and PMF. Besides that, this study also reported that carbon mass fraction and higher heating value (HHV) increase with the increase of torrefaction temperature, but H/C ratio decreases for all torrefied biomass. Among the torrefied products, PKS had the highest carbon mass fraction of 59.9% and PMF had the highest HHV of 22.91 MJ kg^{-1}. In terms of energy yield, PMF produced 90 – 95% yield and PKS produced 78 – 96% yield when torrefied from 240 ℃ to 330 ℃ for 30 min. In addition, the non-condensable gases released during torrefaction reaction include CH_4, CO and CO_2. This study concluded that the biomass had a lot of improvement such as improve in the grindability, higher energy density torrefied products, reduce moisture content and released volatile gases that can used as energy sources through torrefaction treatment.

ABSTRAK

Sebagai pengeksport minyak kelapa sawit kedua terbesar di dunia, penggunaan biomas kelapa sawit di Malaysia sebagai sumber tenaga amat digalakkan. Untuk memastikan biomas kelapa sawit berdaya saing dengan sumber tenaga konvensional seperti arang batu, biomas kelapa sawit perlu melalui proses “torrefaction”. Biomas kelapa sawit yang digunakan dalam projek ini adalah “Palm Kernel Shell, PKS” dan “Palm Mesocrap Fiber, PMF”. Sampel biomas “torrefied” dalam reaktor pada suhu yang berbeza iaitu 240 ℃, 270 ℃, 300 ℃, dan 330 ℃ dengan masa selama 30 min dan 60 min dalam keadaan nadir. Perubahan sifat-sifat “torrefied” biomas termasuk penampilan fizikal, struktur morfologi, kandungan CHNS, nilai pemanasan (HHV), analisis proksimat, hasil jisim dan hasil tenaga. Penampilan fizikal untuk “torrefied” biomas menunjukkan warna yang lebih gelap selaras dengan peningkatan suhu “torrefaction”. Dari segi struktur morfologi, gambar SEM menunjukkan kesan yang lebih jelas didapati pada stuktur permukaan PKS dan PMF pada suhu yang tinggi. Selain daripada itu, kajian ini juga melaporkan kandungan karbon dan nilai pemanasan (HHV) meningkat dengan peningkatan suhu “torrefaction” tetapi keadaan yang sebaliknya berlaku kepada nisbah H/C. Data yang dikutip menunjukkan PKS mempunyai kandungan karbon yang paling tinggi 59.9% dan PMF mempunyai HHV yang tertinggi 22.91 MJ kg^{-1}. Dari segi hasil tenaga, PMF dapat mengekal pada 90 – 95% dan PKS dapat mengekal sebanyak 78 – 96% apabila “torrefied” dari 240 °C hingga 330 ℃ selama 30 min. Di samping itu, gas yang dibebaskan semasa proses “torrefaction” termasuk CH_4, CO dan CO_2. Kajian ini menyimpulkan bahawa biomas mempunyai peningkatkan dari segi qualiti seperti bertambah baik pada “grindability”, ketumpatan tenaga yang tinggi, mengurangkan kadar air dan gas yang dibebaskan semasa “torrefaction” boleh digunakan sebagai sumber tenaga.

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LIST OF SYMBOLS

Wi	Initial weight, g
Wf	Final weight, g
Y_{mass}	Mass yield
Y_{energy}	Energy yield

LIST OF ABBREVIATIONS

EFB	Empty fruit bunches
FC	Fix carbon
GC	Gas chromatography
GCV	Gross calorific value
HHV	Higher heating value
MC	Moisture content
PKS	Palm kernel shell
PMF	Palm mesocrap fiber
TGA	Thermogravimetric analysis
VM	Volatile matter

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Renewable energy is a subject of great interest since it represent the diversification of the energy sources and contribute to sustainable development with continue supply the demand of energy in the world. To reduce the dependency on the fossil fuel, Europe set a target which about 12% primary energy demand are supply by renewable sources (Commission, 1997). Renewable energy sources such as biomass, wind, solar, tide wave and geothermal expected to be fastest growing energy sources due to depletion of fossil fuels and increasing demand of energy. Among the energy sources, biomass is preferable since it act as sustainable carbon carrier energy sources (Acharjee et al., 2011; Van der Stelt et al., 2011). In Malaysia, palm oil wastes are the best among the biomass wastes due to economical factor and availability of raw material. Malaysia has great potential for the exploitation of palm oil wastes since Malaysia is second largest producer and exporter of palm oil. Producers of palm oil produce abundant volume of lignocellulose waste materials as palm kernel shell (PKS), empty fruit bunches (EFB) and palm mesocrap fiber (PMF) (Asadieraghi & Daud, 2015).

1.2 Motivation

A lot of research works in Malaysia has proved that torrefaction pre-treatment able to produce better solid fuels from biomass. According to Chew and Doshi (2011), torrefaction increases the energy density and energetic value, enhanced hydrophobicity and friability, and improve grindability. Torrefaction on palm oil waste (PKS, PMF and EFB) increases the calorific value with produce products that higher carbon content. Besides that, torrefied PMF and PKS retain almost 100% of energy yield while energy yield of torrefied EFB decreases steadily from 83% to 56% with temperature due to poor mass yield (Uemura et al., 2011). Based on Sabil et al. (2013), torrefied PKS has the highest carbon fraction with 58.7% while torrefied PMF has the highest Gross Calorific Value (GCV) with 23.73 MJ kg^{-1}. The energy yield of PKS can be maintained within range of 86-92% at light to severe torrefaction conditions until 280 ℃ and energy yield for EFB and PMF is within range of 70 – 78% at light torrefaction condition until 240 ℃. The particle size of the torrefied biomass has decreased and the particle with more smooth surface which means the torrefied biomass has better grindability (Li et al., 2015). Malaysia researchers had a lot of experimental work on torrefaction of palm oil waste (Chen et al., 2016; Na et al., 2013; Sabil et al., 2013a). Since torrefaction of biomass improve the quality of the biomass to use as bio-coal, this project is carried out to study the optimum condition of torrefaction for PKS and PMF; investigate quality improvement of PKS and PMF with torrefaction pre-treatment.

1.3 Problem Statement

There are several challenges need to overcome in order to fully utilize palm oil waste efficiently. High energy consumption for collection, spread distribution in ash content, lower energy value and high logistic cost are the challenges need to be solved (Uemura et al., 2011). Besides that, tenacious and fibrous structures of biomass resources make it difficult to grind. Reduction about 80 – 90% of energy consumption for grinding torrefied biomass compared to grind untreated biomass (Bach et al., 2013; Van der Stelt et al., 2011). Based on Arias et al. (2008), biomass have several challenges need to overcome in order to be utilized as a fuel, which are high bulk volume, high moisture content, relatively low calorific value, which increase costing on transportation and difficult to grind since biomass are lignocellulosic materials. One of the ways to cope lower energy value and high logistic cost is enforce torrefaction pre-treatment to the palm oil waste. Torrefaction is a thermolysis process that subjects the feedstock to thermal treatment at relatively low temperatures of 200 – 350 ℃ and inert atmosphere. Torrefaction normally allied with roasting, pyrolysis, and thermal pre-treatment (Chew & Doshi, 2011). Some researchers had studied on torrefaction of palm oil waste with analyse the effect of torrefaction on palm oil wastes, the optimum condition for torrefaction, economical potential of torrefaction treatment on palm oil wastes and energy yield of torrefied palm oil wastes. However, the papers about study of volatile released during torrefaction process are limited. Thus, in this project, the study on volatile released during torrefaction was included and the torrefaction effect on the PKS and PMF were investigated.

1.4 Objectives

The following are the objectives of this research:

1) To study the torrefaction effects on physicochemical properties of palm kernel shell (PKS) and palm mesocrap fiber (PMF) at different temperature levels and residence times.
2) To identify the volatile released during the torrefaction.

1.5 Scopes of Study

The following are the scopes of this research:

1) Palm kernel shells (PKS) and palm mesocrap fibers (PMF) were chosen as raw materials.
2) Torrefaction of PKS and PMF carried out in a gas catalytic reactor at 240 ℃, 270 ℃, 300 ℃, and 330 ℃ with an inert condition.
3) The volatile released during torrefaction was collected and analysed by gas chromatography (GC).

4) The torrefied PKS and PMF undergo several analysis such as analyse the mass and energy yield, proximate analysis, ultimate analysis and morphological analysis.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter presents the reviews related to the experimental studies of torrefaction process, a thermal pre-treatment method to convert raw biomass into added value solid product with enhanced fuel properties. The chapter starts with an informative study on the energy demand in Malaysia and potential of biomass as energy source. Then follow by the description of palm oil biomass and its lignocellulosic properties. Besides that, brief explanation of torrefaction pre-treatment on different type of biomass is provided. Furthermore, clarification on the effect of torrefaction and torrefaction condition are supplied.

2.2 Energy demand in Malaysia

Malaysia is a rapidly developing country in the Southeast Asia. With the aim of achieve high-income country target on year 2020, Malaysia must obtain high percentage of Gross Domestic Production (GDP) and this link to increment of energy demand in Malaysia. Based on Chong et al. (2015), GDP of Malaysia grew steadily at an average of 5.8% from 1990 to 2012. Increment of GDP causes Malaysia's energy consumption increase at an average of 6.62% from 1980 to 2012. The historical trend of Malaysia energy consumption based on sectors is provided in Figure 2-1. Thus, it is clearly shows that the main consumption on the energy is production and transportation which related to Malaysia's GDP. The energy in Malaysia are depends on crude oil, natural gas, coal and coke, and hydropower. Coal which is the main energy for industrial to provide heat stream and fluid was imported because Malaysia's coal production cannot fulfil the demand of rapidly growth of industrials. Malaysia coal supply mainly relied on imports from Indonesia and Australia. 92.5% of coal used in 2011 was imported which accounted 31.7% of Malaysia total energy imports as shown in Figure 2-2.

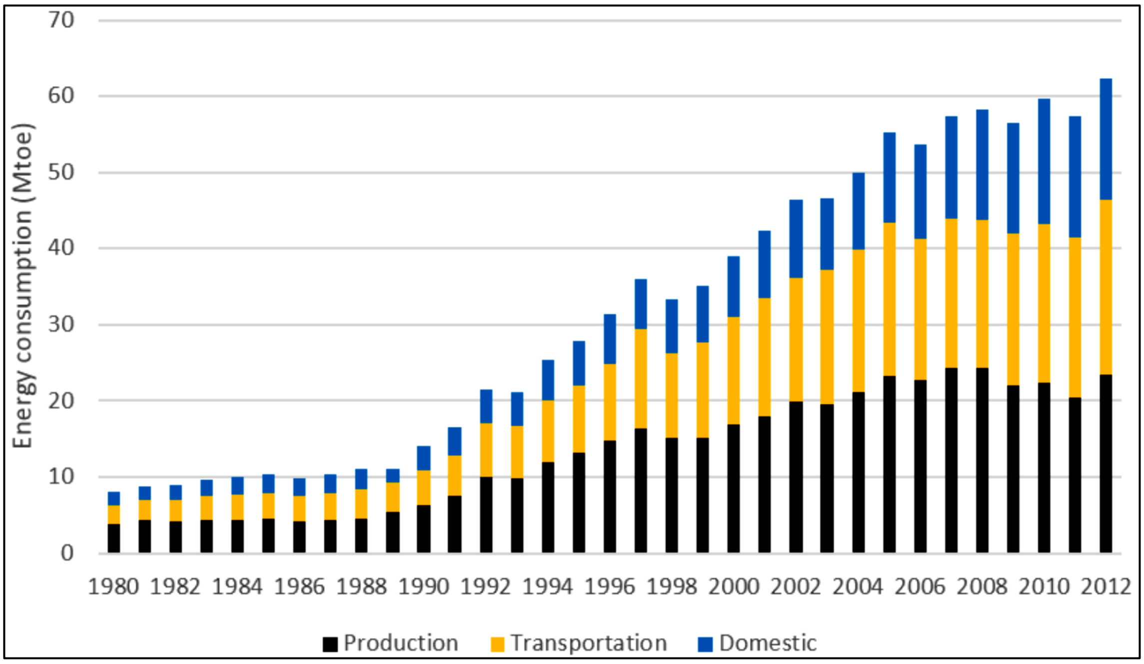


Figure 2-1: Energy consumption of Malaysia expressed by sectors.

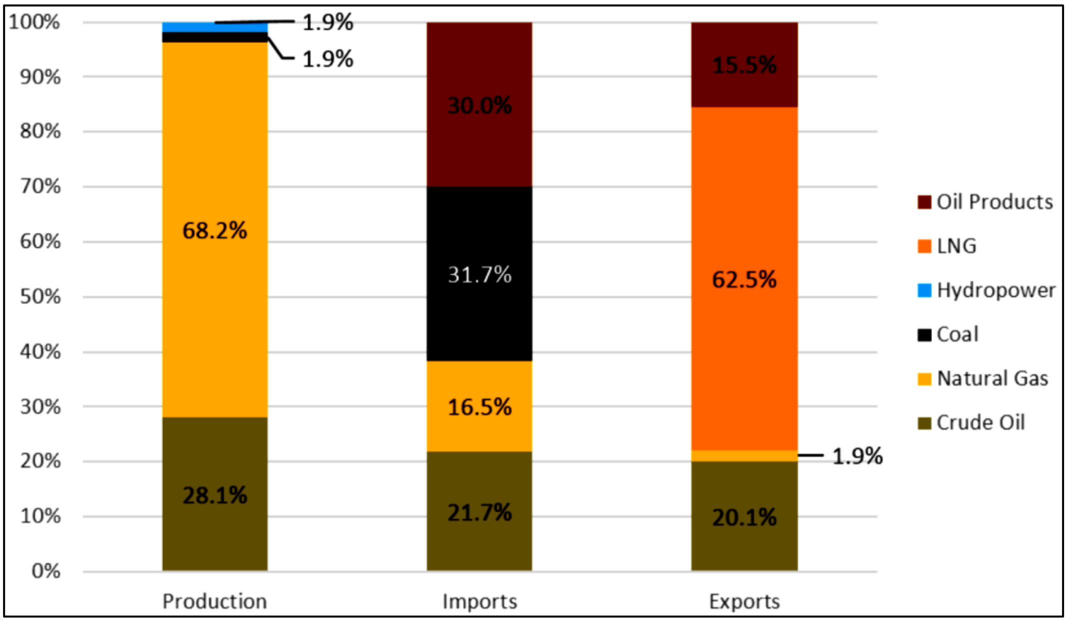


Figure 2-2: The structure of Malaysia's Energy production, imports and exports in 2011.

Besides that, Malaysia energy demand mainly depends on the non-renewable resources which will face depletion. As an example, crude oil production in Malaysia had decreased from 800 bbl/day in year 2003 to 580 bbl/day in year 2011 as shown in Figure 2-3. Malaysian government is looking forward for more reliable and low-cost energy resource to satisfy the domestic demand. In 2009, Malaysian government launched the National Green Technology Policy to provide direction and motivation for Malaysian to continuously enjoy good quality of life and a healthy environment (Pudukudy et al., 2013).

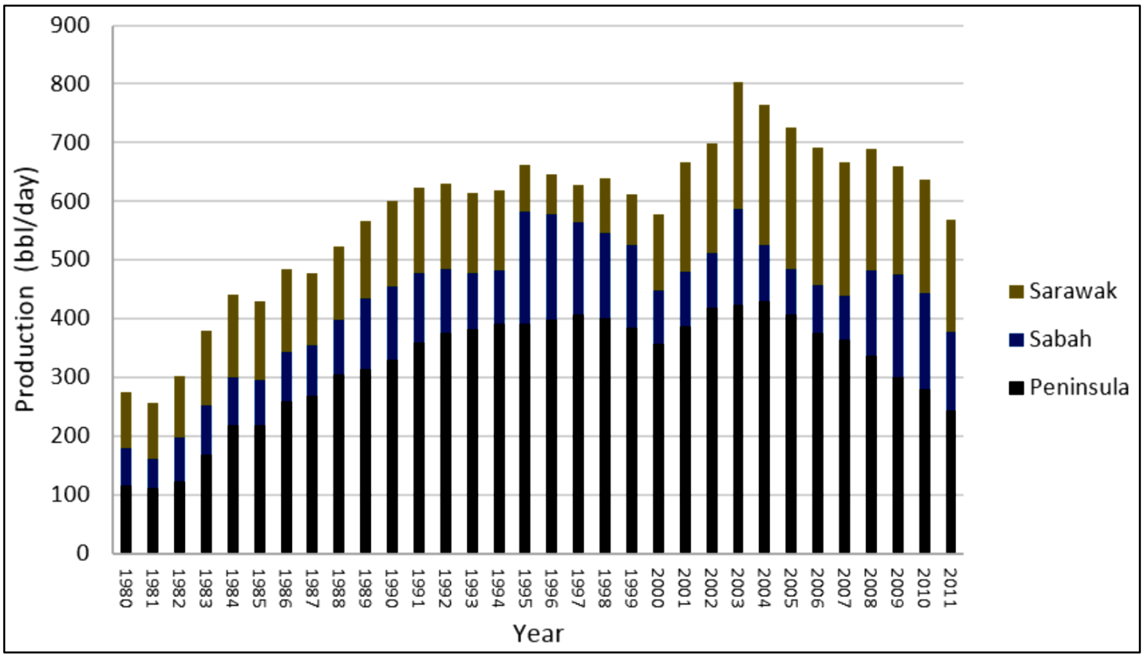


Figure 2-3: Crude oil production in Malaysia from 1980 to 2011.

As a conclusion, by utilization the palm oil biomass to be renewable energy resources is feasible. In order to utilize the palm oil biomass as renewable energy, more research and development should be done on this field.

2.3 Biomass in Malaysia

Malaysia is an agricultural based country which has about 10.31 million hectares land area suitable for agriculture which Peninsula Malaysia region had 6.19 million hectares, Sarawak had 1.81 million hectares and Sabah has 2.31 million hectares.

Agricultural products of Malaysia can be distribute to industrial crops and food crops like palm oil, rubber, cocoa, rice, coconuts, fruit, pepper, tobacco, pineapple, paddy, vegetables and others. Among the agriculture products, oil palm was the main product which contribute 63.4% of the total agriculture products in year 2005 (A. O. Olaniyi, 2013). The amount consumption of palm oil was about 52.1 million tonnes from a total 183.9 million tonnes (17 major oils and fats consume in the world) in year 2012 which reported in Oil World 2013. This fact shows that the demand of palm oil is very high and increase the production of palm oil is encouraged.

2.4 Malaysia palm oil

Malaysia is a tropical country that experiences hot and wet weather throughout the year. This climate suitable for growth of palm oil trees and encourages the development of palm oil cultivation in Malaysia. Indonesia and Malaysia produce about 85% of the world's palm oil. Other producer countries include Thailand, Columbia, Nigeria, Papua New Guinea and Ecuador. Malaysia as the world's second largest palm oil producer after Indonesia which exportation number of palm oil hit up to 18 150 000 MT in year 2015 which has increment about 4.44% in growth rate (Mundi, 2015). Malaysia government very concerns on the palm oil production which million hectares of land is occupied with palm oil plantation. Palm oil is the most important commodity crop in Malaysia, which the palm oil plantation area had increased year by year as shown in Figure 2-4 (PalmOilWorld.org, 2013). The graph shows Malaysia's palm oil plantation area in year 2011 has reach 4.197 million hectares which was about 40.71% of the total land suitable for agricultural in Malaysia.

The increasing in the plantation area of palm oil gives a significant increment to the amount of palm oil production as shown in Figure 2-5. The palm oil production increase steadily which reached 18.9 million tonnes in year 2011 and projected to 19.4 million tonnes in year 2013 (PalmOilWorld.org, 2013). Based on Awalludin et al. (2015), Malaysia recorded a total of $19.9 billion USD export revenue of palm oil products in year 2010 and the value boosted by 34.5% in 2011 to register a record high of $26.8 billion USD.

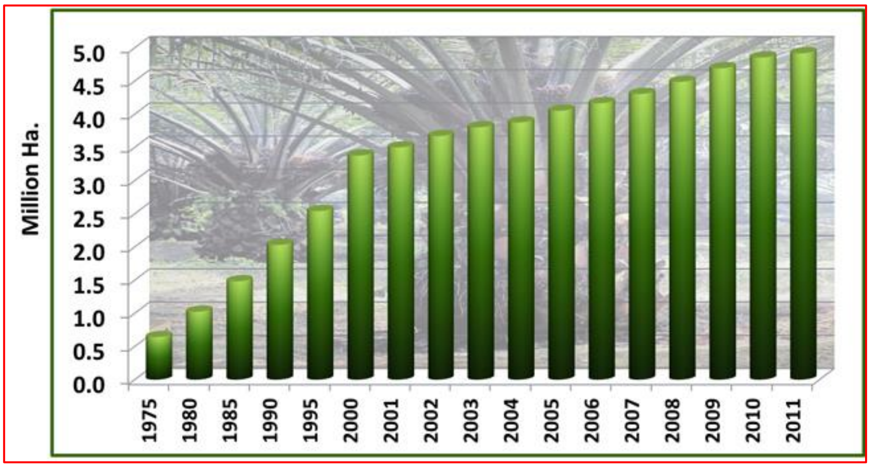


Figure 2-4: Planted area of palm oil in Malaysia from year 1975 to 2011 (PalmOilWorld.org, 2013).

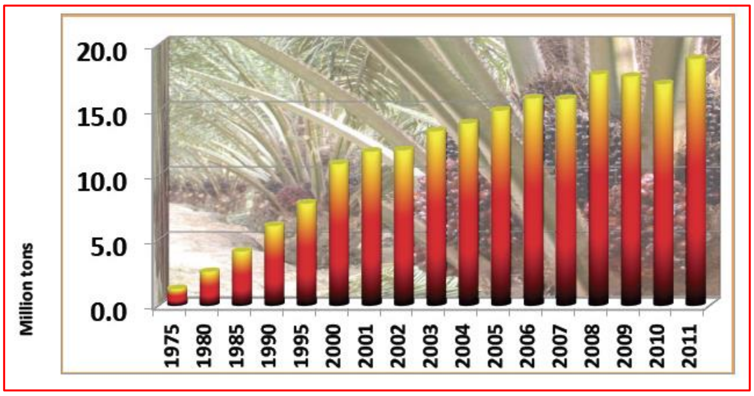


Figure 2-5: Production of crude palm oil in Malaysia from year 1975 to 2011 (Awalludin et al., 2015; PalmOilWorld.org, 2013).

The palm oil industry easily to meet the local fats and oils demand as well as exported to others countries like India, China, European Union (EU), Pakistan, USA, Vietnam and Japan.

As palm oil industries become bigger, a substantial amount of palm oil waste is generated and cause problem of biomass waste overload. Such huge amount of palm oil is produced and exported will cause left over a lot of palm oil waste. Therefore, palm oil waste used as the renewable energy sources is workable and has high potential to replace the conventional energy sources. The palm oil residues that chosen in this project are palm kernel shell (PKS) and palm mesocrap fiber (PMF). About 140 MT (million tones) lignocellulosic wastes which correspond to 17 MT (million tons of oil equivalents) is generated by palm oil industry annually. The total palm oil residue energy potential of 17 MToes able to contribute and decrease the consumption of fossil fuels (Uemura et al., 2011).

The palm oil wastes are from palm oil plantations and palm oil extraction mills. Palm oil plantation produces wastes in the forms of harvested trunks and pruned fronds as shown in Figure 2-6. Besides that, biomasses from palm oil extraction mills are EFB, PMF and PKS as shown in Figure 2-7. On average, five tons of fresh fruit bunches just able to produce one-tonne crude palm oil, so about 4 tons of wastes are produced (Awalludin et al., 2015). In 2012, 83 million dry tons of solid palm oil wastes were produced by Malaysia's palm oil industry. Base on Figure 2-8, the amount of palm oil wastes estimated will be projected to 110 million dry tons by 2020 (AIM, 2013). Without a proper management on the palm oil wastes will cause a lot of pollution. Oil spills will occur if the untreated EFB are disposed into oil palm plantation. Disposal of EFB by incineration means wasting renewable energy sources and heat which able to use for boiler in palm oil mills (Abdullah & Sulaim, 2013). PKS, PMF and EFB are the resources that have huge potential to be used for power generation that not being utilized recently.

Figure 2-6: Palm oil plantation's biomass wastes. (A) Oil palm trunks (OPT) and (B) Oil palm fronds (OPF).

Figure 2-7: Biomass wastes from palm oil mills. (A) Empty fruit bunches (EFB), (B) Palm mesocrap fiber (PMF) and (C) Palm kernel shells (PKS).

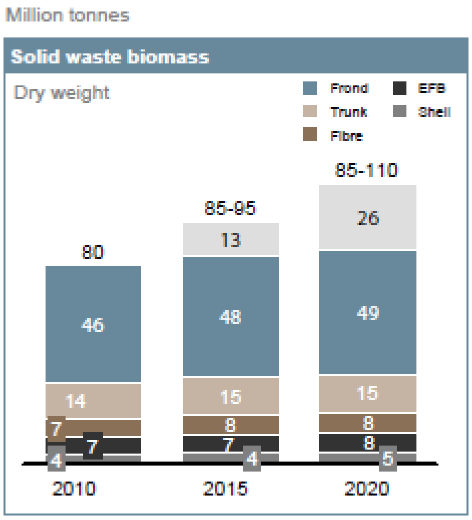


Figure 2-8: The quantity of palm oil wastes produced in 2010, 2015 and estimated value for 2020.

Therefore, palm oil waste used as the renewable energy sources is workable and has high potential to replace the conventional energy sources. The palm oil residues that chosen in this project are palm kernel shell (PKS) and palm mesocrap fiber (PMF). About 140 MT (tons) lignocellulosic wastes which correspond to 17 MT (million tons of oil equivalents) is generated by palm oil industry annually. The total palm oil residue energy potential of 17 MToes able to contribute and decrease the consumption of fossil fuels (Uemura et al., 2011).

2.5 Utilization of palm oil wastes as energy source

Nowadays, global warming and sustainable development are the main concern of the researchers. Scientific data showed that average global temperate increase by more than 2 ℃ would make millions of people lose their lives. Greenhouse gaseous such as carbon dioxide, methane and nitrous oxide are causes of global warming. Nevertheless, carbon dioxide has been acknowledged as the main culprit due to utilization of fossil fuel as a source of energy emits a lot of carbon dioxide (Shuit et al., 2009; Wang et al., 2014). From the research of Lim and Teong (2010), the emissions of greenhouse gases by fossil fuels will increase by 39% in 2030 if no action or alternative solution to replace the fossil fuels. Figure 2-9 shows the total carbon dioxide emissions from fossil fuels in Malaysia was increasing every year. Huge accumulation of greenhouse gases in atmosphere not only cause global warming, it will bring along acid rain and smog. In order to maintain sustainable development and reduce global warming effect, utilization of renewable energy is the best choice.

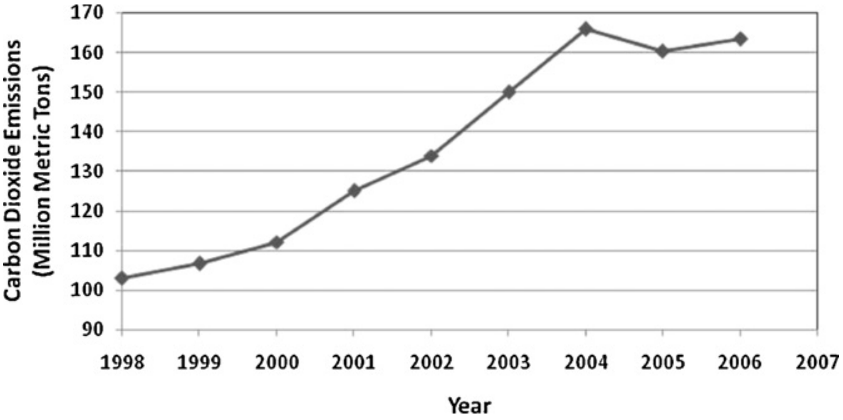


Figure 2-9: Total carbon dioxide emission from consumption of fossil fuels in Malaysia.

Malaysia is a country that has significant amount of agricultural activities which cause biomass be a very promising alternative source of renewable energy. Forest biomass and palm oil residue are potential biomass sources since they have high energy value. Reports of (Ng et al., 2012); Shuit et al. (2009) mention that palm oil plantation play an important role as ‘carbon sink’, palm oil plantation consumes up to 64.5 tonnes of carbon dioxide per hectare per year while virgin rainforest only can assimilate 42.2 tonnes per hectare per year. Converting palm oil wastes into bio-fuel not only overcome fossil fuel crisis but also can help to reduce the greenhouse gas, protect the environment. Palm oil tree as a carbon neutral element because when utilized the palm oil trees through process like combustion or decompose, the amount of carbons released into the environment are equivalent to the amount of carbons absorbed in their lifetime which means there is no net increase of carbon to the environment (Awalludin et al., 2015). Up to year 2001, under Small Renewable Energy Power Program (SREP), 25 out of 62 projects that have been approved, focus on using palm oil waste as fuel source (Ludin NA, 2004). This phenomenon shows that Malaysia is focusing on using palm oil waste as energy source. The palm oil industry has been categorised as the key industry for expansion to achieve economic evolution along with development of greener production processes in Malaysia (Ng et al., 2012). Private and public institutions are actively doing research on palm oil wastes. As a result, used of palm oil wastes is a clean source of energy where minimize negative effect to the environment and produce less secondary wastes. Realisation of palm oil waste’s potential for producing various useful resources can be said as waste converted into wealth.

Malaysia government had launched complete economic growth effort called Malaysian Government’s Economic Transformation Programme (ETP) in October 2010. Improvement and utilization of palm oil wastes and enhancement of related industries is one of the twelve critical factors of ETP. EPT focuses to increase the palm oil production, but at the same time, wastes utilization of palm oil biomass as one of the key factor to achieve the goal. Therefore, second generation biofuels from palm oil wastes is focused to be commercialized (Awalludin et al., 2015). Besides that, in Eight Malaysia Plan in 2001, renewable energy was classified as fifth energy source after the four main primary energy sources like oil, gas, hydropower and coal. Malaysia aims to replace the usage of fossil fuel to other alternative that environment friendly. Palm oil wastes appear to be the potential energy sources due to its abundance, and they are renewable. Therefore, sustainable development with encouraging long term energy project and increase employability rate will achieve by utilization of palm oil wastes as energy sources.

2.6 Chemical composition of palm oil wastes

A comprehensive study on the chemical composition and major organic components in palm oil wastes is essential. Palm oil wastes contain high amount of common organic components such as lignin, cellulose, hemicelluloses and extractives. Palm oil trees carry out photosynthesis process as shown in Figure 2-10. Equation 2.1 shows conversion of CO_2 and sunlight into chemical energy leading to cellulosic biomass (Akhtar & Amin, 2011). The leaves of palm oil plant contain chlorophyll which acts as catalyst to convert the CO_2 and H_2O absorbed to be plant’s food by electrochemical reduction process. The food produced is consumed by the plant for growing purpose.

$$6CO_2 + 5H_2O \xrightarrow{\text{Sunlight}} C_6H_{10}O_5 + 6O_2 \tag{2.1}$$

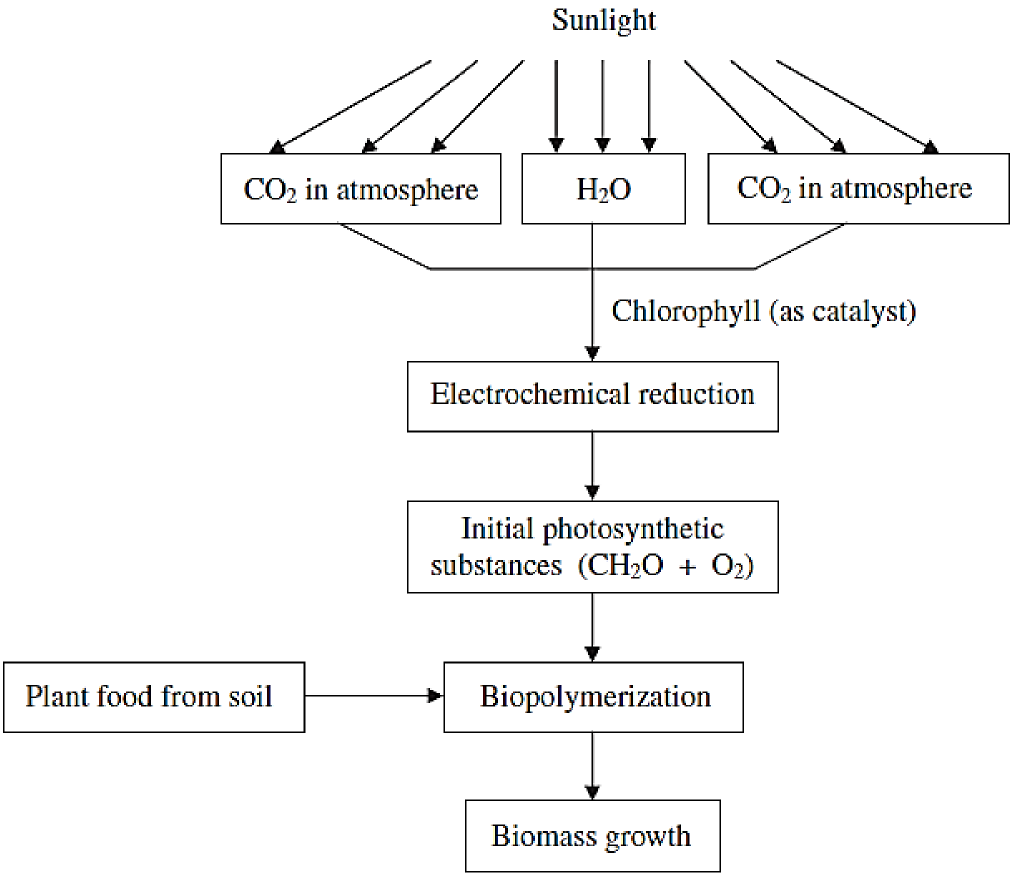


Figure 2-10: Photosynthesis process of biomass growth (Demirbas, 2009).

The chemical composition of palm oil wastes consists of holocellulose (cellulose and hemicellulose), lignin, extractives and ash as shown in Figure 2-11. Holocellulose indicates alpha cellulose (α-cellulose) and hemicellulose as main components of total polysaccharide fraction (Awalludin et al., 2015).

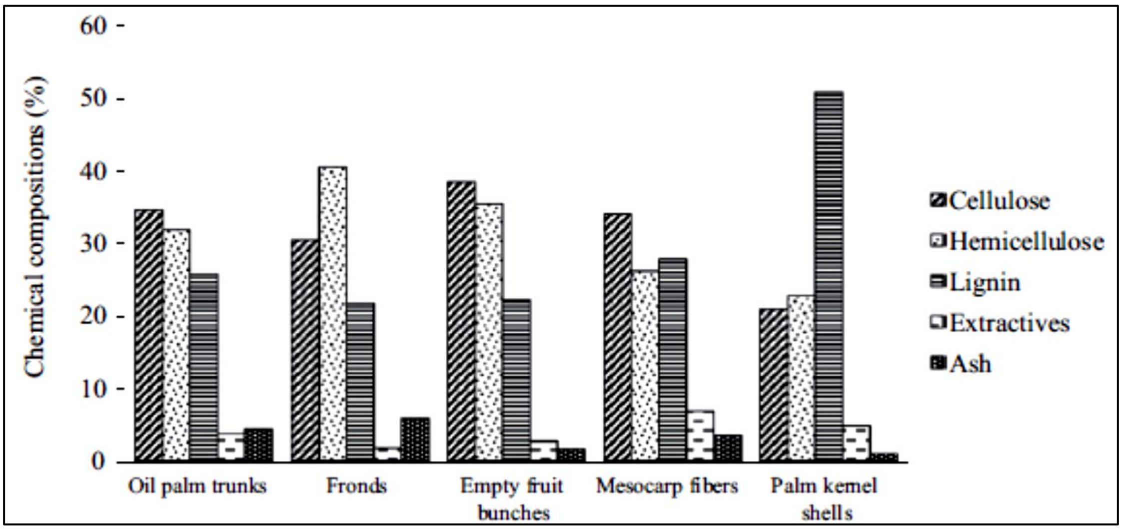


Figure 2-11: Chemical composition of palm oil wastes (Kelly-Yong et al., 2007).

Alpha cellulose is an insoluble polysaccharide having general formula $(C_6H_{10}O_5)_n$ and an average molecular weight range of 300,000 – 500,000. Cellulose is hydrophobic and constitutes approximately 50% of the cell wall material (Yaman, 2004). The chemical structure of palm oil waste's cellulose is shown in Figure 2-12.

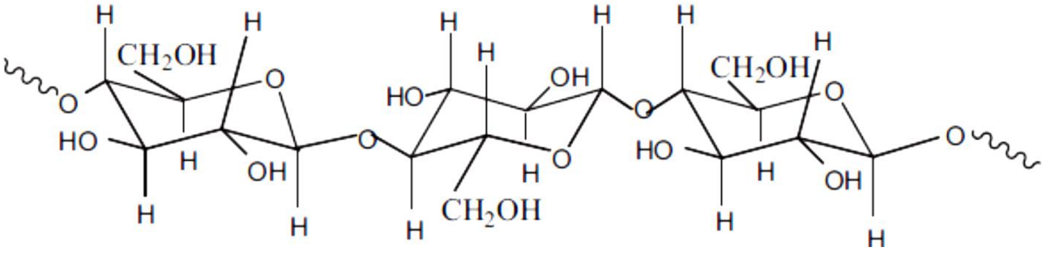


Figure 2-12: Chemical structural of cellulose (Mohammed et al., 2011).

Hemicellulose is complex polysaccharides that play a role in association with cellulose in cell wall with general formula $(C_5H_8O_4)_n$. Hemicellulose is known to be soluble in dilute alkali and its' branched structures which vary among different woody and herbaceous biomass species. Hemicellulose carries 50-200 monomeric units and few simple sugar residues (Yaman, 2004).

Lignin mostly found in the cell walls of woody species biomass and often bound to adjacent cellulose fibers (act as binder) to form a lignocellulosic complex which supporting all cells and microfibrils in the lignocellulosic structure (Awalludin et al., 2015). Lignin is quite resistant to conversion by microbial systems and chemical agents since it is highly branched, substituted and mononuclear aromatic polymers. Lignin occupies about 20% to 40% by weight on dry basis of softwoods and hardwoods (Yaman, 2004). Figure 2-13 shows the general texture structure of the palm oil biomass and the chemical structure of lignin is shown in Figure 2-14.

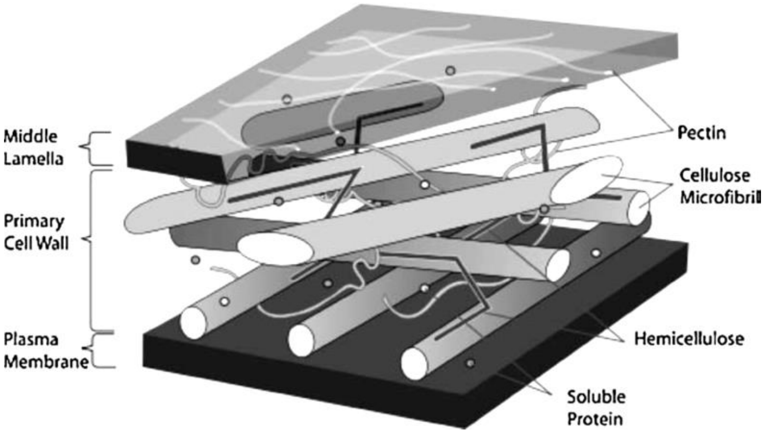


Figure 2-13: Texture structure of biomass (Mohammed et al., 2011)

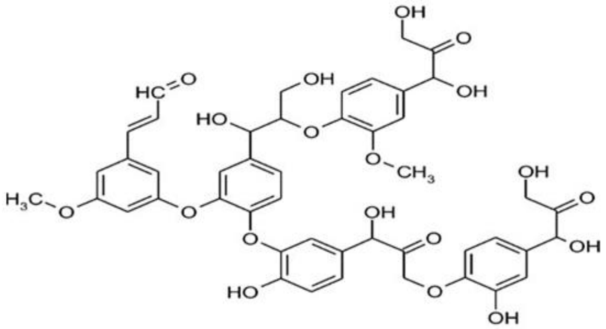


Figure 2-14: Chemical structure of lignin (Mohammed et al., 2011).

Palm oil waste contains less than 10% of extractive and ash. There are less number of researchers study the uses of palm oil extractives. However, quite a number of researches on the usage of palm oil waste’s ash had been carried out. Ash of palm oil waste are used as active adsorbents for dry-type flue gas desulfurization (Zainudin et al., 2005), adsorbent for removal of metal ions from solution (Shawabkeh et al., 2004), adsorbent for removal of reactive blue 19 dye (M. Hasan, 2008) and etc.

2.7 Usage of palm oil wastes

Palm oil wastes are very abundant in Malaysia since Malaysia is the second largest palm oil production country. A lot of researches on the usage of palm oil wastes had been done by researchers of public and private universities. Based on Abdullah and Sulaim (2013), palm oil wastes were utilized as energy sources such as palm oil mills used palm oil biomass as boiler fuel, palm oil mill effluent treated with anaerobic system to produce bio-gas and palm oil briquettes able to generate electricity for large commercial scale. Besides that, the EFB can be used as fertilisers since EFB contains a lot of nutrients and palm oil fibre extracted from EFB used for production of thermoplastic and thermostat composites. Table 2-1 shows the usage of the palm oil wastes based on different part of the palm oil wastes.

Table 2-1: The usage of palm oil wastes.

Author	Raw material	Usage
Abdullah and Sulaim (2013)	➢ Palm oil mills (fibre and shell)	• Boiler fuel to produce process steam for sterilisation in mill complex.
	➢ Palm oil mill effluent (POME)	• Anaerobic treating system produces bio-gas.
	➢ EFB	• Fertiliser & soil conditioning agent (releases nutrients via microorganisms). • Fibrous crop residues which suitable used as paper-making pulp.
	➢ Palm oil trunk	• Used to produce saw-wood, lumber. Palm oil trunk chipped and waxed with resin to produce preformed desk tops and chair seat for schools.
	➢ Palm oil fibre extracted from EFB	• Main material for production of thermoplastic and thermostat composites which has reach commercialization stage.

	➢ Palm oil briquettes	• Used as fuel in producing steam, district heating, and generate electricity for large commercial scale.
Zainudin et al. (2005)	➢ Palm oil ash	• Utilised as adsorbent to remove the pollutant gases such as nitrogen and sulphur oxide.
Mohamed et al. (2010)	➢ Palm oil shell	• Palm oil wastes that rich with lignocellulosic materials are utilized to produce carbon molecular sieve (CMS). Palm oil wastes are chosen because low cost and contain abundant carbon source.
Power (2006)	➢ EFB	• EFB as the raw material for the biomass power plants which plan to build in eastern province of Sabah, Malaysia. 2 biomass power plants can generate 10 MW of electricity.
"Japanese company plans to turn oil palm waste to biofuel in Malaysia" 2006)	➢ Palm oil trunks, palm oil fronds, EFB and PKS	• The palm oil wastes like palm oil trunks, palm oil fronds, EFB and PKS are used as feed stock in a plant to produce bio-ethanol. The plant will be introduced in Malaysia by Japan’s Mitsui Engineering & Shipbuilding Co.Ltd (MES).
Shuit et al. (2009)	➢ EFB	• EFB is used as fuel source to generate electricity. The biomass plant is plan to be built at Jengka, Pahang due to memorandum signed by Tenaga Nasional Berhad (TNB) with Felda Palm Industries Sdn. Bhd. And Japan’s J-Power. • Bioplastics which are similar to petroleum-derived plastic that can be used for production of foil, molds, tins, cups, bottles and other packaging materials. Bioplastic is 100% biodegradable and able to recycle, composted or burned without producing toxic by-product.

From Table 2-1, palm oil wastes have a lot of usage. However, torrefaction pre-treatment will increase the value of the palm oil wastes used as energy resources. Thus, the palm oil wastes should be undergoes torrefaction pre-treatment.

2.8 Torrefaction pre-treatment

The optimum condition to torrefied palm oil wastes is at temperature 300 ℃ and inert condition. Solid fuel produced from oil palm fiber show higher energy density and less volume with torrefied under nitrogen at temperature of 300 ℃ (Lu et al., 2012). Based on W. H. Chen (2011), for the torrefaction temperature of 275 ℃, 52.6 wt% of hemicellulose is lost, while for torrefaction temperature of 300 ℃, only 16.8 wt% of hemicellulose is consumed. The torrefaction temperature has divided into 3 categories, biomass torrefied at temperature 200 ℃ and 225 ℃ pertain light torrefaction; 250 ℃ is mild torrefaction and 275 ℃ and 300 ℃ belong to severe torrefaction(W. H. Chen, 2011). Thus, the range of temperature used in this project was 240 – 330 ℃ belonged to mild and severe torrefaction.

Torrefaction pre-treatment had implemented for a lot of biomass in the world to increase the quality of the biomass fuel. Table 2-2 shows effects of the different type biomass torrefied at specific conditions.

Table 2-2: Torrefaction on different type of biomass and the effects.

Author	Material	Size of raw material	Reactor type and size	Condition	Effect
Arias et al. (2008)	10 g of woody biomass (eucalyptus)	< 5 mm	Horizontal quartz reactor with diameter 50 mm and length 300 mm.	Heat treatment at temperature 240 ℃, 260 ℃ & 280 ℃ in an inert condition with 50 ml/min of N_2.	i) Mass loss due to decomposition of some reactive components of the hemicellulose. ii) Removal of oxygen content about 26% by release of CO_2 and CO which means the O/C ratio decrease and improve the gasification properties of torrefied biomass. iii) The gross calorific values of the torrefied biomass increase by 34%. iv) The higher heating value of torrefied biomass at 240 ℃ yield was 92% and drop to 67% when torrefied at 280 ℃. v) Mild torrefaction treatment at 240 ℃ for 30 min is the best condition since could improve the grinding characteristic and little loss of heating value yield.
Thanapal et al. (2014)	500 g of Mesquite and Juniper samples per batch.	2-4 mm and 4-6 mm.	Batch type reactor.	Temperature from 200 to 300 ℃ and constant flow of 30 SCFH (0.85 m^3/h) of N_2/CO_2.	i) Torrefaction using CO_2 as medium show higher mass loss. ii) The maximum energy yield occur around 250 ℃. iii) Improve the grindability of

					biomass resulting from breakdown of fibres and increased porosity of the treated biomass.
Chin et al. (2013)	50 g of dried wood fine (*Acacia spp, Macaranga spp*), EFB and palm oil trunk.	Diameter range between 10-15 cm.	Tube furnace.	Temperature 200 ℃, 250 ℃ and 300 ℃ for 15 min, 30 min and 45 min with continuously flow of N_2 at flow rate (0.5-1.0 L/min).	i) The extractives content tented to increase when torrefied below 250 ℃, whereas torrefied above 250 ℃ cause the extractives content decreased. ii) Holocellulose content decreased dramatically with increasing severity of torrefaction. iii) Decomposition temperature - Hemicelluloses (225-300 ℃) Cellulose (305-375 ℃) Lignin (250-500 ℃). iv) The energy value ranged from 18.08 to 28.94 MJ/kg which implies the higher heating value of torrefied biomass increased by 0.37% to 67.9%. v) High energy density of torrefied biomass is due to ether and carbon-carbon linkages in lignin and torrefied biomass had high lignin content.
Chen et al. (2016)	20 g of Oil palm fiber (OPF) sample.	Fiber pellets length ad diameter about	Cylindrical chamber.	Severe torrefaction at 275 ℃ – 350 ℃, by flow of N_2 or O_2.	i) Percentage of fixed carbon increase and volatile matter decreased. Percentage of fixed

		30 mm and 8 mm.			carbon higher than volatile matter when torrefied at temperature 300 ℃. ii) Higher fixed carbon percentage indicates higher calorific value and quality of torrefied OPF. iii) The decline in the H/C and O/C ratios are due to dehydration, deoxygenation, and dehydrogenation of OPF where water and light volatiles are released. iv) HHV of OPF increased from 18.37 MJ kg^{-1} (untorrefied) to 20 MJ kg^{-1} (torrefied). v) HHV of OPF torrefied at 350 ℃ is close to HHV of subbituminous coal.
Granados et al. (2014)	10 mg for each type of biomass (sugarcane bagasse, banana rachis, rice husk, palm oil fiber, sawdust and coffee waste)	Particle size of 150 μm (mesh 100)	APT STA 1600LINSEIS-type TGA	Temperature 110 - 250 ℃, inert condition with N_2 supplied at rate 50 ml/min.	i) 180-190 ℃, the hemicelluloses decompose to produce volatiles (CO_2, CO) and low fractions of liquids like acetic acid. ii) Mass loss higher than energy loss leads to densification of biomass, increase the HHV.

A lot of studies about torrefaction are done with different type of biomass as shown in Table 2-2. Torrefaction improves the quality of the biomass in term of increase the HHV value, improve the grindability, increase the porosity of the treated biomass due to breakdown of fiber, and removal of the oxygen content.

2.9 Torrefaction effects

A lot of technologies are proposed and utilized for exploit biomass to produce energy. Example of the technologies are thermochemical (combustion, gasification), biological (anaerobic digestion, fermentation) and chemical processes (esterification) (Arias et al., 2008). In order to make use of palm oil waste as energy source and competitive to conventional energy, torrefaction on palm oil waste is the best choice. Torrefaction is a pre-treatment on biomass at low cost and torrefied products retains 80 – 95% of the energy and 70 – 90% of the mass of original raw biomass (Bates & Ghoniem, 2012). Torrefaction remove the moisture content and thermally degrades the lignocellulosic structure of biomass especially for the reactive hemicellulose fraction (W. H. Chen, 2011). During torrefaction process, the torrefied biomass decrease in mass and increase in energy density at the same time due to water and a part of the volatiles are released (L. Shang et al., 2011; Zheng et al., 2014). Torrefied PKS and PMF showed excellent energy yield values of 100% and 96%, respectively. On the other hand, torrefied EFB exhibited a rather poor yield of 56% (Uemura et al., 2011). According to Sabil et al. (2013a), torrefied PKS has the highest carbon fraction with 58.7% while torrefied PMF has the highest gross calorific value (GCV) with 23.73 MJ kg^{-1}. The research of Sabil et al. (2013b) mentions the GCV and carbon content increase with the increase of torrefaction temperature and the O/C ratio drop, H and O content decrease for all residues. The energy density of fuel pellets produced from torrefied biomass almost similar to low rank coal with amount of 14,000 MJ m^{-3} (Stelte et al., 2013) and Table 2-2 also shows the effects of torrefaction on biomass. Torrefied biomass also showed a significant improvement in hydrophobic properties improving torrefied biomass moisture resistance and potential for outdoor storage (Acharjee et al., 2011; Arias et al., 2008; Sarvaramini et al., 2013). All the results from the research indicate torrefaction is the best choice to increase the quality of palm oil wastes as energy sources.

2.10 Scanning electron microscope (SEM)

SEM is proposed to analyse the raw materials and torrefied materials. SEM uses a focused bean of high-energy electrons to generate a variety of signals at the surface of specimens. Through SEM analysis, information about the sample such as external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the samples able to collected (Center, 2016). According to research of Sabil et al. (2013a), SEM analysis shown the internal structure of EFB and PMF was most affected by torrefaction treatment. Severe torrefaction decomposed the internal structure of EFB and PMF which the sharpen edges on the raw EFB had flattened and the pores on surface of raw PMF had diminished.

2.11 Bomb calorific meter

Bomb calorific meter is used to measure the calorific or energy value of the samples. Bomb calorific meter provide the calorific value in term of high heat value (HHV) which includes the latent heat of vapour released by sample. Low heat value (LHV) is the best data to be compared since it does not contain any contribution like latent heat of vapour. LHV can be obtaining from HHV by the Equation 2-1.

$$LHV = HHV = (21.987_{WH} + 2.443_{WW}) \tag{2-1}$$

Where LHV and HHV are in MJ/kg, $_{WH}$ is the hydrogen mass fraction of the specimen, $_{WW}$ is the free water fraction (Uemura et al., 2011).

2.12 Thermogravimetric analysis (TGA)

TGA is used to analyse the thermal decompositions of main constituents of biomass, namely, hemicellulose, cellulose and lignin, in a torrefaction environment (W. H. Chen, 2011). Besides that, the aim of kinetic evaluation of TGA data is to obtain relatively a simple model to describe the torrefaction of biomass (Lieve Helsen, 2000).

TGA also used to analyse the weight loss of a sample is recorded against temperature under controlled heating rate and gas atmosphere. Differential thermogravimetric analysis (DTG) curves which derived from thermogravimetric (TG) curves have been widely applied to biomass to evaluate pyrolysis kinetic (Yaman, 2004).

2.13 CHNS analyser

CHNS analyser is used to analyse the elemental composition of the compound. Based on Sabil et al. (2013a), the chemical characteristic of the solids biomass are verified using elemental analysis. The elemental analysis is performed using LECO CHNS elemental analyser to measure the elemental value of carbon, hydrogen, nitrogen and sulphur.

2.14 Gas chromatography

The volatile composition is analysed with gas chromatography (GC). The gaseous products were analysed using gas chromatograph with thermal conductivity detector (Awalludin et al., 2015).

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter is discuss about the method and materials used to carry out the torrefaction reaction and the analysis carried out to the torrefied biomass.

3.2 Collection of raw materials

The raw biomasses used in this study were palm mesocrap fiber (PMF) and palm kernel shells (PKS). These palm oil wastes were collected from palm oil plantation in Felda Lepar, Gambang, Pahang.

3.3 Preparation of raw materials

The equipment used for preparation of raw materials consists of *Memmert* Universal Oven located at biological lab of University Malaysia Pahang (UMP), *Retsch* Ultra Centrifugal Mill ZM 200 located at analytical lab of UMP, AY220 Electronic Balance located at analytical lab and normal sieve plate. The raw materials were dried in *Memmert* oven at 100 ℃ for 4 – 8 hours and weighted the dried biomass until constant weighted was achieved. The dry palm oil wastes were grinded with *Retsch* Ultra Centrifugal Mill and sieved into 0.5 – 1.0 mm in diameter (to ensure the raw materials are uniform in a size of diameter). Then, the prepared raw materials were placed in plastic bags and stored in container at room temperature until the torrefaction and analysis were carried out.

3.4 Torrefaction experiment

Torrefaction reactor that located at gas laboratory of UMP was used for the torrefaction experiment. A vertical reactor which was a stainless steel tube with an internal diameter of 22.4 mm and a length of 500 mm was used for torrefaction process. A plate with a hole which located 200 mm above the bottom of tube with a small amount of glass wool on the plate to prevent leakage of biomass sample during torrefaction process. About 2.5 g of the biomass sample (PKS) was weighed by AY220 Electronic Balance and filled it in the reactor. The reactor was flushed with nitrogen gas at flow rate of 10 ml/min for 5 min to provide an inert surrounding. After that, the reactor was heated up to final temperature (240 ℃) with a surrounded electric heater and heating rate was 40 ℃/min. After 30 minutes which was the residence time, the heater was turned off and the reactor was left to cool down to ambient temperature. The experiment was repeated with different final temperatures (270 ℃, 300 ℃ and 330 ℃), different raw materials (PMF) and different residence time (60 min).

3.5 Physical Appearance

The physical appearance of the raw materials and every torrefied products for each temperature of 30 min residence were taken by using Nikon D5200 (Digital DSLR).

3.6 Elemental analysis (CHNS)

Elemental analysis was conducted to measure the C, H, N and S content in the raw palm oil biomass and torrefied biomass. The LECO CHNS elemental analyser was operated with constant helium flow at 1000 ℃. 2 mg of sample was used for each measurement (Sabil et all., 2013). Elemental analysis or ultimate analysis was carried out by Central Laboratory of Universiti Malaysia Pahang which honour with certificate of analysis (COA). The equipment used for this analysis was CHNS model Elementar Bario Macrocube. Elemental analysis was carried for the raw materials samples and torrefied products for each temperature at 30 min residence time.

3.7 Proximate Analysis

Moisture content

The moisture content, ash content and volatile content of raw materials and torrefied biomass was determined during proximate analysis. To identify the moisture content, a sample (3 g) was weighed in crucible and was placed in an electric oven at temperature 105 ℃ for 24 hours (Uemura et al., 2013). After 24 hours, the sample was weighed every one hour till the weight is constant.

$$moisture\ content = \ ((Wi - Wf)/Wi) \times 100 \qquad (3\text{-}1)$$

Where:

Wi – Initial weight, g

Wf – Final weight, g

Ash content

The ash content was measure as follows. A sample (1 g) was weighed in crucible, and was placed in an electric furnace and temperature was raised to 600 ℃. After 3 h, the furnace was turned off and was allowed to cool down. Then, the crucible containing the ash was weighed (Uemura et al., 2013). Return the crucible to the furnace for 1 h at 600 ℃, cool again and reweigh. Repeat this step until the mass of crucible varies by less than 0.3 mg from previous weighing. The ash content was determined follow the E1755-01, Standard Test method for Ash in Biomass.

Volatile content

The volatile matter was analysed follow the prepASH (Practice). A sample (1 g) was weighed in cylindrical silica crucible, and placed in a muffle furnace and the temperature increased to 900 ℃ for 7 minutes. The volatile matter was determined under rigidly controlled standards.

3.8 Surface morphology

Surface morphology of raw materials and torrefied biomass was determined using scanning electron microscope Model 1430 Germany (Sabil et all., 2013). Surface morphology analysis was carried out by using Carl Zeiss Evo 50 Scanning Electron Microscope located at Cariff Research Center Laboratory of UMP. About 10 mg sample was prepared for each analysis. The raw materials and all the torrefied products for every temperature at residence time of 30 min were analysed.

3.9 Volatile analysis

Volatile analysis was carried out by using *AGILENT 6890N* Gas Chromatography Thermal Conductivity Detector (GC-TCD). Volatile analysis was carried out to determine the components of gas produced during torrefaction of the palm oil wastes. The effluent (gas) was collected using gas bag and tested the gas by using Gas Chromatography (GC).

3.10 Measurement

3.10.1 Calorific value determination

Model 1341 Oxygen Bomb Calorimeter was used to determine the calorific value of the torrefied products. The calorific values of raw materials (PMF & PKS) and all the torrefied biomass for each temperature and residence times were measured using a bomb calorimeter to identify the changes after the torrefaction process.

Each analysis consumed about 0.5 g of the sample. The value from bomb calorimeter was high heat value (HHV), which includes the latent heat of vapour emitted from the specimen (Uemura, Omar, Tsutsui, & Yusup, 2011).

3.10.2 Mass and energy yield analysis

The biomass was subject to change in mass and energy yield during the torrefaction process. In present study, Mass and energy yield (Y_{mass} and Y_{energy}) of the torrefied biomass obtained from the following equations (Sabil et al., 2013a).

$$Y_{mass}(\%) = \left(\frac{mass\, after\, torrefaction}{mass\, before\, torrefaction}\right) \times 100 \tag{3-2}$$

$$Y_{energy}(\%) = Y_{mass} \times \frac{higher\ heating\ value\ of\ torrefied\ biomass\ (HHV_{torrefied\ biomass})}{higher\ heating\ value\ of\ raw\ biomass\ (HHV_{raw\, biomass})} \tag{3-3}$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter presents the results and discussions for the research work. The results on physical appearance, moisture content, morphology analysis, elementary analysis, experimental calorific value, mass yield & energy yield and volatile analysis were discussed in detail in this chapter.

4.2 Physical appearance

Physical appearances of the torrefied biomass indicate the level of torrefaction. Based on Figure 4-1, the colour of the biomass became darker as the torrefied temperature increased. Biomass that torrefied at temperature 240 ℃ did not have much different with the raw material. The torrefied PKS and PMF showed the darkest colour when torrefied with 330 ℃. A similar tendency was observed from torrefied of Empty Fruit Bunch (EFB) and woody biomass (Arias et al., 2008; Uemura et al., 2011). Besides that, the torrefied PKS and PMF were lighter in weight, and more brittle (improve in grindability) which same result with torrefied on woody biomass (Kolokolova et al., 2013). The torrefied biomass showed darken colour due to increase of the carbon content. This statement was supported by the results of CHNS analysis, PKS biomass carbon content increased from 47.79% (raw PKS) to 59.92% (torrefied @330 ℃), PMF biomass carbon content increased from 45.2% (raw PMF) to 53.99% (torrefied @330 ℃). Besides that, PKS biomass was darker in colour compared to PMF biomass as shown in Figure 4-1 because PKS contained high density of carbon content (Chin et al., 2013).

	Palm Kernel Shell (PKS)	**Palm Mesocrap Fiber (PMF)**
Raw material		
Torrefied 240 ℃ @ 30 min		
Torrefied 270 ℃ @ 30 min		
Torrefied 300 ℃ @ 30 min		
Torrefied 330 ℃ @ 30 min		

Figure 4-1: The physical appearances of raw materials and torrefied products.

As a conclusion, PKS and PMF biomass colour become darker with increased of the temperature of torrefaction indicated the carbon content of the biomass increasing with the temperature of torrefaction. Besides that, PKS biomass naturally content higher carbon content than PMF biomass which cause PKS biomass was darken in colour.

4.3 Morphological analysis

The morphology of raw materials (PKS & PMF) and all the torrefied products with residence time of 30 min were analysed and the results are presented in Figure 4-2 and Figure 4-3.

Figure 4-2 shows the morphology of the raw PKS and the torrefied products at 240 ℃, 270 ℃, 300 ℃ and 330 ℃ with 30 min residence time. From Figure 4.2, torrefied PKS biomass was clearly reduced in size of particles and loosely packed compared to raw PKS biomass. The particles of PKS biomass torrefied at 330 ℃ showed a major different with reduced in particles size and loosely packed was due to decomposition of lignin content. Based on Basu (2013), the lignocellulosic components decomposed as the temperature below:

Hemicellulose : 225 – 300 ℃
Cellulose : 305 – 375 ℃
Lignin : 250 – 500 ℃

PKS biomass was a high lignin content biomass, so a major changes on the size reduction and sign of decomposed were clearly shown when torrefied at temperature 330 ℃ (Sabil et al., 2013a). Besides that, high temperature torrefaction decomposed the lignocellulosic structures; make the particles' structures weak and loosely packed indicated torrefaction increased the grindability of the products (Arias et al., 2008).

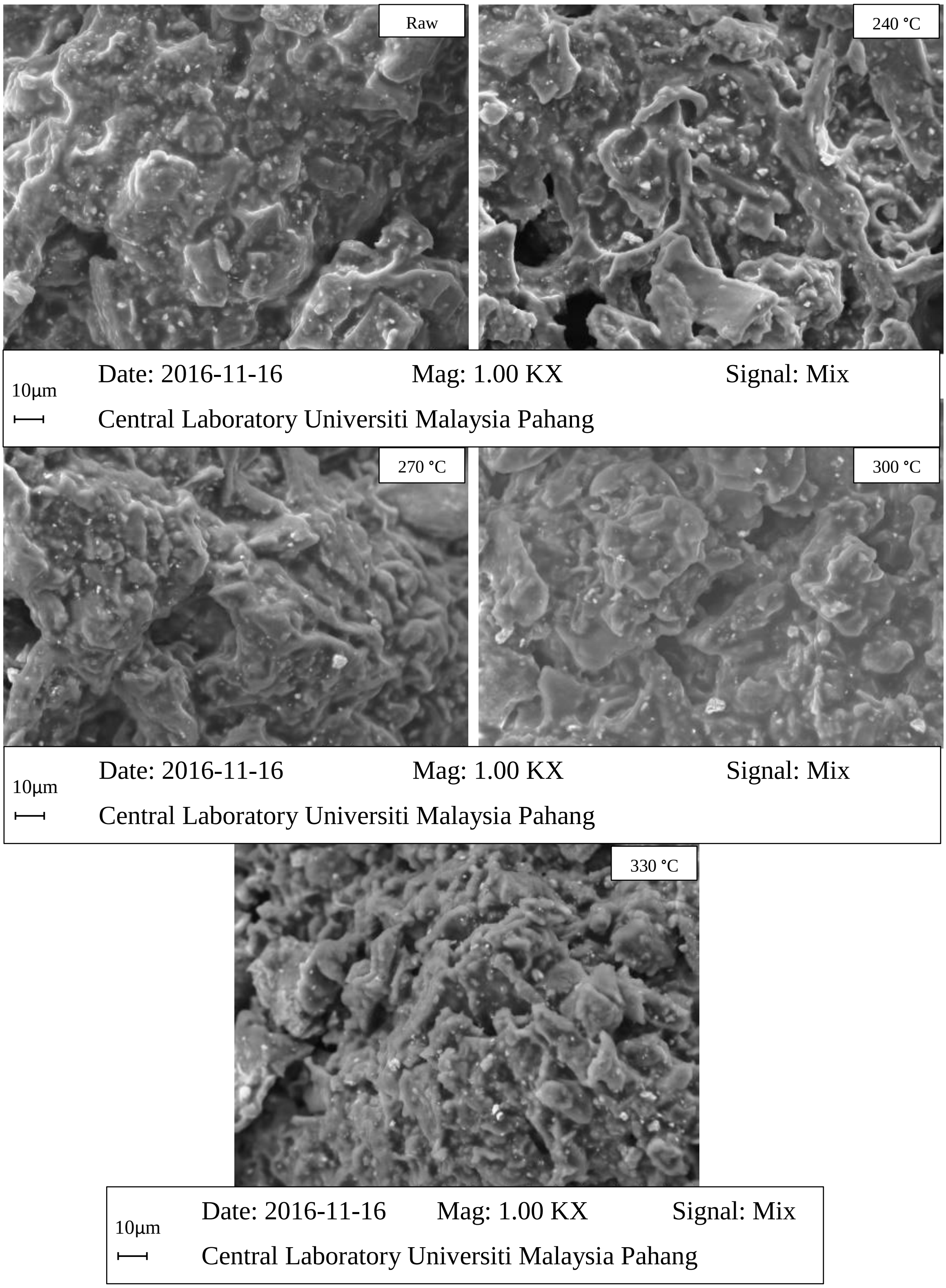
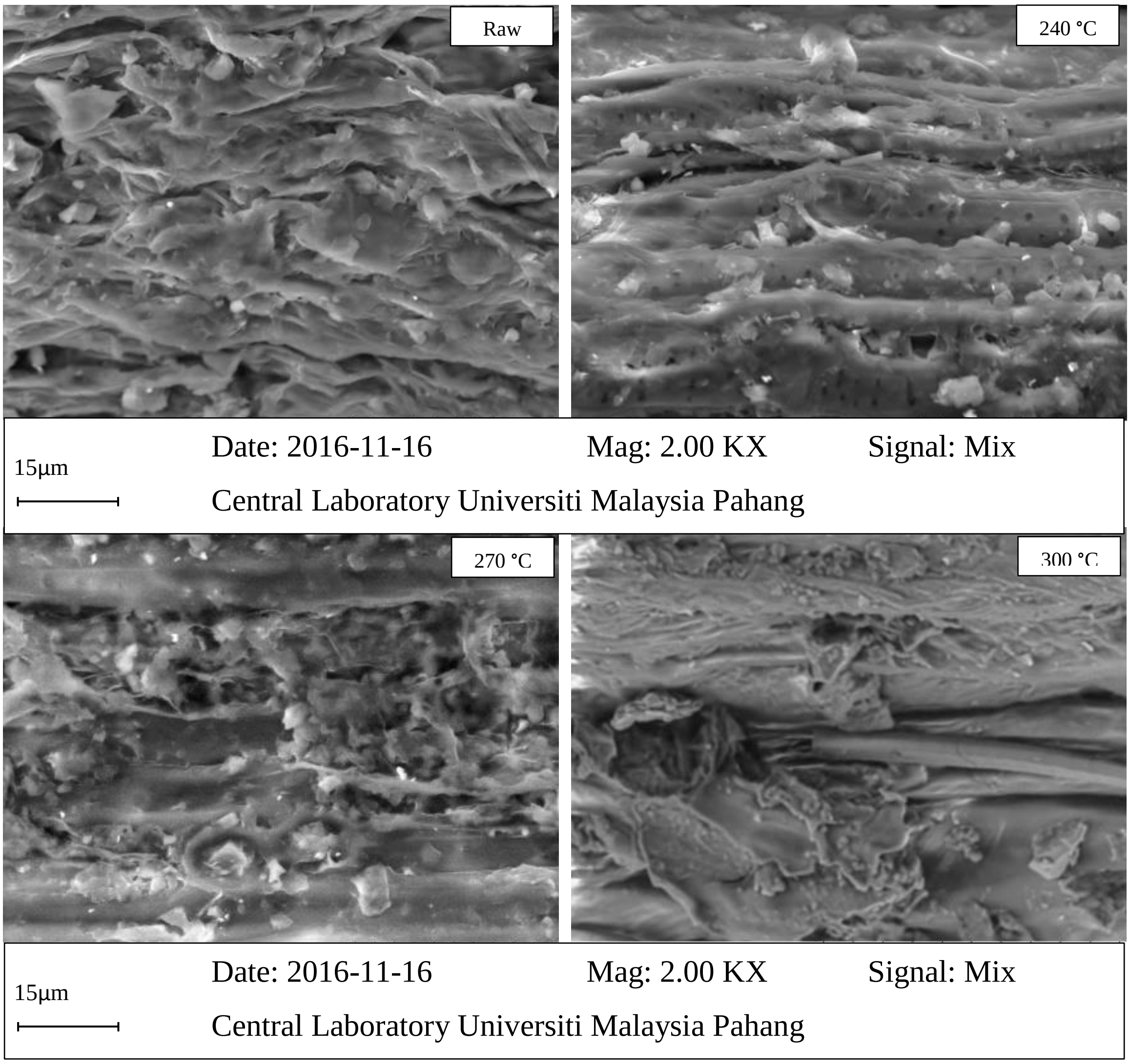


Figure 4-2: SEM images for raw and torrefied PKS.

Figure 4-3 shows the morphology of the raw PMF and the torrefied products at 240 ℃, 270 ℃, 300 ℃ and 330 ℃ with 30 min residence time. PMF was fiber biomass which the particles structure were long cylindrical rod shape as shown in Figure 4-3 and totally different with the particles structures of PKS biomass because PKS was hard shell biomass. Based on Figure 4-3, there were present of tiny pores observed on the surface of the PMF biomass verified PMF was fibrous materials (Sabil et al., 2013a).

Based on Arias et al., (2008), for raw biomass with highly fibrous in nature like PMF had a mixture of large particles and fibers where the fibers formed links between the particles as shown by surface structure of raw PMF biomass in Figure 4-3 and make the biomass hard to be grinded (Arias et al., 2008). However, when the PMF biomass torrefied at higher temperature like 270 – 330 ℃, the linkage was broken and more bigger size pores were observed on the surface structure of PMF torrefied biomass (Sabil et al., 2013a). Broken of the linkage make the particles structures weaken and improved the grindability.



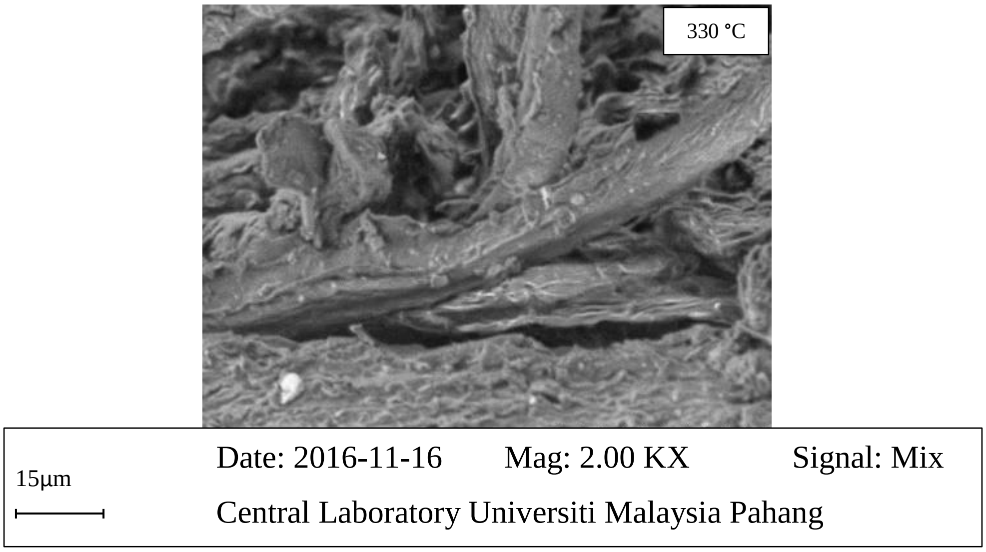


Figure 4-3: SEM images for raw and torrefied PMF.

Section 4.3 concludes torrefaction pre-treatment enhanced the biomass quality by increased the grindability of the biomass. Naturally, biomass was highly fiber content component which make the biomass had low grindability and less competitive to other energy resources like coal. However, this project had proved that biomass was comparative with coal by torrefaction pre-treatment. Torrefaction with higher temperature destroyed the linkage between the molecule and also the cell wall of the biomass. This caused the particles bonding weaken and obviously increased the grindability of the products.

4.4 Proximate analysis

Proximate analysis showed the composition of the biomass in terms of gross components such as moisture (M), volatile matter (VM), ash (ASH), and fixed carbon (FC). Volatile matter can be classified to condensable and non-condensable volatile released during torrefaction reaction. However, only non-condensable volatile was analysed in this study.

Table 4-1 shows the proximate analysis of PKS and PMF with different torrefaction temperature at 30 min residence time. The moisture content plays an important role in selection of the biomass conversion route. Based on Table 4-1, moisture content (MC) of PKS and PMF were 12% and 11% respectively, which were consider low moisture content and they were favored for thermochemical conversion process (Asadieraghi & Daud, 2015).

Table 4-1: Proximate analysis of PKS and PMF.

Biomass	**Condition**	**MC**	**VM**	**ASH**	**FC**
PKS	Raw	12	70	6	12
	240 ℃		67	7	26
	270 ℃		66	8	26
	300 ℃		59	12	29
	330 ℃		50	13	37
PMF	Raw	11	67	6	16
	240 ℃		66	6	28
	270 ℃		65	6	29
	300 ℃		60	7	33
	330 ℃		56	9	35

The volatile matter (VM) of PKS was within range of 50 – 70% while PMF was within 67 – 56%. The volatile matter decreased with increased of torrefaction temperature indicated more volatile was released when torrefaction temperature was high. Besides that, the ash content (ASH) of PKS was slightly higher than PMF at higher torrefaction temperature 330 ℃. In addition, the fix carbon content (FC) for both of the biomass were almost the same and at range 12 – 37%.

4.5 Ultimate analysis and calorific value

Ultimate analysis was carried out for the raw biomass and the torrefied products for every temperature with 30 min residence time. The collected result was shown in Table 4-2.

The value obtained from elemental analysis for PMF and PKS in this work were comparable with reported literature data (Sabil et al., 2013b). The ultimate analysis showed that torrefaction increased the carbon fraction of the torrefied solid while decreased the H fractions. The decreased of H in the torrefied biomass was due to decomposition reactions that took place during torrefaction to produce volatile gases (Sabil et al., 2013a). The N content was exception which remained less than 2 for all torrefaction conditions. Whereas, for S content at any torrefaction conditions, it approximately to zero. Thus, the torrefaction effect on N and S were not significant to be discussed (Sabil et al., 2013b).

Based on the research work by Basu (2013), the hydrogen-to-carbon (H/C) ratio decreased, the effective heating value of the fuel increased. Typically, the H/C ratio of biomass was very high and torrefaction pretreatment able to decrease the H/C ratio due to decomposition of hydrogen in biomass to form volatile gases. Table 4-2 shows the H/C ratios were kept on decreased when temperatures of torrefaction increased. At the same time, the lower the H/C ratio increased the higher heating value (HHV) of the torrefied products. Besides that, the H/C ratio of PKS biomass decreased steadily throughout the torrefaction reaction because PKS was hard shell biomass with mainly consists of lignin which decomposed at higher temperature as discussed in section 4.3. However, a drastic decreased on the H/C ratio of the torrefied PMF at temperature 240 ℃ compared to raw PMF biomass because PMF was fiber biomass that contents a lot of hemicellulose which decomposed at temperature 225 ℃. The H/C ratio of PKS biomass decreased from 0.12 to 0.07 while PMF biomass decreased from 0.20 to 0.06. Similar trend was observed from the projects of other researchers (Sabil et al., 2013a).

Table 4-2: The CHNS analysis result with the Higher Heating Value (HHV) of the raw biomass and torrefied products.

Biomass	**Condition**	**C**	**ΔC (%)**	**H**	**ΔH (%)**	**H/C**	**N**	**S**	**HHV (MJ/kg)**
PKS	Raw	47.79	-	5.95	-	0.12	1.77	0.06	16.15
	240 ℃	51.79	8.37	5.01	-15.78	0.10	1.86	0.08	17.72
	270 ℃	52.35	9.54	5.33	-10.34	0.10	1.63	0.07	19.05
	300 ℃	54.51	14.06	4.55	-23.52	0.08	2.00	0.07	20.92
	330 ℃	59.92	25.38	3.91	-34.26	0.07	2.56	0.09	22.00
PMF	Raw	45.20	-	9.04	-	0.20	3.12	0.11	16.94
	240 ℃	47.70	5.53	3.60	-60.19	0.08	1.35	0.11	18.05
	270 ℃	50.50	11.73	3.59	-60.31	0.07	0.97	0.11	19.17
	300 ℃	53.70	18.81	3.44	-62.01	0.06	1.77	0.12	21.49
	330 ℃	53.99	19.45	3.30	-63.54	0.06	1.78	0.11	22.91

Figure 4-4 shows the carbon content of PKS and PMF biomass referring to the torrefaction temperature with 30 min residence time. Both biomasses showed significant changes especially at higher temperature torrefaction. In the review paper of Tumuluru et al. (2011), the similar result as carbon content increasing with increasing of the torrefaction temperature was discussed. The carbon content increased while hydrogen and oxygen content decreased were due to the formation of water, CO, and CO_2 (Tumuluru et al., 2011). Figure 4-4 shows the carbon contents and calorific values were increased simultaneously with the increased of the temperature for torrefaction. The torrefaction reaction increases the carbon content of biomass in range of 8 – 26% for PKS and 5 – 20% for PMF.

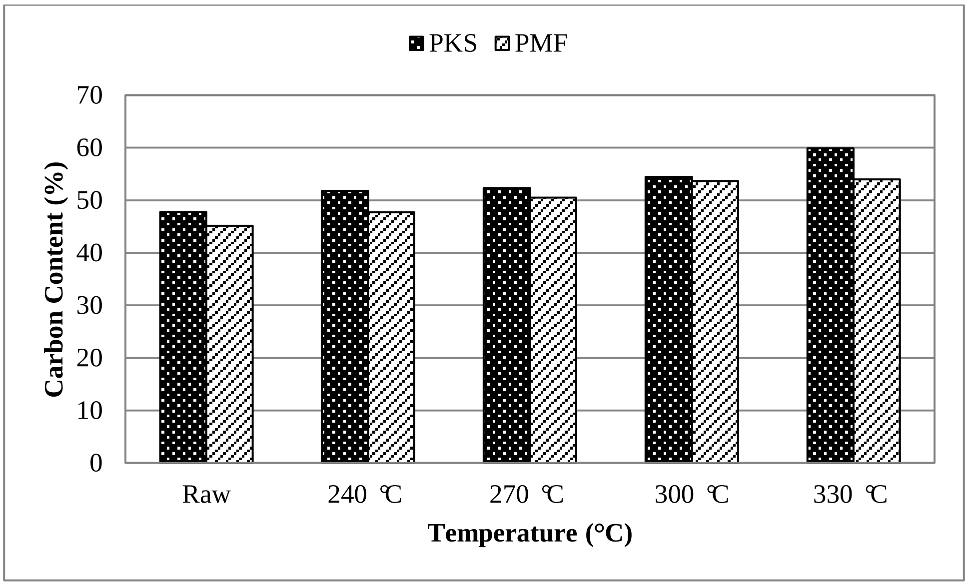


Figure 4-4: Carbon content of PKS and PMF refer to torrefaction temperature for 30 min residence time.

PKS that torrefied at 330 ℃ showed the highest carbon content with 59.92% compared to PMF torrefied at 330 ℃ had carbon content about 53.99% as shown in Figure 4-4. PKS biomass had the largest increment on the carbon content about 25.38% compared to PMF biomass which had increment about 19.45% when both biomasses were torrefied at temperature 330 ℃ and 30 min residence time.

HHV of biomass is an important property of a solid fuel since it is an expression of energy that released when the solid is burnt (Sabil et al., 2013a). Figure 4-5 shows the higher heating value (HHV) of PKS and PMF biomass at different torrefaction temperature with 30 min and 60 min residence time. Obviously, the HHV for both of the biomass was directly proportional to the temperature of torrefaction and residence time. The similar trend also shown in the project carried out by others researchers (Hisham et al., 2016; Sabil et al., 2013a). Biomass loosed relatively more oxygen and hydrogen than carbon during torrefaction process directly increased the calorific value of the torrefied biomass.

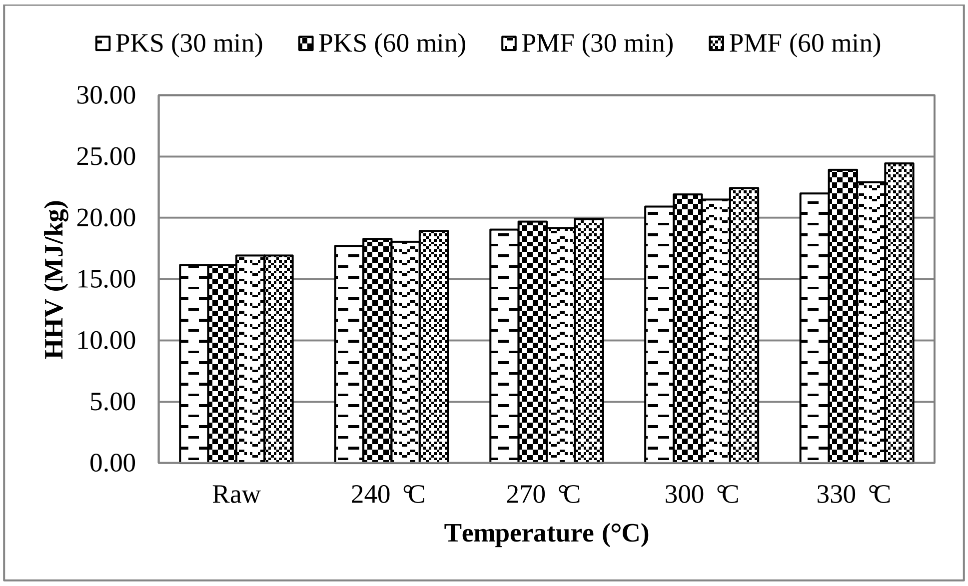


Figure 4-5: Higher heating value (HHV) of PKS and PMF refer to different torrefaction temperature for 30 min and 60 min residence time.

Based on Figure 4-5, increased the temperature of torrefaction for 30 min residence time, and increased the HHV of the biomass in a range of 9 – 37% for PKS and 6 – 36% for PMF. For examples, HHV of PKS biomass increased from 16.15 MJ kg^{-1} to 22.00 MJ kg^{-1} when torrefied at 330 ℃. The same result was obtained for the PMF biomass where the HHV of PMF biomass increased from 16.94 MJ kg^{-1} to 22.91 MJ kg^{-1} when torrefied at 330 ℃. The increased of HHV mainly related to the increased of carbon content of the torrefied biomass (Chin et al., 2013; Sabil et al., 2013a). Besides that, the HHV of the torrefied biomass also depended on the type of biomass (Sabil et al., 2013a).

From Figure 4-5, the increased in the residence time to 60 min, increased the HHV of the torrefied biomass in a range of 3% to 9% when compared to the torrefied biomass with 30 min residence time. It was shown that increased the residence time to 60 min had minor changes on the effect of the torrefaction in term of HHV increment. Based on Basu (2013), there was small effect of residence time on the torrefaction product. However, residence time was not as dominant as the torrefaction temperature. Zheng et al. (2014), in their study had identified the best torrefaction residence time for corncobs was 40 min, not 20 min or 60 min. Arias et al. (2008), the project on investigated the influence of torrefaction on the woody biomass showed the heating value yield remains practically constant from 30 min to 2 hours of torrefaction treatment at temperature of 240 ℃ and 260 ℃. Thus, the residence time influence on the torrefaction was not as significant as the torrefaction temperature.

In Section 4.5, shows the torrefaction pre-treatment increased the calorific value of the torrefied products. The calorific values increased were due to decrease in the ratio of H/C and increased of the carbon content. The decomposition of H element into volatile matters was faster compared to C element, so when torrefaction temperature increased cause decomposition rate of H was faster than C. As a result, the calorific value was increased with the increased of torrefaction temperature and torrefaction able to increase the quality of biomass by increase the calorific value.

4.6 Volatile analysis

During torrefaction of PKS and PMF, the non-condensable gases produced were carbon monoxide (CO), carbon dioxide (CO_2) and methane (CH_4). The volatile released was due to decomposition of the lignocellulosic component such as hemicellulose, lignin and cellulose. Figure 4-6 shows the non-condensable gases obtained from torrefaction of PKS and PMF for 240 – 330 ℃ at 30 min residence time.

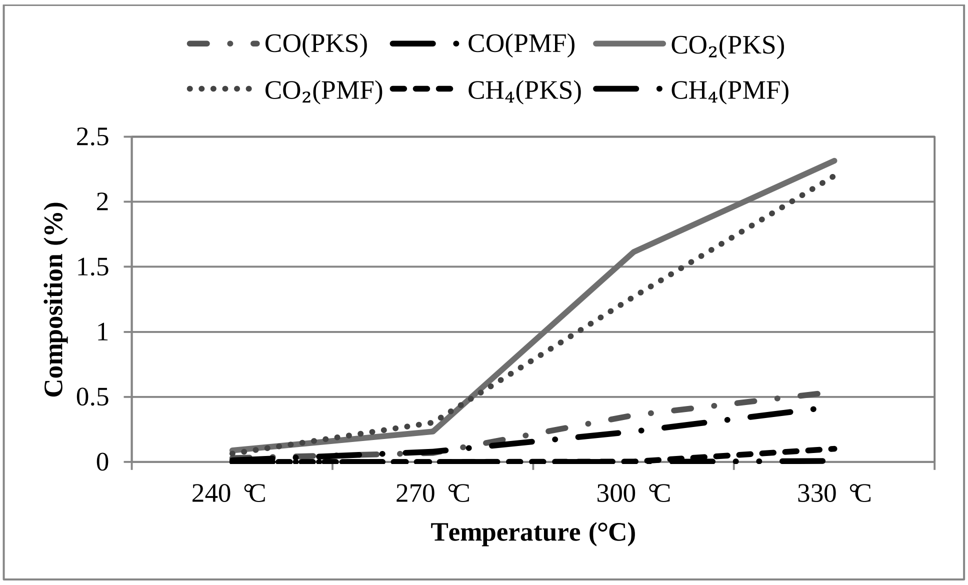


Figure 4-6: The composition of non-condensable gas produced during torrefaction of PKS and PMF at different temperature for 30 min residence time.

From Figure 4-6, when temperature increased, the formation of CO and CO_2 also increased due to degradation of biomass. Basu (2013) mentioned that during 200 – 250 ℃ consider as torrefaction zone for hemicellulose. Most of the inter- and intramolecular hydrogen, C – C and C – O bonds forming condensable liquids and non-condensable gases.

When torrefaction temperature increases to 250 – 330 ℃ is the higher part of torrefaction process. Extension decomposition of the hemicellulose into volatiles occurs. During this stage, the lignin and cellulose also undergo devolatilization and carbonizations which cause the more volatile gases (CO & CO_2) are collected.

When torrefaction temperature up to 330 ℃, PKS produced 0.013% of CH_4, 0.54% of CO and 2.32% of CO_2. At the same condition, PMF produced 0.004% of CH_4, 0.43% of CO and 2.20% of CO_2. Formation of CO_2 was due to decarboxylation and CO mainly produced by CO_2 reacted with H_2O on porous surface of biomass (Dietenberger & Hasburgh, 2016). At 330 ℃, small amount of methane (CH_4) was produced by methanation reaction, where carbon (C) react with hydrogen (H_2) to form CH_4 (Tumuluru et al., 2011). As a result, torrefaction on PKS and PMF released the volatile that content energy value.

4.7 Mass and energy yield

Mass yield gives a measure of the solid yield of the torrefaction process. It defines what fraction of the original mass of biomass would remain in the torrefied product. Change in the hydrocarbon content in biomass is the main concern of torrefaction (Basu, 2013). In biomass energy, torrefaction aimed for production of a fuel that had better properties compared to original biomass. The aim can be achieved without losing too much chemical energy due to release of volatile products during the treatment process. Therefore, the mass fraction and energy yield were considered as the crucial parameters in evaluating a torrefaction process (Sabil et al., 2013a).

Figure 4-7 and Figure 4-8 show the mass yield of torrefied PKS and torrefied PMF deceased with increased of the torrefaction temperature. Previous report showed the similar trends (Hisham et al., 2016; Sabil et al., 2013a, 2013b). The mass yield of torrefied PKS biomass decreased from 87.31% to 57.04% and torrefied PMF biomass decreased from 88.76% to 66.96% when torrefaction temperature increased from 240 ℃ to 330 ℃ for 30 min residence time. The trend of the results for torrefaction of PKS were similar with other researcher projects (Asadullah et al., 2014). Mass yield decreased with increasing of the temperature of torrefaction because more lignocellulosic molecules decomposed into volatile gases and moisture content was removed (Matali et al., 2016; Uemura et al., 2013).

Besides that, increased the residence time of torrefaction caused the mass yield of torrefied biomass to be reduced. When torrefaction carried out at 60 min residence time, torrefied PKS biomass had mass yield in range of 79.47% to 41.99% and mass yield of torrefied PMF biomass within 88.76% to 65.90%. The torrefied products with 60 min residence time had lower mass yield compared to the products that torrefied at 30 min residence time. The same trend was observed from other researchers projects (Hisham et al., 2016).

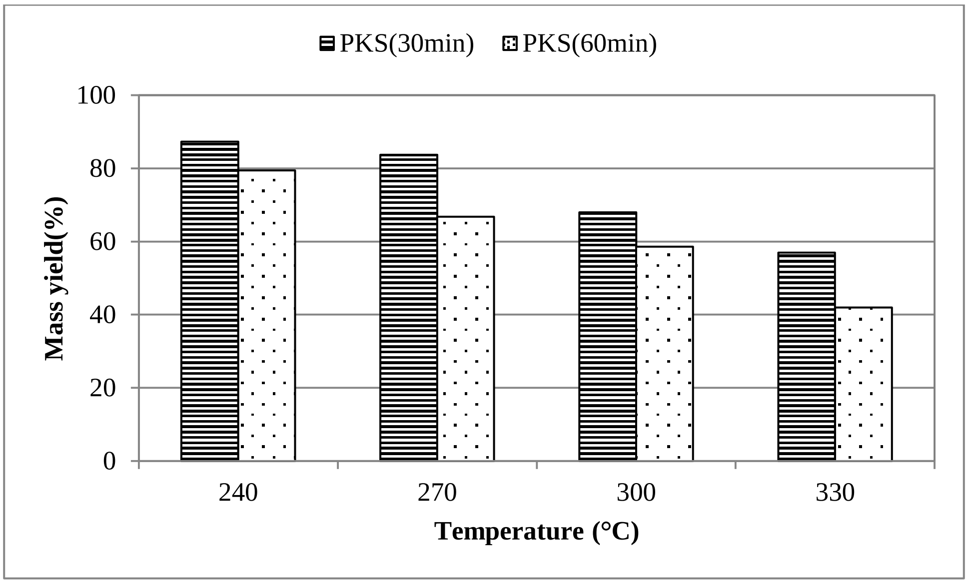


Figure 4-7: Mass yield of torrefied PKS at different temperature for 30 min and 60 min residence times.

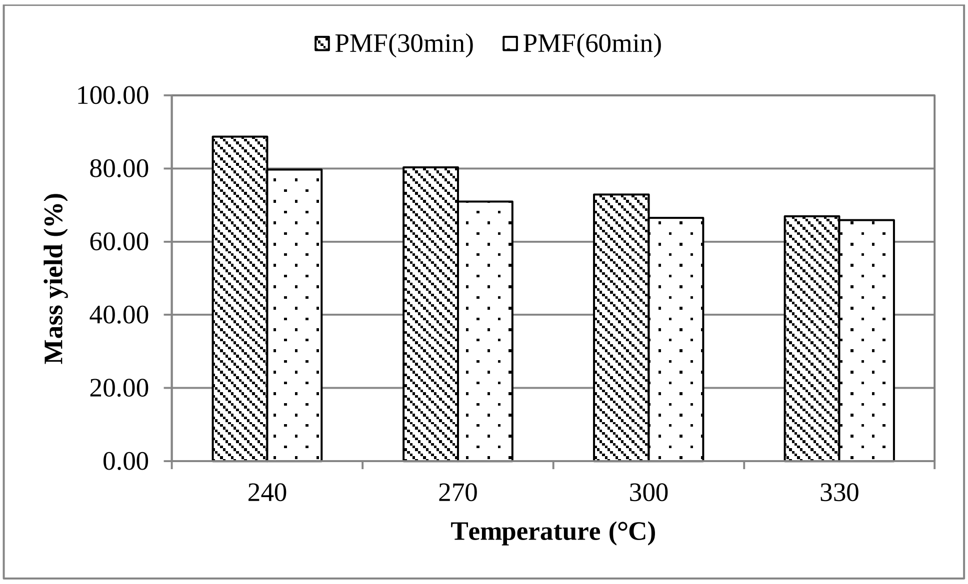


Figure 4-8: Mass yield of torrefied PMF at different temperature for 30 min and 60 min residence times.

The mass yield of the torrefied biomass was affected by the size of the particles. The PKS biomass and PMF biomass had the same diameter which about 1 mm to 500 µm, but PMF biomass length was longer than PKS biomass. Based on Basu (2013), the size of biomass particles could affect the torrefaction yield (mass yield). Torrefaction involved convective heat transfer from the reactor to the biomass surface, conduction of the heat into the biomass interior. Thus, the heat was easily transfer to the interior of

PKS biomass and caused the mass yield of torrefied PKS biomass was lower compared to torrefied PMF biomass. For examples, the mass yield of torrefied PKS biomass at temperature 330 ℃ and 30 min residence time was 57.04% which was lower about 10% compared to mass yield of torrefied PMF biomass with the same condition.

Based on Figure 4-9 and Figure 4-10, basically the energy yield of PKS and PMF decreased with increased of the torrefaction temperature. The results obtained were consistently with other study (Poudel et al., 2016; Uemura et al., 2011). The energy yields of torrefied PKS biomass show drastically drop when torrefaction temperature increased to 330 ℃ for both 30 min and 60 min residence times because the mass yield at 330 ℃ was quite low compared to others torrefaction temperature. However, the energy yield for torrefied PMF biomass was maintained at the range of 82% - 95% for both residence times. The main factor that the energy yield was retained because the mass yield of the torrefied PMF biomass was higher compared to torrefied PKS biomass due to the large particles size of PMF biomass. As a comparison, the data collated by Sabil et al., (2013b) showed the energy yield for torrefied PKS biomass at 300 ℃ was 72.4% which is 7% lower than our findings report as Figure 4-9. The different in energy yield mainly caused by different in residence time for torrefaction since in their study used (2hr) and this study (1hr).

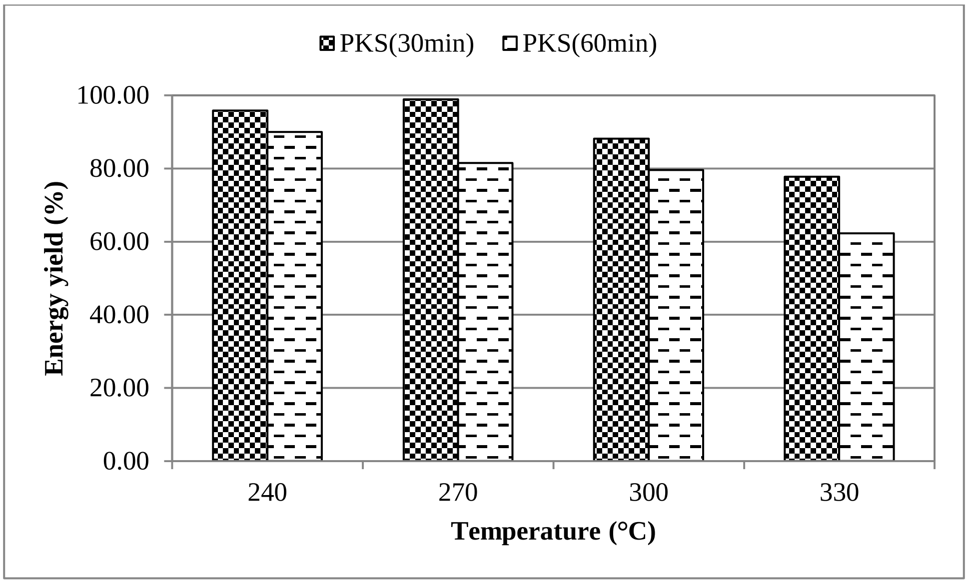


Figure 4-9: Energy yield of torrefied PKS at different temperature for 30 min and 60 min residence times.

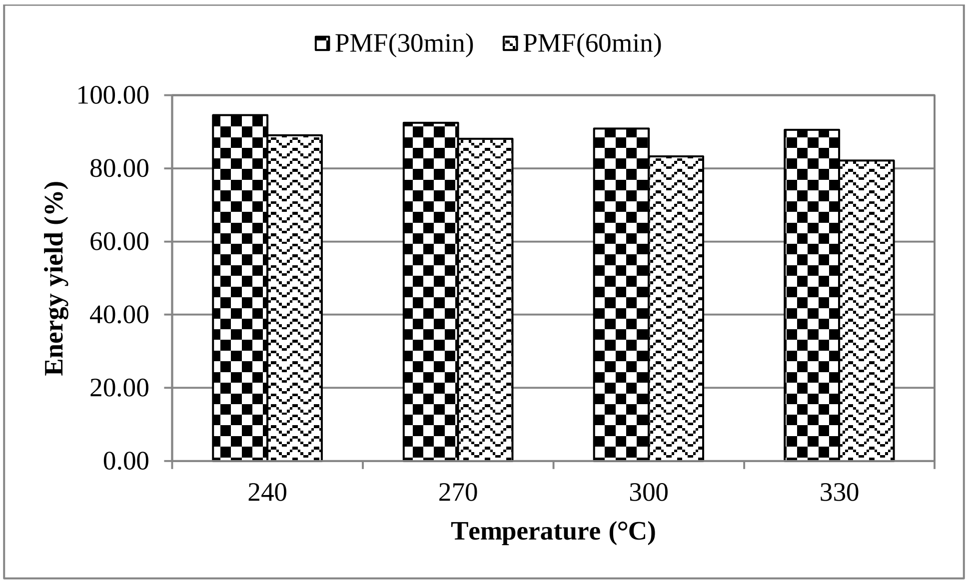


Figure 4-10: Energy yield of torrefied PMF at different temperature for 30 min and 60 min residence times.

In Section 4.6 shows torrefaction able to increase the quality of the biomass in order to utilize as energy sources. Torrefaction able to decrease the mass yield by removed the moisture content and also decomposed the lignocellulosic component to be volatile matter make the torrefied products to be lighter which reduced the transportation cost for transport the torrefied products. Besides that, the energy yield for the torrefied products were maintained in the range of 80% to 95% for both PKS and PMF biomass when torrefaction at temperature of 240 ℃ to 300 ℃ with 30 min residence time. Thus, the results showed the torrefied products were cost saving in term of transportation (light product) and content high energy value.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In conclusion, the influence of torrefaction process on the PKS and PMF biomass had been investigated. From physical appearance, the colour of the torrefied biomass became darken with increased of the torrefaction temperature because the carbon content of the biomass increased with increased of torrefied temperature. It had been shown that the CHNS content and HHV of torrefied biomass increased as the torrefaction temperature increased. From the results obtained, PKS had the highest carbon fraction with 59.92% while HHV of PMF was the highest about 22.91 MJ kg^{-1} for 330 ℃ torrefaction temperature and 30 min residence time. In term of mass yield, torrefied PKS had the lowest mass yield which about 57% when torrefied at 330 ℃ for 30 min. Besides that, energy yield of PMF was able to maintain at 90 – 95 % when torrefied from 240 – 330 ℃ for 30 min. However, the energy yield of torrefied PKS just able to maintain within 78 – 90% for the same torrefaction condition. In addition, the SEM images showed the particles for biomass that torrefied at higher temperature were loosely packed and eventually increased the grindability of the products.

The increased in the residence time to 60 min, increased the HHV of the torrefied biomass in a range of 3% to 9% when compared to the torrefied biomass with 30 min residence time. It was shown that increased the residence time to 60 min had minor changes on the effect of the torrefaction in term of HHV increment. Thus, the residence time influence on the torrefaction was not as significant as the torrefaction temperature.

Torrefaction of PKS and PMF also produced non condensable gases such as CO, CO_2 and CH_4 which were another sources of energy. In general, torrefaction had increased the qualities of biomass to be utilized as bio-coal such as higher calorific value, increase grindability, reduce the moisture content and volatile released can be used as energy sources.

5.2 Recommendation

The following recommendation should be considered throughout this research works. First of all, proper pre-treatment of freshly obtained PKS and PMF should be done accordingly. Once collected, open drying should be implemented for remove the moisture content of biomass to prevent the biomass from damaged by fungus. Improper drying will cause whole batch of raw materials cannot be used.

Besides that, if researchers wish to compare the effect of torrefaction on different biomass, palletisation should be done on the raw materials in order to confirm the sizes of the raw materials are the same.

Furthermore, during the torrefaction process, flushing of nitrogen was compulsory to ensure that the process was carried out in the absence of oxygen. Also, the tubular reactor should be cleaned after each experiment to prevent stain which can cause corrosion in the interior surface of the reactor.

In addition, the time taken for cooling process after torrefaction can be shortened by direct blowing with portable fan which effectively reduced the progress delay.

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APPENDIX

Figure A-1 shows the gas catalytic reactor used to carry out the torrefaction reaction.

Figure A-1: Gas catalytic reactor.

Table A-1: Higher heating value of PKS and PMF for 30 min and 60 min residence time.

Residence time		**30 Min**		**60 Min**	
Biomass	Condition	HHV (MJ/kg)	ΔHHV (%)	HHV (MJ/kg)	ΔHHV (%)
PKS	Raw	16.15	-	16.15	-
	240 ℃	17.72	9.76	18.28	13.22
	270 ℃	19.05	18.00	19.69	21.93
	300 ℃	20.92	29.56	21.92	35.74
	330 ℃	22.00	36.23	23.92	48.16
PMF	Raw	16.94	-	16.94	-
	240 ℃	18.05	6.51	18.93	11.73
	270 ℃	19.17	13.12	19.90	17.44
	300 ℃	21.49	26.87	22.42	32.36
	330 ℃	22.91	35.22	24.44	44.28

Table A-2: Gas chromatography data for volatile released during torrefaction.

		Composition (%)		
Biomass	Condition	CO(PKS)	CO_2(PKS)	CH_4(PKS)
PKS	240 ℃	0.03	0.089	0
	270 ℃	0.07	0.235	0
	300 ℃	0.36	1.613	0.004
	330 ℃	0.54	2.316	0.101
		CO(PMF)	CO_2(PMF)	CH_4(PMF)
PMF	240 ℃ - 30 min	0.012	0.065	0
	270 ℃ - 30 min	0.078	0.302	0
	300 ℃ - 30min	0.234	1.27	0
	330 ℃ - 30 min	0.425	2.2	0.008

Table A-3: Manual data of torrefaction of PKS

240 °C (30 min)	
Mass	(g)
Reactor - R	140.6096
Glass wool - G	0.0627
(R+G)	140.6715
Biomass - B	2.5037
(R+G+B) initial	143.1761
(R+G+B) final	142.8583
m biomass (i)	2.5046
m biomass (f)	2.1868
Non Torrefied B	0.0488
Torrefied B	2.115

240 °C (30 min)	
Mass	(g)
Reactor - R	140.697
Glass wool - G	0.0698
(R+G)	140.7411
Biomass - B	2.512
(R+G+B) initial	143.246
(R+G+B) final	143.0423
m biomass (i)	2.5049
m biomass (f)	2.3012
Non Torrefied B	0
Torrefied B	2.1912

240 °C (60 min)	
Mass	(g)
Reactor - R	140.7123
Glass wool - G	0.0846
(R+G)	140.7957
Biomass - B	2.5294
(R+G+B) initial	143.3274
(R+G+B) final	142.8076
m biomass (i)	2.5317
m biomass (f)	2.0119
Non Torrefied B	0
Torrefied B	1.9909

270 °C (30 min)	
Mass	(g)
Reactor - R	140.6229
Glass wool - G	0.0711
(R+G)	140.691
Biomass - B	2.4914
(R+G+B) initial	143.176
(R+G+B) final	142.7725
m biomass (i)	2.485
m biomass (f)	2.0815
Non Torrefied B	0
Torrefied B	2.0435

270 °C (60 min)	
Mass	(g)
Reactor - R	140.7057
Glass wool - G	0.0799
(R+G)	140.786
Biomass - B	2.5596
(R+G+B) initial	143.3534
(R+G+B) final	142.5013
m biomass (i)	2.5674
m biomass (f)	1.7153
Non Torrefied B	0
Torrefied B	1.7058

300 °C (30 min)	
Mass	(g)
Reactor - R	140.6324
Glass wool - G	0.0786
(R+G)	140.7091
Biomass - B	2.4938
(R+G+B) initial	143.2017
(R+G+B) final	142.4046
m biomass (i)	2.4926
m biomass (f)	1.6955
Non Torrefied B	0
Torrefied B	1.6931

300 °C (60 min)	
Mass	(g)
Reactor - R	140.7397
Glass wool - G	0.0692
(R+G)	140.8104
Biomass - B	2.5714
(R+G+B) initial	143.3818
(R+G+B) final	142.3178
m biomass (i)	2.5714
m biomass (f)	1.5074
Non Torrefied B	0
Torrefied B	1.4493

330 °C (30 min)	
Mass	(g)
Reactor - R	140.6054
Glass wool - G	0.0635
(R+G)	140.6683
Biomass - B	2.5015
(R+G+B) initial	143.1601
(R+G+B) final	142.0895
m biomass (i)	2.4918
m biomass (f)	1.4212
Non Torrefied B	0
Torrefied B	1.3732

330 °C (60 min)	
Mass	(g)
Reactor - R	140.7446
Glass wool - G	0.1001
(R+G)	140.8383
Biomass - B	2.5816
(R+G+B) initial	143.4202
(R+G+B) final	141.9225
m biomass (i)	2.5819
m biomass (f)	1.0842
Non Torrefied B	0
Torrefied B	1.0374

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Table A-4: Manual data of torrefaction of PMF

240 °C (30 min)	
Mass	(g)
Reactor - R	140.6283
Glass wool - G	0.0621
(R+G)	140.689
Biomass - B	1.6216
(R+G+B) initial	142.3009
(R+G+B) final	142.1521
m biomass (i)	1.6105
m biomass (f)	1.4617
Non Torrefied B	0.5283
Torrefied B	0.9484

240 °C (60 min)	
Mass	(g)
Reactor - R	140.7117
Glass wool - G	0.0746
(R+G)	140.7839
Biomass - B	1.6328
(R+G+B) initial	142.3973
(R+G+B) final	142.071
m biomass (i)	1.611
m biomass (f)	1.2847
Non Torrefied B	0
Torrefied B	1.2643

270 °C (30 min)	
Mass	(g)
Reactor - R	140.5458
Glass wool - G	-
(R+G)	140.6193
Biomass - B	1.6042
(R+G+B) initial	142.2187
(R+G+B) final	141.9041
m biomass (i)	1.5994
m biomass (f)	1.2848
Non Torrefied B	0
Torrefied B	1.2848

270 °C (30 min)	
Mass	(g)
Reactor - R	140.6096
Glass wool - G	0.0801
(R+G)	140.6909
Biomass - B	1.6037
(R+G+B) initial	142.2893
(R+G+B) final	141.9732
m biomass (i)	1.5984
m biomass (f)	1.2823
Non Torrified B	0
Torrified B	1.2823

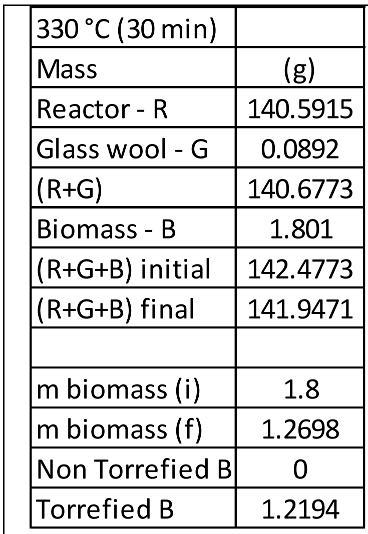
270 °C (60 min)	
Mass	(g)
Reactor - R	140.7038
Glass wool - G	0.081
(R+G)	140.7821
Biomass - B	1.6293
(R+G+B) initial	142.3866
(R+G+B) final	141.9205
m biomass (i)	1.6045
m biomass (f)	1.1384
Non Torrefied B	0
Torrefied B	1.08

300 °C (30 min)	
Mass	(g)
Reactor - R	140.5708
Glass wool - G	0.0965
(R+G)	140.6629
Biomass - B	1.6052
(R+G+B) initial	142.2591
(R+G+B) final	141.7243
m biomass (i)	1.5962
m biomass (f)	1.0614
Non Torrefied B	0.1699
Torrefied B	0.8715

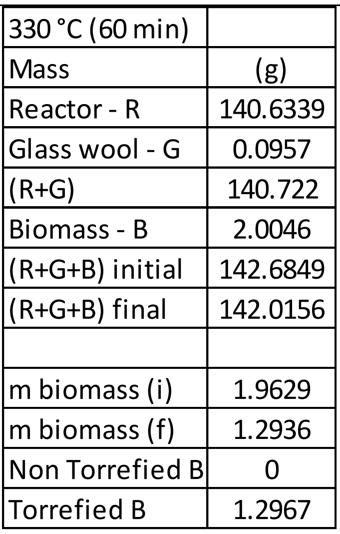
300 °C (30 min)	
Mass	(g)
Reactor - R	140.6226
Glass wool - G	0.0638
(R+G)	140.6822
Biomass - B	1.6169
(R+G+B) initial	142.2816
(R+G+B) final	141.8478
m biomass (i)	1.5994
m biomass (f)	1.1656
Non Torrefied B	0
Torrefied B	1.0544

300 °C (60 min)	
Mass	(g)
Reactor - R	140.7296
Glass wool - G	0.0532
(R+G)	140.7816
Biomass - B	1.6373
(R+G+B) initial	142.4011
(R+G+B) final	141.8596
m biomass (i)	1.6195
m biomass (f)	1.078
Non Torrefied B	
Torrefied B	1.0531

330 °C (30 min)	
Mass	(g)
Reactor - R	140.5819
Glass wool - G	0.0825
(R+G)	140.6624
Biomass - B	1.8061
(R+G+B) initial	142.4542
(R+G+B) final	141.8621
m biomass (i)	1.7918
m biomass (f)	1.1997
Non Torrefied B	0.0309
Torrefied B	1.146



330 °C (30 min)	
Mass	(g)
Reactor - R	140.5915
Glass wool - G	0.0892
(R+G)	140.6773
Biomass - B	1.801
(R+G+B) initial	142.4773
(R+G+B) final	141.9471
m biomass (i)	1.8
m biomass (f)	1.2698
Non Torrefied B	0
Torrefied B	1.2194



330 °C (60 min)	
Mass	(g)
Reactor - R	140.6339
Glass wool - G	0.0957
(R+G)	140.722
Biomass - B	2.0046
(R+G+B) initial	142.6849
(R+G+B) final	142.0156
m biomass (i)	1.9629
m biomass (f)	1.2936
Non Torrefied B	0
Torrefied B	1.2967