A STUDY ON THE FAST PYROLYSIS OF JACKFRUIT PEEL TO BIO-OIL IN A DROP-TYPE FIXED BED REACTOR

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by

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LIST OF ABBREVIATIONS

CHNS/O	Carbon, Hydrogen, Nitrogen, Sulphur / Oxygen
CO_2	Carbon Dioxide
FTIR	Fourier Transform infrared spectroscopy
GC-MS	Gas Chromatography–Mass Spectrometry
GHG	Greenhouse Gases
HHV	High Heating Value
JFP	Jackfruit Peel
MSW	Municipal Solid Wastes
N_2	Nitrogen gas
NaOH	Sodium Hydroxide
TCC	Thermochemical Conversion
TGA	Thermogravimetric Analysis

KAJIAN MENGENAI PIROLISIS PANTAS TERHADAP KULIT BUAH NANGKA UNTUK MENGHASILKAN MINYAK DALAM REAKTOR LAPISAN TETAP "DROP-TYPE"

ABSTRAK

Permintaan terhadap tenaga terus meningkat kesan perkembangan pesat populasi dunia dan isu ini membawa kepada pengurangan bahan api fosil. Bagi mengatasi masalah tenaga krisis, kajian ini telah menjalankan pirolisis pantas terhadap kulit buah nangka untuk menghasilkan minyak dalam reaktor lapisan tetap "drop-type". Hal ini kerana, biojisim dianggap sebagai sumber yang sangat berkesan untuk diperbaharui berbanding dengan bahan api fosil konvensional di mana ia boleh digunakan untuk pengeluaran tenaga yang berpotensi yang dapat dikekalkan dan mengurangkan pencemaran alam sekitar. Eksperimen ini telah dijalankan pada suhu yang berbeza (350-650 ^{o}C), saiz sample (0.25-2 mm) dan kadar aliran gas nitrogen (200-400 ml/min). Penghasilan minyak tertinggi (57.86 wt%) diperoleh pada suhu 550 ^{o}C dengan saiz sample 0.5-1 mm dan kadar aliran gas nitrogen sebanyak 200 mL/min. Ujikaji awal yang dijalankan terhadap kulit buah nangka menggunakan thermogravimetric analyzer (TGA) adalah bertujuan untuk menentukan analisis hampiran. Kemudian, komposisi unsur dan nilai pemanasan yang lebih tinggi daripada kulit buah nangka dan minyak (550 ^{o}C) telah ditentukan dan dibandingkan. Di samping itu, analisis FTIR dan analisis GC-MS dijalankan terhadap minyak untuk menyiasat kumpulan berfungsi dan sifat-sifat kimia minyak masing-masing. Sifat- sifat kimia daripada penghasilan minyak menunjukan bahawa minyak ini mengaplikasikan dalam loji kimia yang boleh berguna sebagai bahan mentah kimia dan digunakan sebagai bahan bakar pembakaran untuk elektrik.

A STUDY ON THE FAST PYROLYSIS OF JACKFRUIT PEEL TO BIO-OIL IN A DROP-TYPE FIXED BED REACTOR

ABSTRACT

Energy demand is increasing due to rapid growth in population and leads to depletion of fossil fuels. To prevent the energy crisis, this study explores fast pyrolysis of Jackfruit peel into bio-oil in a drop-type fixed bed reactor. This is because, the biomass considered very effective renewable resources compared to conventional fossil fuels where it can be used for energy production which potentially sustainable and reduce environmental pollution. Fast pyrolysis serves as promising techniques to dispose of agriculture waste and to get bio-oil, bio-char and syngas simultaneously. The experiment was carried out at different reaction temperature (350-650 ^{o}C), particle size (0.25-2 mm) and nitrogen flow rate (200-400 mL/min). The highest bio-oil yield (57.86 wt%) was obtained at 550 ^{o}C with Jackfruit Peel (JFP) waste size of 0.5-1 mm and 200 ml/min of nitrogen gas flow rate. Preliminary experiment was conducted using thermogravimetric analyzer (TGA) to determine the proximate analysis of JFP. Then, elemental composition and higher heating value of the feedstock and bio-oil (550 ^{o}C) were determined and compared. Additionally, the FTIR analysis and GC-MS analysis were carried out on bio-oil to investigate the functional group and chemical composition of bio-oil respectively. The chemical characterization of bio-oil results provide some promising insight into the application of bio-oil in chemical plant, which could be useful as a chemical feedstock and used as combustion fuels for electricity.

CHAPTER ONE

INTRODUCTION

1.1 Background

Energy sources are an important role in the world's future which can be stored, converted and amplified for our daily use. Fossil fuel play very important role in human daily life such as transportation fuel, heating, cooking and generates electricity. Energy production from fossil fuels results in high greenhouse gas emissions towards atmosphere. Fossil fuels, renewable sources and nuclear sources are the energy sources where strongly affects current and future energy supply systems. Malaysia energy consumption has grown from insignificant levels in 1980 to an annual output of nearly 60 million ton of oil equivalent in the year 2012 as illustrated in Figure 1.1. (by fuel type) and Figure 1.2 (by sector type) (Chong et al., 2015). Figure 1.1 illustrated energy demand in Malaysia by coal, oil product, natural gas and electricity. Figure 1.2 clearly shows the industry sector was the highest growth rate followed by transportation and domestic in energy demand. In addition, the future energy demand is expected to rise at the rate of 5-7.9% per year for the next 20 years in industrial, transportation and power generation sector (Ong et al., 2011).

But nowadays, the natural resources drastically depleted leading to serious energy crisis. The main reasons for the depletion of natural resources are rapid population increases and lead to high consumption of resources. Figure 1.3 shows the future energy depletion from fossil fuels in 2011 until 2081. Rapid population, energy demand and supply can causes high amount of fossil fuels consumed. Fossil fuels will therefore run out earlier. Since, fossil fuels are an incredibly dense form of energy, and they took millions of years to produce. And when they are depletes, they are gone forever. Declining availability of fossil fuels may lead also increases in fuel prices and declining security.

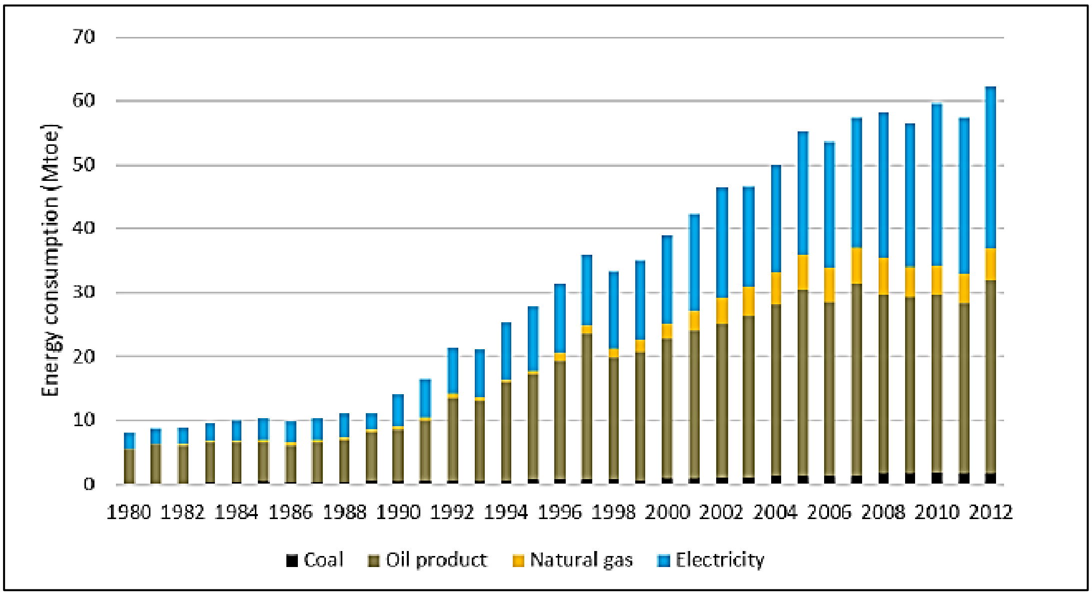

Figure 1.1: Malaysia energy consumption expressed by fuel type (Chong et al., 2015).

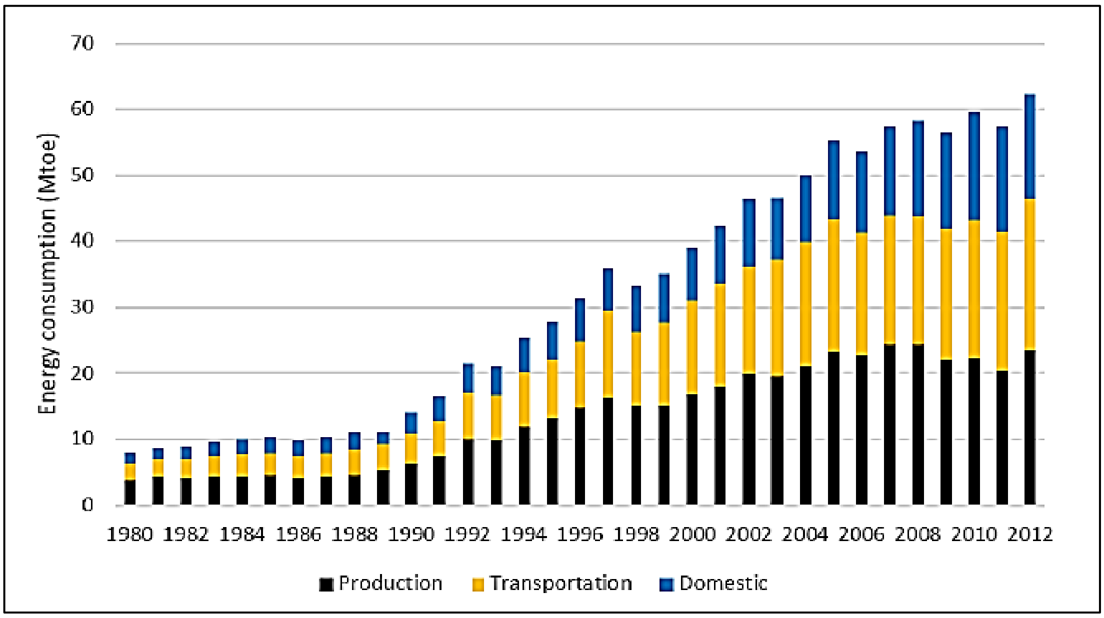

Figure 1.2: Malaysia energy consumption expressed by sector type (Chong et al., 2015).

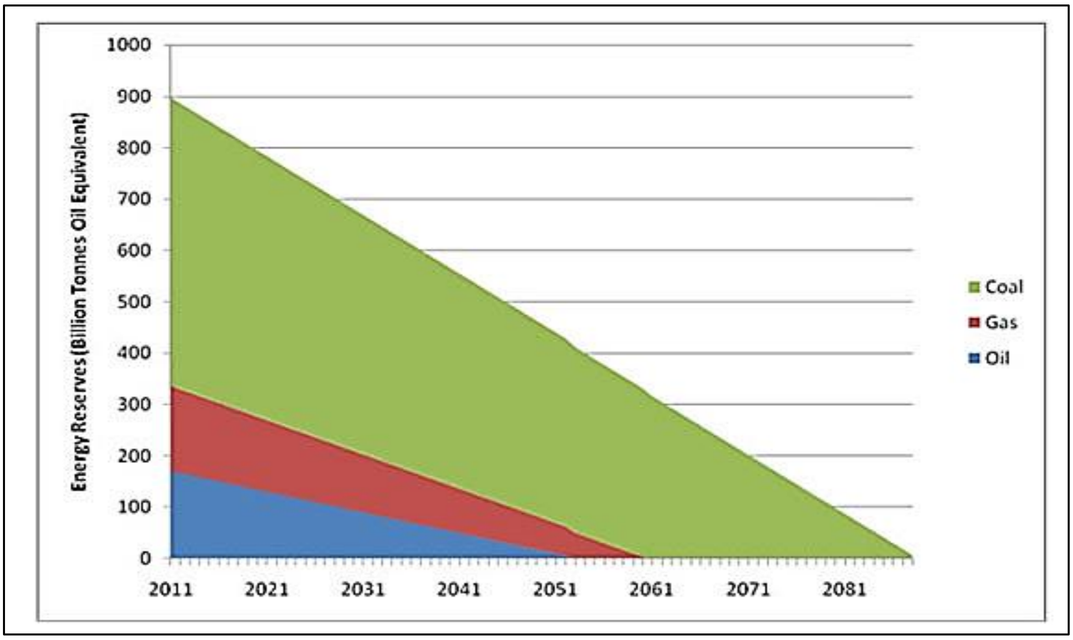

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Figure 1.3: Future energy reserves for coal, gas and oil (Höök et al., 2012).

The rapid consumption will affect the environment either by usage of natural resources or by increasing pollution such as emission of carbon dioxide (CO_2), nitrogen oxides (NO_x), and other greenhouse gases (GHG). Besides, the problem of pollution, the energy from fossil fuels also is very cost effective (Benipal et al., 2016).

Energy crisis is the main reason to study and should be research different kinds of renewable alternative energies. Bio-oil is one of the renewable alternative energy where usable for heating, power generation, chemical feedstock and transportation fuel with sustainability and low pollution emission to the environment. Bio-oil can be derived from biomass where can replace fossil fuel. Biomass are widely used as biofuel feedstock due to its numerous advantages with the resources widely distributed and renewable in nature (Isa and Ganda, 2018). Biomass is commercially competitive and is making relatively fast progress with wind and geothermal energy (Demirbas, 2009).The bio-oil produces low environmental impact and considered a source of clean energy when compared to fossil fuels.

There are various biomass resources in the world, such as microalgaes, woods and agricultural wastes. In Malaysia, agricultural wastes produce annually and potentially an attractive feedstock for producing energy. Major agricultural products are oil palms, paddy husk, sugarcane bagasse and fruit wastes (Ozturk et al., 2017, Chuah et al., 2006). For the purpose of reducing environmental pollution brought by the agricultural wastes disposal such as direct burning, incineration and landfilling, many researchers have studied on thermochemical conversion (TCC) methods, such as pyrolysis, combustion, liquidation, and gasification, to convert them into liquid fuels, bio char and gas obtain effective bioenergy or chemical feedstock (Panwar et al., 2012, Zhang et al., 2010).

Among the thermochemical conversion routes, fast pyrolysis is promising alternatives that are renewable and reduce emissions such as CO_2 and other greenhouse gases (GHG) (Krutof and Hawboldt, 2016). The major product of the fast pyrolysis is a liquid that recognized as bio-oil and by-products of this process are bio-char and non-condensable gases. Bio-oil as liquid fuel can be readily stored and transported, also has a high potential to upgrade and convert with gasoline and diesel (Mortensen et al., 2011). The pyrolysis oils from fast pyrolysis are composed of a range of chemicals including cyclopentanone, methoxy phenol, acetic acid, methanol, acetone, furfural, phenol (aromatic ring), formic acid, levoglucosan, guaiacol and their alkylated phenol derivatives. Several researches are reported that maximum bio-oil yields from fast pyrolysis obtained up to 80% (Manurung et al., 2009, Heo et al., 2010b, Xiu and Shahbazi, 2012).

1.2 Problem Statement

Energy crisis is the main cause to explore different kinds of renewable alternative energies, one of which is bio-oil. There are many renewable resources such as solar, wind, wave, geothermal, hydroelectric and nuclear. Nowadays, biomass considered very effective renewable resources where it can be used for energy production which potentially sustainable and reduce environmental pollution. In particular, Malaysia is an agricultural country whose millions of tons of agricultural wastes produced that is not used and is disposed as waste in landfills. Therefore, agricultural wastes are an attractive feedstock for producing sustainable energy.

Fast pyrolysis is a thermochemical conversion and is one of the most promising approaches for the conversion of biomass into high value-added products such as bio-oil, bio char and gases. Fast pyrolysis is an advanced process in which biomass is rapidly heated to moderate temperature around 500 °C in the absence of oxygen. Biomass conversion by fast pyrolysis has many environmental and economic advantages over fossil fuels. In addition, the liquid bio-oil formed by fast pyrolysis has heating value about half that conventional fuel oil.

In this study, fast pyrolysis of Jackfruit peel into bio-oil was researched since its volatile matter and carbon content are quite high to produce maximum yield of bio-oil. So far, the study on fast pyrolysis behavior of Jackfruit peel is not reported. Fast pyrolysis process was chosen since it is flexible and simple process for production of bio-oil, biochar and syngas with absence of oxygen. Therefore, a study on the effects of operating parameters such as reaction temperature, biomass particle size and nitrogen flow on production and characterization of bio-oil yield from Jackfruit peel via fast pyrolysis was conducted. At same by utilizing the wastes into usable products can reduce disposal cost.

Research Objectives

The objectives are:

I. To investigate fast pyrolysis of Jackfruit peel to bio-oil in a drop- type fixed bed reactor at various experimental parameters such as reaction temperature (350-650 ^{o}C), particle size (0.25-2 mm) and nitrogen flow (200-400 mL/min).

II. To characterize the pyrolysis products under the best pyrolysis conditions using Elemental Analyzer, FTIR, and GC–MS.

1.4 Research Scope

In this study, Jackfruit Peels were collected from a Market at Parit Buntar, Malaysia. After that, the collected wastes were washed, dried and sieved before the experiment. The fine particle size (0.25 mm) of samples was characterized using Elemental Analyzer, Thermogravimetric Analyzer (TGA) and Bomb Calorimeter. The characterizations were done to observe and study the properties of Jackfruit Peel in terms of ultimate analysis, proximate analysis and heating value respectively. Then, chemical composition such as cellulose, hemicellulose, lignin and extractive studies were performed by calculation according to the experimental method. The biomass was pyrolysed with operating parameters such as reaction temperature, particle size and nitrogen flow to yield maximum liquid fuel which is bio-oil. First, the biomass was undergo fast pyrolysis with 200-400 mL/min of nitrogen flow at 550 ^{O}C and 0.25-0.5 mm of particle size where to analysed suitable nitrogen gas flow to produce high yield of bio-oil. The second group of experiments was performed with four particle sizes, namely, <0.25, 0.25-0.5, 0.5-1, 1-2 mm at 550 ^{O}C pyrolysis temperature and suitable nitrogen flow gas. Then, a final experiment was performed with four pyrolysis temperature such as 350, 450, 550, and 650 ^{O}C at nitrogen flow and particle size. The experiments were repeated at least thrice to confirm the reproducibility. Lastly, the products (bio-oil and gas) were collected for suitable operating parameters and characterized using Elemental Analyzer, GC-MS, Bomb Calorimeter, FTIR and TGA.

1.5 Organization of Thesis

This thesis consists of five main chapters and each chapter contributes to the sequence of this study. The following are the contents for each chapter in this study:

Chapter 1 introduces the overview of this research and how fast pyrolysis is significant for the production bio-oil from jackfruit peel as agricultural waste. In general, this chapter outlines the background of fast pyrolysis of agricultural waste to potential energy, the problem statement, objectives and scope of research along with the organization of thesis.

Chapter 2 briefly presents the previous discoveries and reviews available from scientific records and references that are related to this research topic. The discussion focused on the study of fast pyrolysis on agricultural wastes as biomass energy and utilizing this type of biomass resources for energy. In general, this chapter outlines the overview and elaboration biomass as source of energy and in particular, agricultural waste. Then, a review on Jackfruit Peel is one of the agricultural wastes for energy utilization. After that, discussion focused on the studies of biomass conversion into energy and in particular, pyrolysis process. Next, an extensive review on fast pyrolysis and influence of experimental parameters on products yield.

Chapter 3 covers the overall experimental aspects of the research project including the Jackfruit Peel preparation, chemicals required, description of equipment and Jackfruit Peel characterization methods, and experimental rig set-up for fast pyrolysis studies. Then, a description of the experimental methodology along with the bio-oil and bio char characterization method used in this research project is presented.

Safety and environmental precautions were designated to ensure a safer and sustainable research environment.

Chapter 4 refers to the experimental results and discussions of the data obtained. Further elaboration on the effect of different operating parameters such as reaction temperature (350-650 ^{o}C), particle size (0.25-2 mm) and nitrogen flow (200-400 mL/min) on product yields from fast pyrolysis of Jackfruit Peel. Then the characteristics of the obtained pyrolysis oil and gas were studied.

Chapter 5 concludes all the findings achieved in this research study. Recommendations for future studies on this research topic are included as well.

CHAPTER TWO

LITERATURE REVIEW

2.1 Biomass as Source of Energy

All the earth's living matter name as biomass. The term 'biomass' refers to forestry, purposely grown agricultural crops, trees and plants and organic, agro-industrial and domestic wastes (Demirbas, 2009). Biomass mainly consists of carbon, hydrogen, oxygen, nitrogen and less proportion of sulphur. Biomass is living organisms where it can absorb and stored solar energy by photosynthesis where turn it into biomass energy. That biomass energy can be utilized by burning it directly or using various processes to obtain potential fuels. Biomass is considered one of the most alternative energy sources to produce more valuable bio-oil and also its sustainable way for avoiding environmental pollution (Maisano et al., 2017).

There are various types of biomass that would be used to produce bio-oil, include wood wastes, agricultural wastes, bagasse, sawdust, grass, waste from food processing, municipal solid wastes (MSW), animal wastes, aquatic plants, bio materials, and algae etc. Table 2.1 shows the global renewable energy scenario from 2001 to 2040 (Demirbas, 2009). According to European Renewable Energy Council (EREC) in 2006 47.7% of the global energy contribution will come from renewables in 2040. In Table 2.1 clearly states that biomass is the most used renewable energy source now and in the future followed by large hydro, geothermal, small hydro, wind, solar thermal, photovoltaic, etc.

Table 2.1: Global renewable energy scenario from 2001 to 2040 (Demirbas, 2009).

Global renewable energy scenario by 2040					
	2001	2010	2020	2030	2040
Total consumption(Mtoe)	10,038	10,549	11,425	12,352	13,310
Biomass	1,080	1,313	1,791	2,483	3.271
Large hydro	22.7	266	309	341	358
Geothermal	43.2	86	186	333	493
Small hydro	9.5	19	49	106	189
Wind	4.7	44	266	542	688
Solar thermal	4.1	15	66	244	480
Photovoltaic	0.2	2	24	221	784
Solar thermal electricity	0.1	0.4	3	16	68
Marine (tidal/wave/ocean)	0.05	0.1	0.4	3	20
Total renewable energy sources	1,365.5	1,745.5	2,694.4	4,289	6,351
Renewable energy sources contribution (%)	13.6	16.6	23.6	34.7	47.7

Mtoe = Million ton of oil equivalent.

Due to environmental considerations and the increasing demands of energy worldwide, utilization of biomass for energy uses is gaining great attention (Zhang et al., 2007). In Malaysia, biomass is considered to be an sustainable replacement for fossil fuels because 75% of the country's land is covered by tropical forests and agricultural sites (Mekhilef et al., 2011). A very small amount of sulphur contains in biomass compared to conventional fossil fuels. Therefore, combustion of bio-fuel produces less dangerous gas emissions such as nitrogen oxides (NO_x), sulphur dioxide (SO_2) and soot compared to conventional fossil fuels (Tsai et al., 2007).

Total production of biomass in Malaysia is approximately 168 million tons metric per tons of year (Ozturk et al., 2017). Biomass in Malaysia contributes about 14% of the approximately 340 million barrels of oil equivalent of energy used annually. There are five major sectors that contribute wastes to the biomass energy in Malaysia such as forestry (wood products), rubber cultivation, cocoa cultivation, sugar cane cultivation and oil palm cultivation. Table 2.2 shows the quantity of biomass production, generation and potential capacity in Malaysia (Chuah et al., 2006)

Table 2.2: Biomass in Malaysia production, generation and potential capacity (Chuah et al., 2006).

Sector	Quantity (kton/yr)	Potential Annual Generation (GWh)	Potential capacity (MW)
Rice Mills	424	263	30
Wood industry	2117	598	68
Palm oil mills	17980	3197	365
Bagasse	300	218	25
Palm Oil Mill Effluent (POME)	20881	4276	488
Total	31500	1587	177

2.2 Agricultural Waste as Source of Biomass

In the South-East Asian region, Malaysia is recognized as one of the leading agricultural commodity producers (Ozturk et al., 2017). The most common agricultural residue is the rice husk, sugar cane fiber (bagasse), coconut husk, groundnut shell and straw. In developing countries animal manure considered agricultural waste to produce heat or gas (Demirbas, 2001). Table 2.3 present quantity of biomass produced in Malaysia in 2007. It shows that the agricultural waste is most used renewable energy source followed by forest residue and municipal solid waste in 2007 (Goh et al., 2010).

Many researchers have been carried out in manipulating these agricultural waste as biomass source into source of energy because agricultural wastes considered to be one of the most sustainable carbon sources (Collard and Blin, 2014). Different varieties of agricultural wastes that have been tested for pyrolysis include rice (Huang et al., 2016), corn and wheat (Lanzetta and Blasi, 1998), cotton (Ayşe Eren, 2002), rape (Karaosmanoğlu and Tetik, 1999), bagasse (Zandersons et al., 1999), banana leaves (Sellin et al., 2016), grape residue (Li et al., 2016).

Pattiya, (2011b) has reported Thailand is an agricultural country and has various biomass sources available for utilization. Besides, he reported that among the agricultural wastes research on cassava plantations is the great interest since the residues contain high exploitable energy and are abundant in supply. Therefore he studied production of bio-oil via fast pyrolysis of cassava rhizome and cassava stalk in a fluidised bed reactor without a hot vapour filtration unit (Pattiya, 2011a). Results showed that the maximum yields of the liquid bio-oils derived from the stalk and rhizome were 62 wt.% and 65 wt.% respectively.

Table 2.3: Quantity of biomass produced in Malaysia in 2007 (Goh et al., 2010).

Type	Quantity (kt)	Source	Source (kt)	MC (wt%)	DW (kt)
Agricultural waste					
Oil palm fronds	46837	Oil palm FFB	8192	60	18735
EPFB	18022			65	6308
Oil palm fibers	11059			42	6414
Oil palm shells	4506			7	419
Oil palm trunks	10827			759	2609
Paddy straw	880	Replanting paddy		11	783
Rice husk	484		2375	0	440
Banana residues	530	Banana	265	107	473
Sugarcane bagasse	234	Sugarcane	730	50	117
Coconut husk	171	Coconut	505	115	151

Table 2.3: *Continued*

Type	Quantity (kt)	Source	Source (kt)	MC (wt%)	DW (kt)
Pineapple waste	48	Pineapple for factories	69	612	19
Forest residues					
Logging residues	2649	Logs	264	12	2332
Plywood residues	2492	Plywood	2492	12	2193
Sawmill residues	116	Sawn timber	1418	12	1021
Municipal solid waste					
*Organic waste	4653	MSW	6744	575	1978

[MC= Moisture content; DW= Dry weight; MSW= Municipal solid waste; Fresh fruit brunches (FFB); Empty palm fruit brunch (EPFB)]

*Organic waste: all organic materials including food waste and paper cardboards.

Hawash et al., (2017) studied on pyrolysis of seven agricultural wastes to determine the quality of bio-oil and bio-char. He concluded that agricultural wastes have good potential for alternative fuel production. Figure 2.1 present the char, bio-oil and gas yields from pyrolysis products of seven biomass wastes at 500 ^{o}C. Figure below illustrated jatropha seeds gave high bio-oil yield, due to its contained highest volatile content (Hawash et al., 2017)

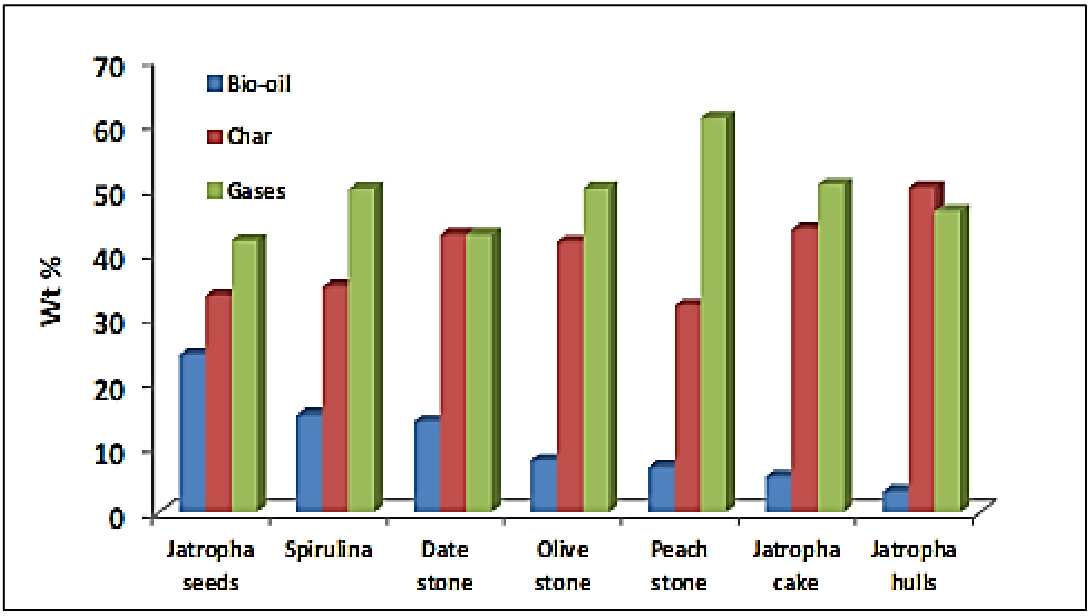

Figure 2. 1: Weight percentage of different products from pyrolysis of different agricultural wastes (Hawash et al., 2017).

2.3 Jackfruit Peel as Agricultural Waste

This study is about biomass potential energy from agricultural waste which is Jackfruit Peel (JFP). Jackfruit commonly known as Artocarpus heterophyllus Lam belongs to the family Moraceae is a fairly large sized tree and bears the largest fruit among the edible fruits (Kaushal and Sharma, 2016). Jackfruit Peel is a solid waste and grows in many of the countries of south-east Asia. Major jackfruit producers are

Malaysia and Sri Lanka (Sidhu, 2012). The common name for Jackfruit Peel in Malaysia is *nangka*.

In Southern Asia the jackfruit is very popular and relatively cheaper. Since Jackfruit Peel is no in-season or out-of season, it can be harvested all year long. Moreover, Malaysia people like to eat the Jackfruit and also used to cook with curry. The jackfruit weight was approximately 23–50 kg, 60-90 cm in length and 59% of the fruit's outer peel is composed of fibre, which rich in calcium and pectin. A mature tree produces up to 700 fruits annually, each weighing 0.5 to 50kg. (Hameed, 2009, Foo and Hameed, 2012). When fully ripe, the rind of the compound fruit is greenish yellow and opened jackfruit smells of pineapple and banana. Inside, the fruit is made up of large, yellow bulbs enclosing an oval light-brown seeds When the jackfruit cuts into half it can produce sticky and white latex (Sidhu, 2012). Normally, the jackfruits are selling in the market and a lot of people buying it for eat and cook. These things indicate high demand of Jackfruit in Malaysia and its lead to high output of jackfruit peel waste.

Jackfruit peel wastes have no economic value. In fact it creates a serious problem of disposal for local environments. Therefore, conversion of jackfruit peel into bio-oil and char by direct burning would increase its economic value, help reduce the cost of waste disposal, and provide a potentially inexpensive raw material for liquid fuel (Prahas et al., 2008). Figure 2.2 shows Jackfruit's fruiting brach, cut fruit and flakes (Sidhu, 2012) whereas Table 2.4 illustrate the area, production and productivity of Jackfruit in Asia (Haq, 2003b). Soetardjia et al., (2014) carried out a research on Jackfruit peel to produce bio-oil by pyrolysis process since it have high volatile matter (74%) followed by carbon (63.6%) and less amount of ash (2%) which leads to high yield of bio-oil.

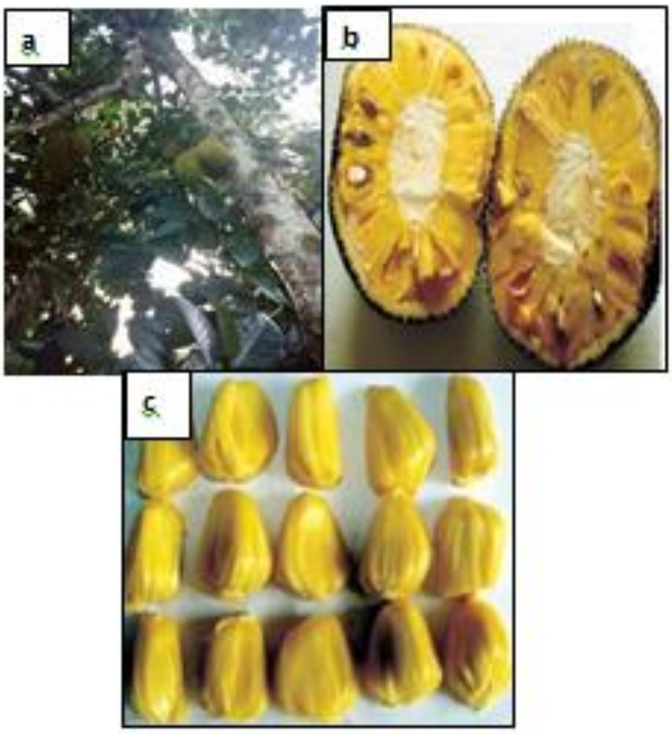

Figure 2.2: Jackfruit part a) Fruiting branch, b) Cut fruit, c) Flakes (Sidhu, 2012).

Table 2.4: Area, production and productivity of Jackfruit in Asia (Haq, 2003b).

Country	Area (ha, $x10^3$)	Production (t, $x10^3$)	Productivity (t/ha)
Bangaladesh	10 (2006)	926	8.20
India	102 (1992)	1436	1.40
Indonesia	50 (1987)	340	9
Malaysia	5 (1987)	13	10
Nepal	2.17 (2002-2003	17.16	1.60
Srilanka	50 (2011)	-	-
Thailand	37 (1987)	392	10

ha, $x10^3$= Thousand Hectares, t, $x10^3$= Thousand Ton, t/ha = ton/hectares

2.4 Bio–oil

Bio-oil is also named as pyrolysis oil, bio-crude, wood oil or wood distillate (Mohan et al., 2006b). It is a dark brown, free flowing organic liquid mixture, which generally consist of a great amount of water (usually 15– 35 wt%) and hundreds of organic compounds, such as acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, alkenes, nitrogen compounds and miscellaneous oxygenates (Rezaei et al., 2014), as well as solid particles (Milne et al., 1997). Commonly, the bio-oil ranges between 15 and 20 MJ/kg which is only 40–50% of the conventional petroleum fuels HHV (42–45 MJ/kg) (Demirbas, 2007). Table 2.5 presents the heating value of pyrolysis oil from various feedstock. This is due to the higher amount of oxygen content which is in the extent of 35-40wt% on dry basis weight. Normally, bio-oil transformed by pyrolysis process contains lower sulphur because plant biomass contains inconsiderable amounts of sulphur. Bio-oil fuels can reduce NO_x emissions than diesel oil in a gas turbine which is more than 50% (Xiu and Shahbazi, 2012).

Table 2.5: Bio-oil heating value from various feedstocks.

Type of Biomass	**Heating value (MJ/kg)**	**References**
Orange peels	18.350	(Aboagye et al., 2017)
Palm oil sludge	22.2	(Gopakumar et al., 2015)
Durian Shell	25.76	(Tan et al., 2017)
Sugarcane Waste	23.5	(Islam et al., 2010)
Rice husk	24.8	(Heo et al., 2010a)

Bio-oils can be used as combustion fuels for electricity. At same time, it's also can used for heat production in boilers, furnaces, and combustors, diesel engines (Solantausta et al., 1993). For practical application in engines further upgrading of the bio-oils is required (Balat, 2011). Transportation liquid fuels from bio-oils has been revealed after upgrading through catalytic cracking technologies (Mortensen et al., 2011) and high-pressure hydro processing (Zhang et al., 2009b). In addition, bio-oils can be used as a feedstock for production of chemicals, such as phenols for resin production, additives in fertilising and pharmaceutical industries, flavouring agents (such as glycol aldehyde) in food industries (Balat, 2011). Table 2.6 described some physical and characteristics of pyrolysis oil (Jahirul et al., 2012).

Table 2. 6: Physical properties and characteristics of pyrolysis bio-oil (Jahirul et al., 2012).

Properties	**Pyrolysis Oil Characteristics**
Appearance	Dark red-brown to dark green
Odor	Distinctive odor—pungent smoky smell
Density	Very high compared to fossil fuel
Viscosity	Can vary from as low as 25 centistokes (cSt) to as high as 1000 cSt
Heating Value	Significantly lower than fossil oil
Aging	Viscosity increase, volatility decrease, phase separation and deposition of gum occur with time
Miscibility	Miscible with polar solvent but totally immiscible with petroleum fuel

2.5 Biomass Conversion

Biomass can be converted either directly or indirectly to produce energy products, such as biofuel. There are diverse technologies, which differ in their efficiency, level of development, investment, operation and maintenance costs, and labor requirements to convert the potential energy content of biomass into useful forms of energy. The conversion of biomass waste into useful energy can be achieved through thermochemical and biochemical processes. The biochemical and thermochemical conversion technologies degrade biomass using various enzymes and using heat respectively. A varied range of products obtained through biomass conversion technologies, including thermochemical, and biochemical are presented in Figure 2.3 (Akhtari et al., 2014).

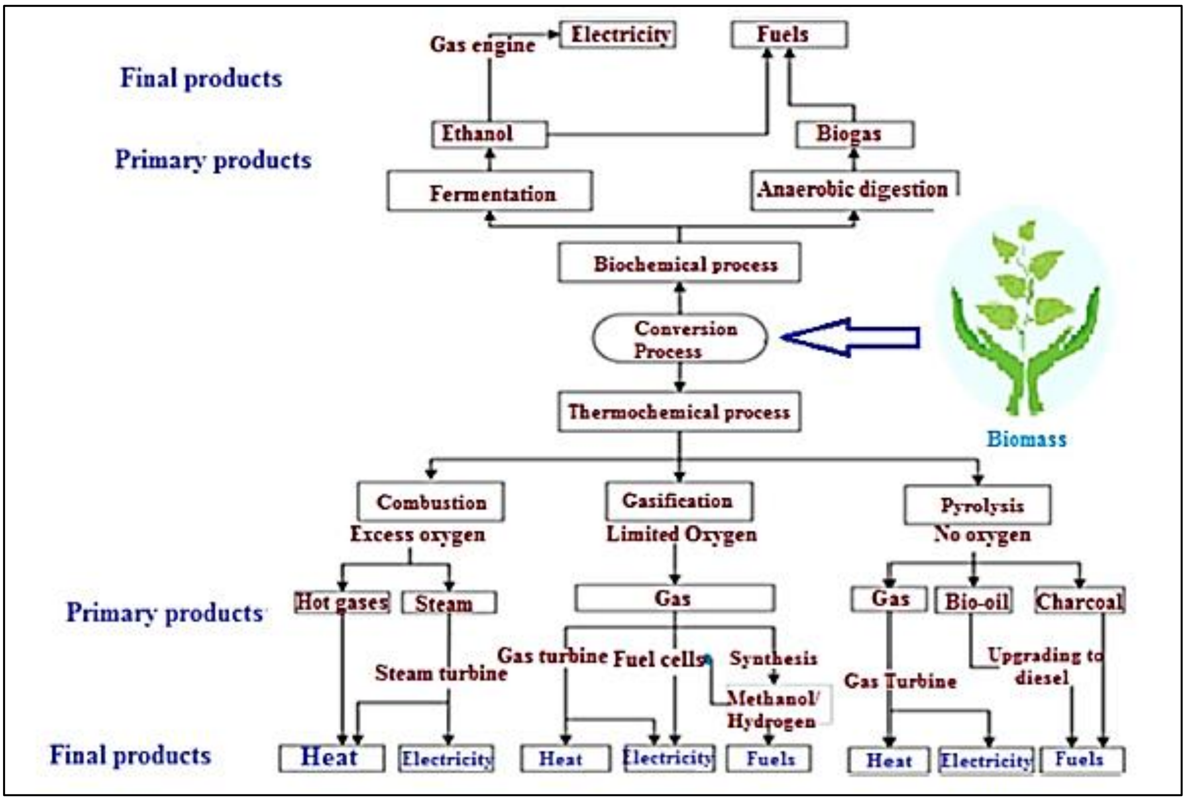

Figure 2.3: : Biomass conversion processes and their products (Akhtari et al., 2014).

A lot of researchers carried out thermochemical conversion technologies to convert biomass into biofuels. Gasification, combustion and pyrolysis are thermochemical conversion processes.

Gasification is happened at high temperature in order to optimize gas production to use in gas turbines to produce electricity. It is an exothermic partial oxidation of biomass for high yields of gaseous products such as syngas or producer gas which rich in CO, H_2, CH_4, and CO_2 (Milne et al., 1998). The gas can be cleaned and used as an engine fuel or upgraded to liquid fuels or chemical feed stocks through biological or catalytic upgrading via the Fischer-Tropsch process (Datar et al., 2004).

The direct combustion of biomass is still the dominant bioenergy pathway for global (Gaul, 2012). Complete combustion involves the production of heat when it's completely oxidize to CO_2 and H_2O. However, the reactions that take place during biomass combustion are complex (Jenkins et al., 1998). This process leads to incomplete combustion and release environmental air pollutants such as CH_4, CO, and particulate matter (PM) which are very harmful to living organisms. In addition, sulfur and nitrogen, are associated with emission of SO_X and NO_X which causes acid rain.

Pyrolysis is the thermal decomposition of biomass into liquid, gaseous and solid by heating the biomass to about 400-600 ^oC in the absence of oxygen. Pyrolysis is an endothermic reaction. The liquid product is a heterogeneous mixture characterized by high oxygen content and alkalinity, which can be upgraded to fuels or chemicals (Field et al., 2013, Demirbas, 2001).

2.6 Pyrolysis

Pyrolysis is a promising thermochemical technology, more favourable and economical for converting biomass into energy fuels (Ferrera-Lorenzo et al., 2014, Soetardjia et al., 2014). Moreover, pyrolysis produces high energy fuels with less pollution, making it the most effective processes for biomass conversion ad eventually replacing non-renewable fossil fuel resources. The biomass pyrolysis reaction is accomplished in the absence of oxygen and in a typical temperature range of 450–600 ^{o}C (Guizani et al., 2017).

Depending on the heating rate, pyrolysis can be divided into three types including slow, flash and fast pyrolysis. Slow pyrolysis uses lower biomass particle heating rates (5-80 ^{o}C min^{-1}) and longer vapor residence times, enhancing the production of tars and char. The flash pyrolysis process is characterized by higher heating rates and shorter residence time resulting high bio-oil yield. Fast pyrolysis requires high biomass particle heating rates (100-120 ^{o}C min^{-1}) and short vapor residence times, thus producing directly a liquid fuel (Demirbas, 2001).

Many studies have already been carried out on energy utilizations, which were introduced pyrolysis processes for the treatment of waste biomass materials for the production of bio-oil due to its cost effective and easily can handle operation. Francavilla et al., (2015) was carried out pyrolysis of G. gracilis (macroalgae) residue in order to investigate the production of bio-oil and bio char within a pyrolysis temperature range of 400–600 ^{o}C. Results showed that the bio-oil yield is high (65 wt%) at temperature 500 ^{o}C and bio char yield ranged between 33 wt% (400 ^{o}C) and 26.5 wt% (600^{o}C).

Soetardji et al., (2014) have carried out slow pyrolysis of Jackfruit Peel in a fixed-bed reactor at a range of temperature of 400-600 ^{o}C, heating rate range between 10-50 ^{o}C/min, and a range of nitrogen flow between 2-4 L/min. Results showed that the highest bio-oil yield (52.6%) was obtained at 550 ^{o}C with nitrogen flow rate of 4 L/min and heating rate of 50 ^{o}C/min.

Duman et al., (2011) have studied on the slow and fast pyrolysis of cherry seeds (CWS) and cherry seeds shells (CSS) in fixed-bed and fluidized bed reactors at different pyrolysis temperatures. They was investigated the influence of reactor type and temperature on the yields and composition of products. In the case of fast pyrolysis, the result showed maximum bio-oil yield was 44 wt% at pyrolysis temperature of 500 ^{o}C for both CWS and CSS, whereas the slow pyrolysis of CWS and CSS, the bio yields were of 21 and 15 wt% obtained at 500 ^{o}C respectively. The characterization of bio-oils were analyzed for slow pyrolysis and fast pyrolysis of both CWS and CSS at maximum yield condition which are can be used as a fuel for combustion systems in industry and can be evaluated as a chemical feedstock respectively. Therefore pyrolysis is considered to be an appropriate method to convert biomass into high value-added products such as bio-oil and gas (Jiang et al., 2017, Soetardjia et al., 2014).

2.7 Fast Pyrolysis

Among the pyrolysis conversion technologies, fast pyrolysis is a productive and efficient method since high yield and quality of liquid fuels could be obtained quickly (Anex et al., 2010, Mortensen et al., 2011). In fast pyrolysis, once the desired temperature of reactor reached biomass drops into the reactor to decomposes very quickly and generate high amount of vapors and condense it to produce bio-oil liquid. At the end of the reaction there is small amount of charcoal and gases are produced (Fan et al., 2017). Technically, to improve the yield and quality of desired products the parameter conditions in the fast pyrolysis process are easy to be adjusted.

Biomass fast pyrolysis has been explored by various researchers across the worldwide to yield bio-oil which is easier to places of productive usage (Fan et al., 2017, Maher and Bressler, 2007). Yanik et al., (2007) study on fast pyrolysis of three agricultural wastes (corncob, straw and oreganum stalks) at 500°C in a fluidized bed reactor. The result showed that the oil yields varied between 35 and 41%, depending on biomass type. This is due to different volatile matter according to type of biomass. Liu et al., (2009) have studied on fast pyrolysis of corn straw in a bench-scale fluidized bed reactor. In his experiment, the maximum bio-oil yield was 42 wt% at 525 ^{o}C pyrolysis temperature, <45 mm biomass particle size, 0.8s vapors residence time (Liu et al., 2009).

Tan et al., (2017) studied on fast pyrolysis of durian in a drop-type fixed bed reactor physicochemical properties of the products. The experiment was carried out with different particle sizes (up to 5 mm) and reaction temperatures (250–650 ^{o}C). The highest bio-oil yield was obtained at 650 ^{o}C (57.45 wt%) with 1–2 mm of particle size. Fast pyrolysis of Corn straw in a bench-scale fluidized bed reactor was studied by Liu et al., (2009). In the experiments, the influence of pyrolysis temperature (450-550 ^{O}C), biomass particle size (0.45-2 mm), and vapors residence time (0.8-1.6 s) on the product distribution was investigated. The results shows maximum bio-oil yield was 42.00 wt% at 525 ^{o}C pyrolysis temperature, <0.45 mm of biomass particle size, 0.8 s of vapors residence time. The product of bio-oil analysis with GC-MS showed that, the bio-oil was the mixture of complex organic compounds with higher amount of oxygenated compounds. Table 2.7 shows the summarize literature review of fast pyrolysis of biomass.