SYNGAS PRODUCTION FROM MICROWAVE PLASMA GASIFICATION OF OIL PALM CHAR

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ABSTRACT

Gasification is heating-up of solid or liquid carbonaceous material with some gasifying agent to produce gaseous fuel. Conventional gasification normally operates at higher pressure than atmospheric pressure and requires heat up during startup compared to microwave gasification. In this study, both microwave gasification and microwave plasma test rigs were designed to produce syngas from char. A quartz reactor of 600mm length and 20mm internal diameter with swirling gas inlet was designed as the gasification reactor. CO_2 was used as a gasifying agent for syngas production. Oil palm empty fruit bunch (EFB) char and oil palm shell (OPS) char were used as the carbonaceous materials. The flow rate of CO_2 varied from 1 to 4 lpm. The microwave output power was supplied continuously at 800W for 5 min. The syngas was analysed using gas chromatograph (GC) Agilent 6890 fitted with packed column, Thermal Conductivity Detector (TCD), and capillary column for measuring volumetric concentration of CH_4, CO_2, CO, and H_2. From the study, it was found that EFB char is better than OPS char as gasification fuel due to high porosity and surface area that will increase the char reactivity towards CO_2. For plasma gasification, the temperature increment promoted by the addition of microwave absorber using activated carbon (AC) increased the CO composition. The optimum condition for microwave char gasification of EFB was 3 lpm with 25 wt% AC that produced syngas with 1.23 vol% CH_4, 20.88 vol% CO_2, 43.83 vol% CO, 34.06 vol% H_2 and the calorific value of 9.40 MJ/kg. For OPS it was at 2 lpm with 1.12 vol% CH_4, 35.11 vol% CO_2, 35.42 vol% CO, 28.35 vol% H_2 and the calorific value of 7.32 MJ/kg. The highest carbon conversion efficiency for EFB and OPS chars were 76.02% and 67.72%, respectively. CO_2 flowrates affected the carbon conversion efficiency because it is related to reactivity of different type of char. As EFB char has higher surface area and larger pores than OPS char, the ability to adsorb the gasifying gas is better than OPS, thus resulting in higher carbon conversion. The best gasification efficiency was 72.34% at 3 lpm, 10 wt% AC for EFB with 12% unreacted carbon. For OPS, the maximum gasification efficiency was 69.09% at 2 lpm, 10 wt% AC with 18% unreacted carbon. In conclusion, plasma gasification of oil palm waste is an alternative for solid waste treatment that uses less energy, time, and cost.

ABSTRAK

Gasifikasi ialah proses pemanasan bahan berkarbon pepejal atau cecair dengan menggunakan beberapa ejen gasifikasi untuk menghasilkan bahan api gas. Gasifikasi konvensional biasanya beroperasi pada tekanan tinggi dan memerlukan masa yang lama untuk pemanasan, berbeza dengan gasifikasi gelombang mikro. Dalam kajian ini, rig gasifikasi gelombang mikro dan gasifikasi telah direka untuk menghasilkan gas daripada arang. Sebuah reaktor dari kaca quartz dengan panjang 600 mm dan diameter dalaman 20 mm dengan aliran masuk pusaran direka sebagai reaktor gasifikasi. CO_2 digunakan sebagai agen gasifikasi untuk pengeluaran gas. Tandan buah kosong (EFB) dan tempurung kelapa sawit (OPS) digunakan sebagai bahan berkarbon. Kadar alir gas CO_2 ditetapkan pada 1 hingga 4 lpm. 800 W kuasa disalurkan pada ketuhar gelombang mikro selama 5 minit. Gas sintetik dianalisis dengan alat gas kromatograf (GC) Agilent 6890 dilengkapi dengan turus jenis terpadat, TCD, dan turus kapilari untuk mengukur komposisi CH_4, CO_2, CO, and H_2. Dari kajian, didapati arang EFB lebih bagus dari arang OPS dalam gasifikasi kerana kadar keporosan dan luas permukaan yang tinggi. Bagi gasifikasi plasma, kenaikan suhu kesan dari penambahan karbon teraktif ke dalam arang telah meningkatkan juga komposisi CO yang terhasil. Kondisi optimum untuk gasifikasi gelombang mikro bagi arang EFB adalah 3 lpm dengan 25% AC gas sintesis dengan komposisi 1.23 vol% CH_4, 20.88 vol% CO_2, 43.83 vol% CO, 34.06 vol% H_2 dan 9.40 MJ/kg nilai kalori gas. Untuk OPS pula ialah pada 2 lpm dengan komposisi 1.12 vol% CH_4, 35.11 vol% CO_2, 35.42 vol% CO, 28.35 vol% H_2 dan 7.32 MJ/kg nilai kalori gas. Kecekapan penukaran karbon tertinggi untuk EFB dan OPS adalah masing-masing 76.02% dan 67.72%. Kadar alir CO_2 memberi kesan kepada kecekapan penukaran karbon kerana ia berkait dengan reaktiviti jenis arang berbeza. Oleh kerana arang EFB mempunyai luas permukaan dan liang yang lebih besar dari OPS, maka kecekapan penukaran karbonnya adalah lebih tinggi. Kecekapan gasifikasi EFB adalah 72.34% pada 3 lpm, 10 wt% AC dengan 12% karbon tidak terbakar. Untuk OPS, kecekapan gasifikasi terbaik adalah 69.09% pada 2 lpm, 10 wt% AC dengan 18% karbon tidak terbakar. Kesimpulannya, gasifikasi plasma sisa kelapa sawit adalah alternatif untuk rawatan sisa pepejal yang menjimatkan tenaga, masa, dan kos.

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LIST OF ABBREVIATIONS

AC	-	Activated carbon
BET	-	Brunauer Emmet Teller
CNTs	-	Carbon nanotubes
CV	-	Calorific value
DC	-	Direct currents
EFB	-	Empty fruit bunches
GC	-	Gas chromatography
HFSS	-	High frequency structure simulator
HV	-	Heating value
LPG	-	Liquefied petroleum gas
MSW	-	Municipal solid waste
MW	-	Microwave
MWDPG	-	Microwave-induced drying, pyrolysis, and gasification
OPF	-	Oil palm fiber
OPS	-	Oil palm shell
PAH	-	Polycyclic aromatic hydrocarbons
PCBs	-	Polychlorinated biphenyls
PE	-	Polyethylene
POME	-	Palm oil mill effluents
PSA	-	Pressure swing adsorption
RF	-	Radio frequency
RVC	-	Reticulated vitreous carbon
SGY	-	Specific gas yield
TCD	-	Thermal conductivity detector
TGA	-	Thermogravimetric analysis
WGS	-	Water gas shift

LIST OF SYMBOLS

K	-	Equilibrium constant
m	-	Mass
n	-	Moles
P	-	Power
Q	-	Volumetric flowrates
R	-	Rate of reactions
S	-	Surface area
T	-	Temperature
t	-	Time
V	-	Volume
W	-	Weight
X	-	Conversion
x	-	Volume fraction
η	-	Efficiency
ξ	-	Extend of reaction
ϕ	-	Concentration

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Municipal solid waste (MSW), or more commonly known as solid waste are generated daily from the industrial sector, agricultural sector, and generally discarded by the society. The rapid population growth, as well as trend in urbanisation and socioeconomic demands are increasing in parallel to the generation of solid waste. The problem of waste management is becoming a withstanding concern to the global citizen. In the light of this situation, this research proposes an elegant solution to contain the situation, as well as providing an alternative green energy which has the potential to replace the depleting natural resources. By converting these wastes into syngas or synthesis gas; we might be able to replace natural gas for industrial, and everyday energy applied by the masses. For instance, syngas may be burned directly in gas engines, used to produce methanol and hydrogen, or converted via the Fischer-Tropsch process into synthetic liquid fuel (Laurence and Ashenafi, 2012).

Syngas is created by the process of gasification. Gasification is heating-up of solid or liquid carbonaceous material with some gasifying agent to produce a gaseous fuel (Ahmed and Gupta, 2009). Carbonaceous fuels such as coals and biomass commonly use in gasification to produce syngas. The heating value of the gases produced is generally low to medium. Combustion is excluded because the product flue gas has no residual heating value from complete combustion of the fuel. Meanwhile, partial oxidation of fuel or fuel-rich combustion, and hydrogenation are included. The oxidant or gasifying agent in partial oxidation process could be steam, carbon dioxide, air or oxygen, or some mixture of two or more gasifying agents. The oxidant is chosen according to the desired chemical composition of the syngas and efficiency (Ahmed and Gupta, 2009). The high-temperature process refines corrosive ash elements such as chloride and potassium, allowing clean syngas production ready to be used.

Even though conventional gasification is a clean energy technology, it also has some disadvantages. Plasma gasification can compensate for these weaknesses as it is operated under atmospheric pressure and requires a short time to elevate to a higher temperature than conventional gasifier using external electric energy. Conventional gasification technologies maintain the high temperature required for the gasification through partial oxidation of fuels. Plasma gasification technology, however, achieves a gasification reaction temperature by using a high-temperature plasma flame generated using external electric energy (Yoon and Lee, 2011). Plasma gasification technology is commonly referred to as "true gasification" or "pure gasification" because it leads to a pure gasification reaction with a rare occurrence of combustion (Mountouris *et al.*, 2008). Using this technology promotes chemical reactions due to the generation of active particles, including radicals and ions to reduce reaction times (Kanilo *et al.*, 2003).

With the growth of palm oil production in Malaysia, the amount of residues generated will also increase. The oil palm industry is currently producing the largest amount of biomass in Malaysia with 85.5% out of more than 70 million tonnes (Shuit *et al.*, 2009). The type of biomass produced from oil palm industry includes empty fruit bunches (EFB), oil palm fiber (OPF), oil palm shell (OPS), wet shell, palm kernel, fronds and trunks. Due to the huge amount of biomass generated yearly, Malaysia has the potential to utilize the biomass efficiently and effectively to other value added products. Plasma gasification will be able to convert these oil palm biomass to syngas that can be useful in the energy sector. This clearly shows the potential of oil palm biomass as one of the major sources of energy in Malaysia. Its renewable nature makes it even a more important energy source.

1.2 Problem Statement

Solid waste management is often fragmented, and lacks coherence for countries and cities across the globe. Even present, the system has been often negligent to basic environmental preservation and have serious environmental risks. The inconsistent standards, and lack of any scientific basis to the designs of such solid waste management led to general environmental degradation, and contributes directly to climate change. Gasification of biomass char would offer an opportunity for conversion of biomass wastes into value-added products in an environmentally friendly process. The greenhouse gas, CO_2 will be reduced to fuel gas, CO. In Malaysia about 50 million tons of Palm Oil Mill Effluents (POME) and about 40 million tons of Oil Palm Biomass are generated from the palm oil industries every year. The current management practice poses significant environmental problems as much of the waste is disposed by biomass burning of end product emit greenhouse gas into the atmosphere and leave high organic content on the grounds (Alam and Ainuddin, 2007). These wastes, when not treated properly as such will lead to grave consequences to the population and the environment.

Gasification is a clean energy technology that generates syngas consisting of hydrogen and carbon monoxide through the partial oxidation of a fuel source (Yoon and Lee, 2011). However, the conventional gasification process had many arising problems. It operates at high pressure and requires a long time to heat up during startup. Bartels *et al.* (2010) reviewed 8 types of conventional gasification with different gasifier design. The gasification pressure range was between 70 to 120 bar which is very high pressure. Stassen and Knoef (1995) compared between operation parameters of fixed bed gasifiers and list out the startup time for gasifier between 10 to 60 minutes. In microwave heating systems, rapid and selective material heating can be achieved in only a few minutes with instantaneous start-up and close-down of the processes (Kasin, 2006). In conventional gasification, heat is transferred from the surface towards the center of the material by convection, conduction, or radiation, so the heat transfer is inconsistent. As for microwave plasma gasification, the electromagnetic energy is converted to thermal energy inside the material thus provides a selective and higher heating rate (Fernández *et al.*, 2011; Domínguez *et al.*, 2008).

Microwave plasma gasification is ideal for high temperature heterogenous gas-solid reactions. Microwave absorbers are used to absorb the microwave energy and transfer it to the fuel material. The ratio of microwave absorber to char in plasma gasification plays an important role in achieving optimum product yield (Guo *et al.*, 2008; Salema and Ani, 2011; Bu *et al.*, 2011). It is predicted that an increase in the activated carbon percentage might increase the temperature of gasification reaction temperature. At extremely elevated temperature, the char can be gasified within a few seconds without any intermediate reactions (Zhang *et al.*, 2010). Microwave plasma gasification will definitely contribute to the energy industries in providing clean gas alternative as well as engaging a solution for greenhouse gas emission.

1.3 Objectives of the Study

Based on the issues of conventional gasification mentioned above, this research will compensate the problems by using microwave plasma gasification. The objectives of this research are:

i. To investigate the CO_2 microwave gasification of EFB and OPS oil palm chars, and optimize the char reaction rate through the implementation of different CO_2 flowrates.

ii. To characterize and analyse the microwave plasma gasification products with respect to the addition of activated carbon as microwave absorber to the oil palm chars using CO_2 as gasifying agent.

1.4 Scopes of the Study

Biomass that were used in this research are Empty Fruit Bunch (EFB) and Oil Palm Shell (OPS). The waste biomass were obtained from the Federal Land Development Authority (FELDA) oil palm mill in Kulai, Johor. The biomass undergo pyrolysis in a conventional oven to produce char. A domestic microwave oven with 800kW power and 2.45GHz frequency was modified to set up a vertical quartz reactor inside the microwave cavity. The biomass char was positioned in the center of the microwave to undergo plasma gasification experiment. Nitrogen was used as the carrier gas and CO_2 as the gasifying agent. The effects of CO_2 flowrates, char types, and activated carbon to the syngas produced was investigated. The gas specific yield, conversion efficiency, and gas heating value was calculated from the result of syngas analysis. The biomass and char were analysed for proximate analysis, ultimate analysis, and the Brunauer- Emmet- Teller (BET) surface area.

Two types of char which is EFB and OPS was studied because of their different physical and chemical properties. The char sample size for the gasification experiment was 5g as it is the amount that fit perfectly in the reactor. The flow rate of CO_2 was ranging from 1-4 lpm and nitrogen was fixed at 3 lpm. The microwave was run for 5 minutes only to prevent overheating of equipment as plasma gasification produced high temperature.

1.5 Significance of Study

This study can help improve the current POME treatment which is using conventional gasification. By using microwave plasma gasification, the char reaction rate can be increased tremendously. This developing technology has attracted researchers all over the world as it optimized the fuel and energy consumption with short processing time. The usage of microwave energy in gasification is promising due to the enhanced chemical reaction and improved yield obtained compared to conventional gasification. Generating energy requires precious natural resources, for instance, coal, oil or gas. Converting waste to energy will help us preserve these resources and make them last longer in the future. Therefore, the findings from this study will contribute a significant improvement in the CO_2 microwave gasification process.

1.6 Report Outline

There are five chapters in this report. The first chapter is an introduction to the thesis. It presents the background of the study, problem statement, objectives and scopes of study, the significance of the study, and report outline. Chapter 2 presents a literature review on solid waste treatment, plasma treatment and processing, carbonaceous solid, and parameter of the study. In Chapter 3, reports on material and method including experimental procedures for biomass and char preparation, and microwave plasma gasification are presented. The results and discussion are presented in Chapter 4. This depicts the discussion on the effect of CO_2 flow rates and char type to syngas composition, analysis of syngas produced, effect of activated carbon to reaction temperature profile, gas specific yield, carbon conversion efficiency, and gas heating value. It also covers the characterization of biochar for the gasification. The final chapter provides conclusions for this study and recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

2.1.1 Overview on Solid Waste Treatment

Enormous amount of solid wastes generated daily from municipal solid waste (MSW), industrial sector, agricultural sector and forest sector globally. These wastes can be converted into syngas which is potentially able to replace natural gas for industrial and energy application. Various thermal processes, such as pyrolysis, vitrification, gasification, and incineration, can be used for treating these hazardous wastes. The objective of the treatment is to breakdown the organic fraction and converts the inorganic fraction so that it could be reused or disposed properly as an inert silicate slag (Colombo *et al.*, 2003; Sabbas *et al.*, 2003; Kuo *et al.*, 2006).

Alternatively, combustion of solid wastes could be used to process organic wastes, enabling energy recovery (Vaidyanathan *et al.*, 2007). However this is only applicable to wastes that do not contain hazardous or toxic substances. In which case, the plasma treatment could be used to treat these toxic wastes and benefit from their recoverable energy content. As well, the plasma is a safer and more ecofriendly option. This is because, the plasma arcs have high temperature, and consequently this will reduce any potential for undesirable byproducts to be generated. This is observable in the syngas produced.

2.1.2 Malaysian Solid Waste Data

2.1.2.1 Sources and Types of Waste Generation in Malaysia

In Malaysia, waste materials are generated daily in the form of MSW, sewage sludge, industrial waste, agricultural waste, and clinical waste. These waste contain pollutant such as heavy metals and agrochemicals that can contaminate the nature. Some of the factors that contribute to waste generation in Malaysia are industrialization achievements of the nation, population growth, and increase in the disposable products, significantly adding to the growing amounts of paper and plastic refuse. These factors have also contributed to the rise in pollutants dumped into rivers and seas (Gregory, 1996). Fauziah and Agamuthu (2003) have predicted the generation of sectoral waste of Kuala Lumpur (tonnes/day) for the year 2009 until 2023. Saeed *et al.* (2008) stated that sectoral waste in Malaysia is made up of waste from residential (48%), street cleansing (11%), commercial (24%), institutional (6%), construction and industry (4%), and landscape (7%). *Figure 2.1* shows sectoral MSW generated from 2009 to 2023.

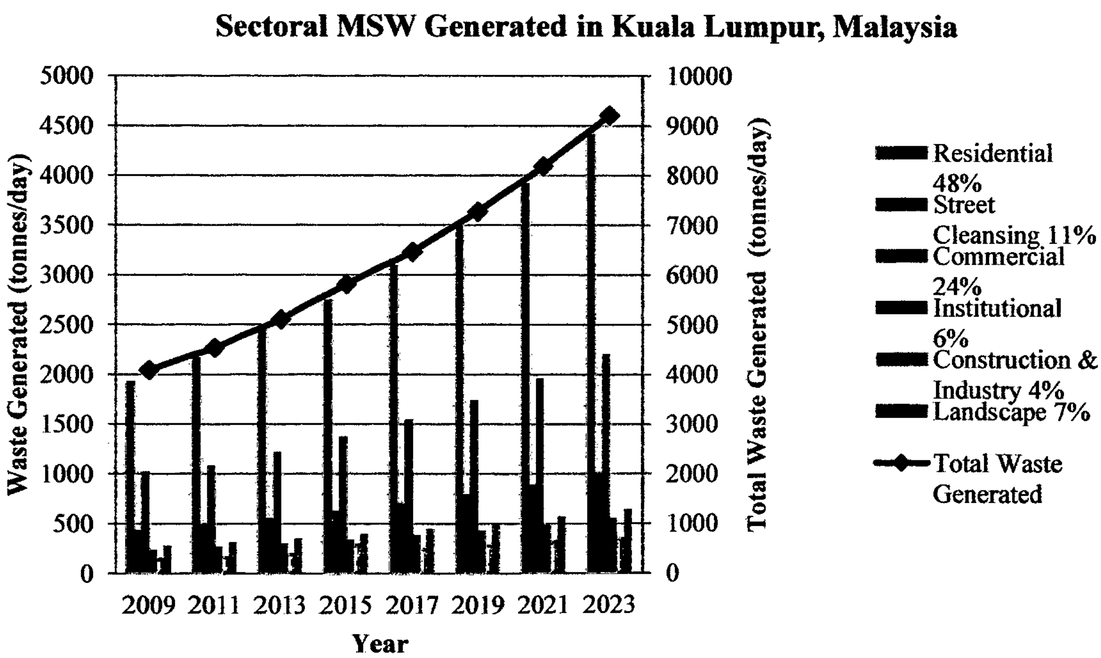

Figure 2.1 Sectoral MSW Generated in Kuala Lumpur, Malaysia (Fauziah and Agamuthu, 2003)

2.1.2.2 Municipal Solid Waste (MSW)

Ghazali *et al.* (1996) estimated that waste in Malaysia is projected to rise to 1 million tonnes per year and an average of 0.95 kg/person/day by 2000. This estimation is based on the facts that human population are growing and so is the standard of living. Koe and Aziz (1995) stated that in 1995, Malaysians generated 5.5 million tonnes of domestic and commercial waste, exclusive of toxic material. Solid waste contains materials such as organic matter, plastics, glass and metals. A research on authorized coastal disposal sites by Koe and Aziz (1995) indicated that solid waste composed of the following materials: organic garbage (56%), paper (25%), plastics (8%), metals (6%), and glass (3%). *Figure 2.2* shows the daily generation of MSW in three highly populated states in Malaysia, namely Kuala Lumpur, Pulau Pinang, and Johor. The predicted results from year 2014 above is calculated using assumptions and formula proposed by Saeed *et al.* (2008). *Figure 2.3* shows the composition of MSW generated in Kuala Lumpur in 2002 as presented by Kathiravale and Yunus (2008) from Malaysian Institute for Nuclear Technology Research (MINT). The average composition as shown on *Figure 2.3* is that the organic content is around 40% with another 20% being inorganic.

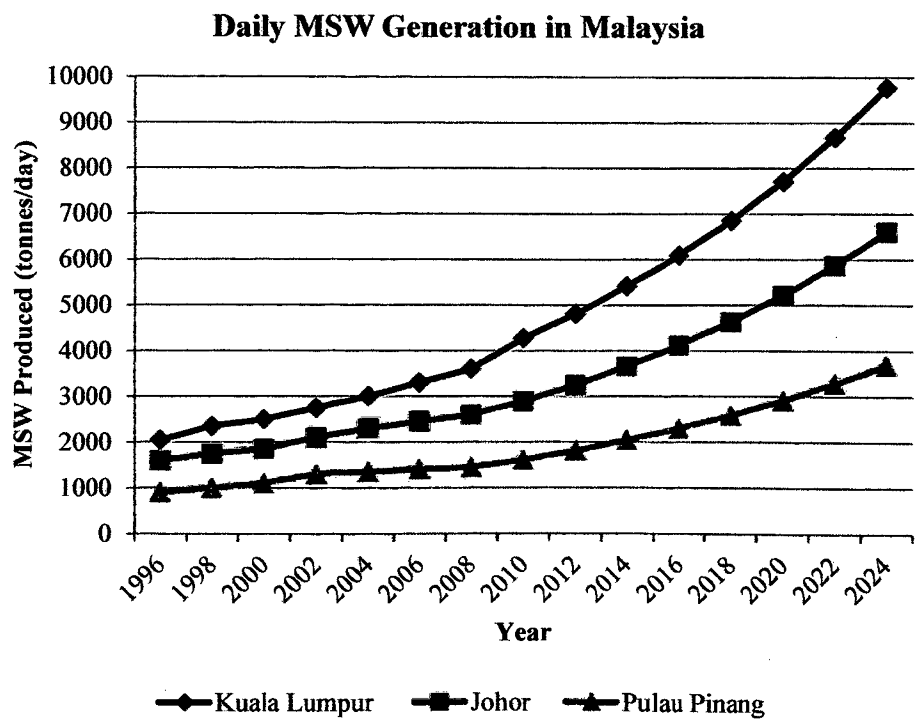

Figure 2.2 Daily MSW generation in Malaysia (Saeed *et al.*, 2008)

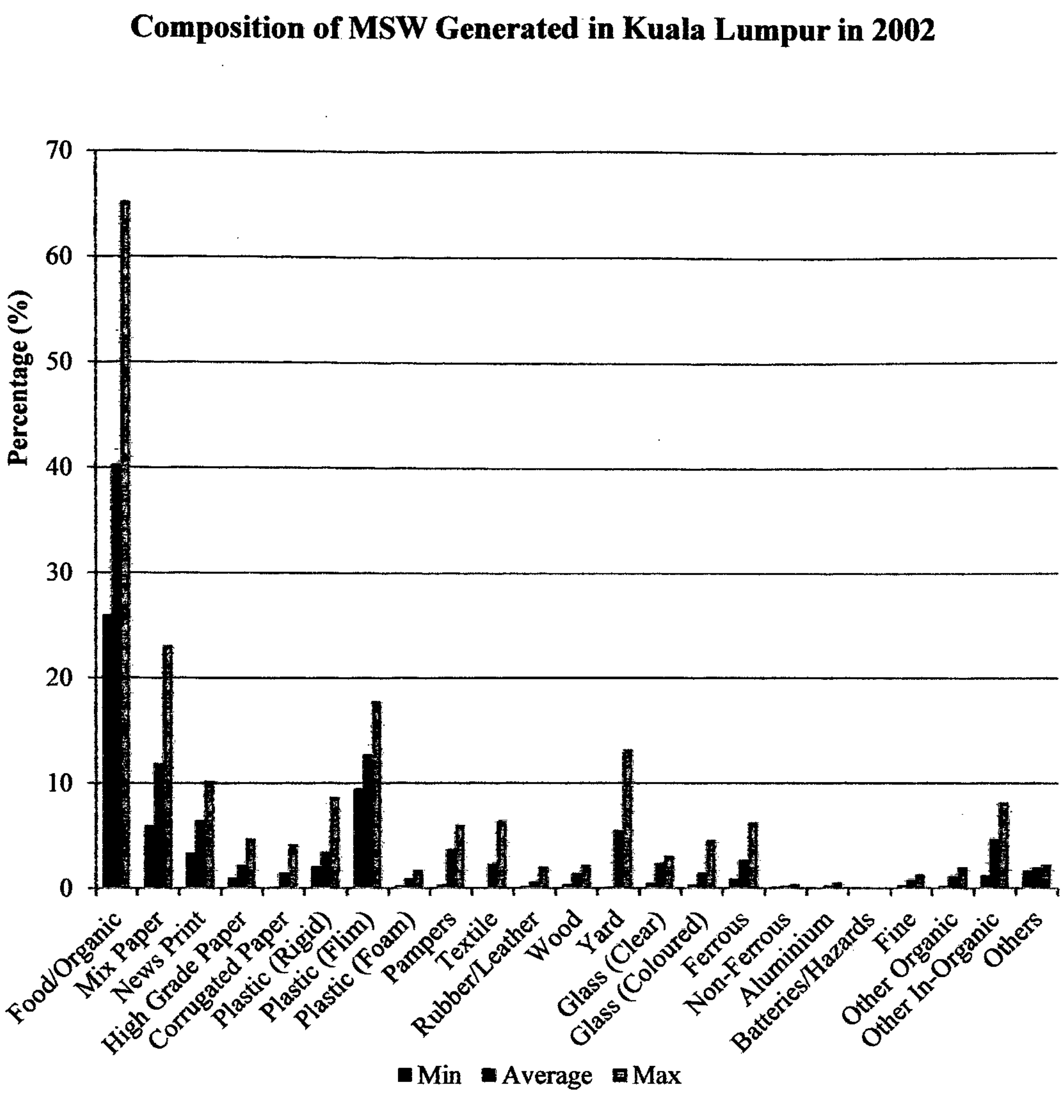

Figure 2.3 Composition of MSW Generated in Kuala Lumpur in 2002 (Kathiravale and Yunus, 2008)

2.1.2.3 Sewage Sludge

Koe and Aziz (1995) stated that domestic sewage is a major source of organic pollutants in coastal waters from both urban and rural populations in South East Asia 366 tonnes of domestic sewage is generated per day, 80% of the national daily output. The number increases by 20% from 1986 to 1990 according to Law *et al.* (1992). Malaysia produces 5 million cubic meters of domestic sludge. By the year 2022, Indah Water Konsortioum (1997) estimated that the amount will be increased to 7 million cubic meters per year. According to Goto (2013), estimated sludge amount produced in Malaysia can be derived from the summation of the water production. In generally, the ratio of the coagulant/water production is around 0.0205. If the water production is Q_W (tonnes), the sludge amount can be estimated as Equation 2.1:

$$\text{Sewage Sludge Amount (tonnes)} = Q_W \times 0.0205 \tag{2.1}$$

However, the ratio of the coagulant/water production changes from 0.05(max) to 0.007(min) according to the quality of the water resources or the operation situation grade of the treatment in each water treatment site. Statistic of water production in Malaysia can be referred from National Water Service Commission Malaysia (2011).

2.1.2.4 Industrial Waste

Department of Environment, Malaysia (2011) specified that the main source of hazardous waste are metal finishing, electroplating, chemical, electronics, printing and packaging industries. According to Guven (2001) , industrial process in a country will depend on the nature of the industrial base. Waste generated may consist of pure substances or as complex mixtures of varying composition and in varying physicochemical states. General factory rubbish, organic waste from food processing, acids, alkalis, metallic sludges and tarry residues are examples of industrial waste. Waste that is hazardous or potentially toxic, will require special handling, treatment and disposal. Table 2.1 shows the quantity of scheduled waste generated by industry from the year 2004 to 2011.

Table 2.1 Quantity of Scheduled Waste Generated by Industry from Year 2004 to 2011 (National Water Service Commission, 2011)

Year	MT/Year
2004	469,584
2005	548,916
2006	1,103,457
2007	1,138,840
2008	1,304,899
2009	1,705,308
2010	1,880,929
2011	1,622,031

2.1.2.5 Agricultural Wastes

Some example of agricultural waste are horticultural and forestry waste, comprise crop residues, animal manure, diseased carcasses, unwanted agrochemicals and 'empty' containers. Guven (2001) argues that estimates of agricultural waste arising are rare, but they are generally thought of as contributing a significant proportion of the total waste matter in the developed world. According to Law *et al.* (1992), in Peninsular Malaysia, estimated a total of 4.2 million tonnes of crop residues and 2.3 million tonnes of livestock waste is produced in the 90s. Crop residues such as rejected agricultural materials in the form of straws, leaves, and other by-products, which are burned, dumped and disposed of, account for nearly half of all agricultural production. *Figure 2.4* illustrates the production of agricultural waste in Malaysia in 1997 generated from the production of rice, palm oil, rubber, coconut and forest products. Waste from palm oil are also known as biomass waste. Types of oil palm biomass and quantity produced in the year 2012 in Malaysia are shown on Table 2.2.

CHAPTER 1

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Microwave plasma gasification is ideal for high temperature heterogenous gas-solid reactions. Microwave absorbers are used to absorb the microwave energy and

CHAPTER 3

RESEARCH METHODOLOGY

3.1 Introduction

This chapter describes the materials and methodology in the microwave plasma gasification experiments and how the data was analyse. Preparation and characterization of the biomass, gasification rig design and experiment, and product gas analysis will be discussed further in this chapter.

3.2 Flowchart of Experiment

The process and steps of microwave plasma gasification experiments carried out is illustrated in a flowchart in *Figure 3.1*. This flowchart shows the steps involved in this study including materials preparation, design of microwave plasma rig, char characterization, microwave plasma gasification experiment, and syngas analysis.

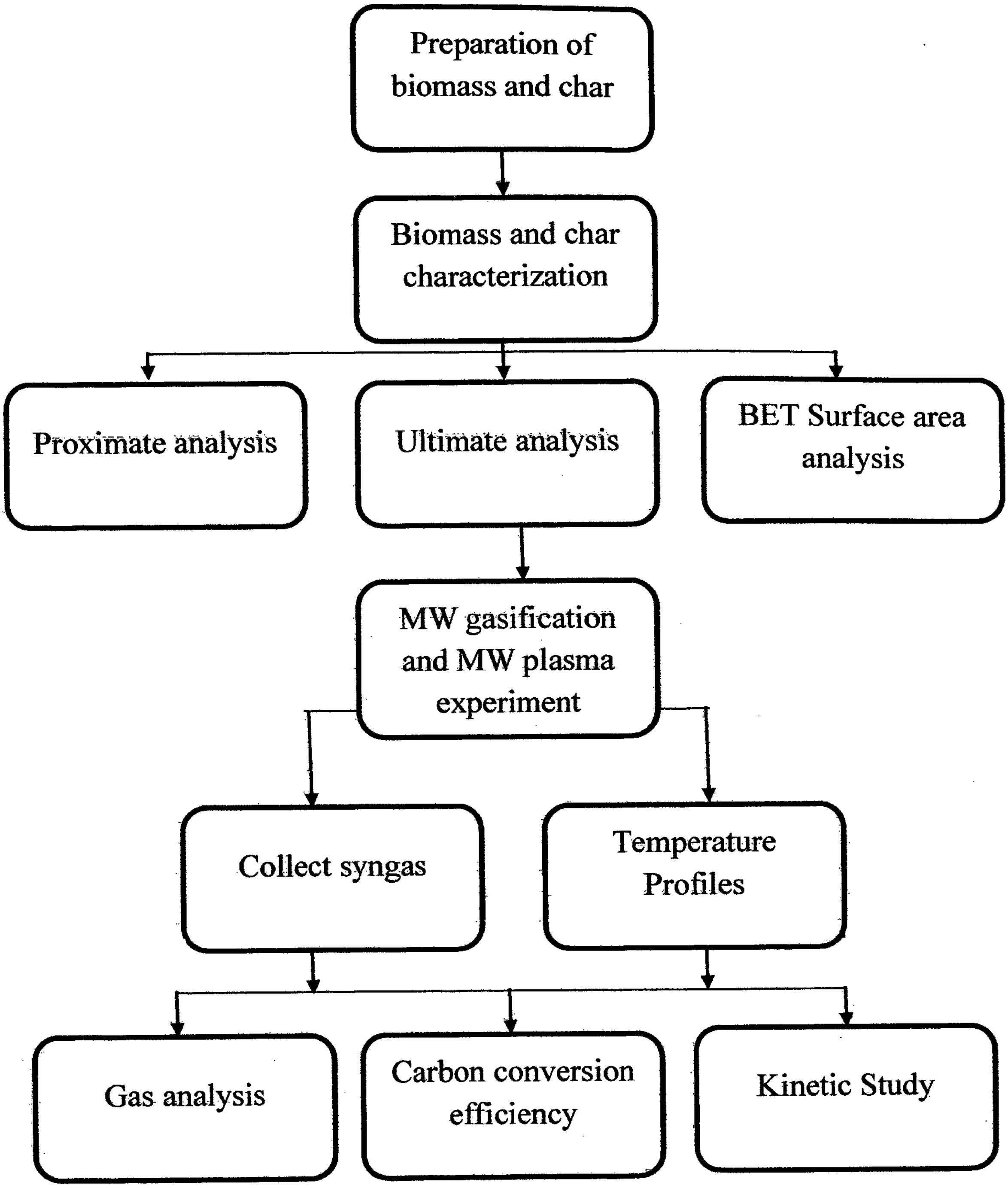

Figure 3.1 Research Flow Diagram

3.3 Materials

3.3.1 Preparation of Biomass

The two types of palm biomass received - the empty fruit bunch (EFB) and oil palm shell (OPS) were obtained from the Federal Land Development Authority (FELDA) oil palm mill in Kulai, Johor. Both biomass were dried in a conventional oven at 105°C for 24 hours to remove the water content. After that, the biomass was grinded as the raw biomass size are not suitable for the pyrolysis. Grinding the biomass to a smaller size will increase the surface area for reaction to occur. EFB and OPS were grinded and sieved to 1.18 to 2.00 mm. *Figure 3.2* shows the EFB and OPS biomass after the grinding and sieving process. The grinder machine from Polymer Lab, Faculty of Chemical Engineering, UTM, is shown in *Figure 3.3*.

Figure 3.2 EFB and OPS biomass

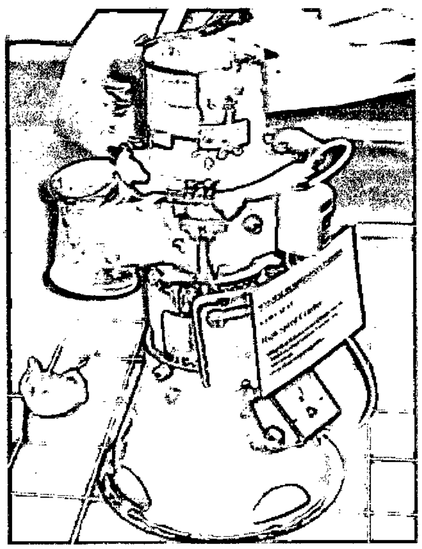

Figure 3.3 Grinder Machine

3.3.2 Preparation of Char

Pyrolysis of biomass is done to convert the biomass into char. A fixed bed furnace is used in this process. The whole system is a vertical furnace with an inlet gas flow from below. This pyrolysis rig consists of temperature controller, heating