PREPARATION OF BIOCHAR FROM PALM OIL MILL EFFLUENT (POME) SLUDGE BY MICROWAVE PYROLYSIS

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PREPARATION OF BIOCHAR FROM PALM OIL MILL EFFLUENT (POME) SLUDGE BY MICROWAVE PYROLYSIS

by

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LIST OF ABBREVIATIONS

BET	Brunauer, Emmett and Teller
BOD	Biological oxygen demand
COD	Chemical oxygen demand
DCFC	Direct Carbon Fuel Cell
EFB	Empty fruit bunches
FTIR	Fourier Transformation Infrared Spectrometer
GDP	Gross domestic product
GHG	Greenhouse Gases
HTC	Hydrothermal carbonization
HTG	Hydrothermal gasification
HTL	Hydrothermal liquefaction
MFC	Microbial fuel cell
OPS	Oil palm shell
POME	Palm oil mill effluent
S_{BET}	BET Surface Area
SEM	Scanning Electron Microscope
SNG	Synthetic natural gas

PENYEDIAAN BIOARANG DARIPADA ENAP CEMAR EFLUEN KILANG MINYAK KELAPA SAWIT (POME) OLEH PIROLISIS GELOMBANG MIKRO

ABSTRAK

Ciri-ciri dan aplikasi penjerapan Bioarang yang dihasilkan daripada enap cemar Efluen Kilang Minyak Sawit (POME) secara pirolisis gelombang mikro telah dibentangkan dalam laporan ini. Kajian ini dijalankan untuk mengkaji penghasilan Bioarang daripada enap cemar POME secara pirolisis gelombang mikro, kesan kuasa gelombang mikro, dan masa sinaran ke atas hasil Bioarang dan ciri-cirinya. Selain itu, kajian ini juga bertujuan untuk menilai kebolehlaksanaan penggunaan Bioarang untuk mengurangkan kekeruhan POME dengan menyingkirkan bahan cemar warna dalam POME. Pirolisis gelombang mikro dengan menggunakan gas Nitrogen (N_2) sebagai gas pembersih untuk menghasilkan Bioarang. Keadaan persediaan pirolisis optimum bagi Bioarang untuk pengurangan kekeruhan terbaik prestasi POME adalah pada kuasa gelombang mikro 700W dan 20 minit masa sinaran. Keadaan persediaan pirolisis ini mempunyai hasil Bioarang sebanyak 57.82% peratusan berat, menghasilkan Bioarang dengan pengurangan kekeruhan POME setinggi 75.01%. Selain itu, Bioarang yang dihasilkan daripada keadaan persediaan pirolisis optimum mempunyai S_{BET} 70.2238 m^2/g. Keluasan mikropori dan isipadu mikropori Bioarang ialah 16.8293 m^2/g dan 0.008874 sm^3/g. Bioarang mempunyai permukaan berliang, yang menunjukkan kepada keluasan permukaan luar Bioarang yang tinggi, menjadikannya mempunyai keupayaan penjerapan yang baik. Tidak seperti enap cemar POME kering, ia tidak mempunyai permukaan berliang untuk dijadikan tapak penjerapan bagi penjerapan bahan cemar organik dan bahan cemar warna. Kajian ini menunjukkan bahawa enap cemar POME yang

dikeringkan merupakan antara sisa yang berpotensi untuk ditukarkan kepada Bioarang melalui pirolisis gelombang mikro untuk tujuan penjerapan.

PREPARATION OF BIOCHAR FROM PALM OIL MILL EFFLUENT (POME) SLUDGE BY MICROWAVE PYROLYSIS

ABSTRACT

The characteristics and adsorption application of biochar produced from Palm Oil Mill Effluent (POME) Sludge by microwave pyrolysis has been presented in this report. This study was carried out to study the production of biochar from POME sludge by microwave pyrolysis, the effect of microwave power, and radiation time on the biochar yield and its characteristics. Besides, this study was also aimed to evaluate the feasibility of using biochar to reduce turbidity of POME by removing the colour contaminants in POME. Microwave pyrolysis by using Nitrogen (N_2) gas as purge gas was used to produce biochar. The optimum pyrolysis setup condition of the biochar for best turbidity reduction of POME performance is at a microwave power of 700W and 20 mins radiation time. This pyrolysis setup condition has a biochar yield of 57.82 wt%, producing biochar with turbidity reduction of POME as high as 75.01%. Besides, the biochar produced from the optimum pyrolysis setup condition has a S_{BET} of 70.2238 m^2/g. The micropore area and micropore volume of biochar is 16.8293 m^2/g and 0.008874 cm^3/g. The biochar has porous surface, which indicates to the high external surface area of the biochar, making it to have good adsorption capability. Unlike the dried POME sludge, it has no porous surface to be as adsorption site for the adsorption of organic contaminants and colour contaminants. This study showed that the dried POME sludge is a potential waste to be converted into biochar by microwave pyrolysis for adsorption purposes.

CHAPTER 1

INTRODUCTION

Malaysia is well-known for its tropical weather that receives substantial sunlight and rainwater throughout the year. This supremacy has allowed the fast-growing development of the local agriculture sector, particularly the palm oil industry. The palm oil industry in Malaysia has been served as the backbone of Malaysia's agriculture sector. In 2019, Malaysia exported around 17.4 million metric tons of palm oil and palm-based products. These exports were valued at approximately 67.5 billion Malaysian ringgit. Overall, the palm oil industry contributed around 36.9 billion ringgits to Malaysia's total gross domestic product (GDP), about a 2.7% yield of its GDP (Raudhah, 2021). The Malaysia's palm oil industry produced a large number of by products, such as empty fruit bunches (EFB), palm fibre, and shell, all of which can be used as a source of energy. As a result, it is critical for the palm oil industry to be sustainable in order to increase its long-term profitability and viability (Chuah *et al.*, 2006). However, the long-term viability of palm oil production has always been questioned. This is due to the controversy that palm oil plantations have serious negative environmental consequences, such as deforestation and greenhouse gas (GHG) emissions, as a result of over-exploitation of peat land for oil palm plantations. Besides, palm oil mills also contribute to environmental degradation through the production of palm oil mill effluent (POME), which is produced during the palm oil milling process (Lam and Lee, 2011).

The rapid development of the palm oil industry increases the production of POME drastically. POME is a brown slurry composed of 4-5% solids, mainly organic, 0.5-1% residual oil and grease, about 95% water, and contains a high concentration of organic nitrogen (Onyla *et al.*, 2001). This wastewater could potentially induce disastrous pollution to the environment and wipe out aquatic species if not properly treated due to high chemical oxygen demand (COD) of POME. As the production of POME increasing, the accumulation of the suspended solids, nutrients, oil and grease, and organic matters in POME along the open treatment ponds lead to more POME sludge produced.

POME sludge is the product of the anaerobic treatment of the POME from the anaerobic and aerobic pond. It is a good nutrient source as it has high composition of phosphorus (1.25 ± 0.1%), potassium (5.16 ± 2.2%), calcium (2.55 ± 0.1%), and magnesium (1.41 ± 0.2%). The POME sludge is almost neutral with a pH range of 7.4 to 7.6. Besides, it contains high BOD (15180.0 mg/L) and COD (40563.0 mg/L) level, high carbon (37.51 ± 5.1%) and nitrogen (4.68 ± 0.7%) content, indicating high amount of organic matter (Baharuddin *et al.*, 2010). The untreated POME sludge causes pollution to the environment by releasing methane and carbon dioxide gases. This is because the anaerobic bacteria in the POME sludge carry out anaerobic digestion if the POME sludge does not undergo any treatment. Therefore, the POME sludge needs to be further treated and processed to produce products for other applications, such as biochar, fertilizer and soil remediation.

Biochar is a carbon rich solid produced from thermochemical decomposition of biomass. The biochar is inexpensive and environmental-friendly, yet it can be used for variety of purposes, such as soil remediation, waste management, wastewater treatment, greenhouse gas capture and heavy metals adsorption (Cha *et al.*, 2016). Its composition varies according to the raw biomass material and the characteristics of the carbonization process (Kambo and Dutta, 2015). There are different processes for the biochar production, such as pyrolysis, gasification, and hydrothermal carbonization. The different processes produce different yield and characteristics of biochar (Cha *et al.*, 2016).

Pyrolysis is a thermochemical process takes place over a temperature range between 150 to 400 °C in the absence of oxygen gas atmosphere, decomposing the thermally weak constituents of biomass, producing biochar, bio-oil, and non-condensable gases. Parameters such as reaction temperature, pressure, holding time and temperature rising rate determine the product composition (Cha *et al.*, 2016). There are three types of pyrolysis, which are slow or conventional pyrolysis, fast pyrolysis, and microwave pyrolysis. Slow pyrolysis and fast pyrolysis are differed from their temperature rising rate or heating rate. Biomass is heated slowly to 500 °C, with vapor residence times vary from 5 to 30 minutes for slow pyrolysis. On the other hand, fast pyrolysis necessitates dry feedstock (less than 10 wt% moisture), rapid heat transfer, and rapid temperature rise by heating small biomass particles (1 to 2 mm) to a temperature range between 400 to 500 °C in one second or a maximum vapor residence time of 5 seconds (Mohan *et al.*, 2014). Besides, microwave pyrolysis has various advantages over conventional pyrolysis, including high safety and automation, rapid heating rate, volumetric heating, no physical contact with heat, selective space heating, and ease of operation with high safety and automation (Yu *et al.*, 2014). Microwaves are electromagnetic waves that cause molecular motion by causing ionic species to relocate or causing polar molecules to rotate and generate thermal energy due to intermolecular friction. Microwave wavelengths ranged from 30 cm to 1 mm, with frequencies ranging from 300 MHz to 300 GHz. Material that can absorb energy is called absorber or dielectric, and the absorber in the microwave pyrolysis is the biomass with high moisture and organic matter content (Jones *et al.*, 2002a).

Gasification refers to the partial combustion of solids. This process produces a gas fuel that can be used to generate direct heat or electricity. The product compositions are controlled by temperature, particle size, residence time, pressure, gas composition, and the identity of the catalyst (Mohan *et al.*, 2014).

Hydrothermal carbonization (HTC) of biomass at high temperature and pressure in water, producing a slurry consisting of char and water, as known as the hydrochar. In a hydrothermal process, biomass is mixed with water in a closed reactor, and the temperature is raised after a set period of time to achieve stability. To keep water in a liquid state above 100 °C, the pressure is also increased. Biochar, bio-oil, and gaseous products including carbon monoxide, carbon dioxide, methane, and hydrogen gases are the major results of the hydrothermal carbonization process below 250 °C, 250 to 400 °C, and beyond 400 °C, respectively, depending on the temperature under saturated pressure. Hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and hydrothermal gasification (HTG) are the terms used to describe the hydrothermal processes at different temperature ranges. The carbon content of char produced by the HTC technique is higher than that of char produced by dry processes. According to research, the primary parameters controlling the properties of the products are reaction temperature, pressure, residence duration, and water-to-biomass ratio (Cha *et al.*, 2016).

The comparison of the products distribution of the discussed thermochemical processes can be illustrated in Figure 1.1. It shows that the desired product of different thermochemical processes. The desired products of slow pyrolysis, fast pyrolysis, and gasification are solid char, liquid bio-oil, and non-condensable gases, respectively (Mohan *et al.*, 2014).

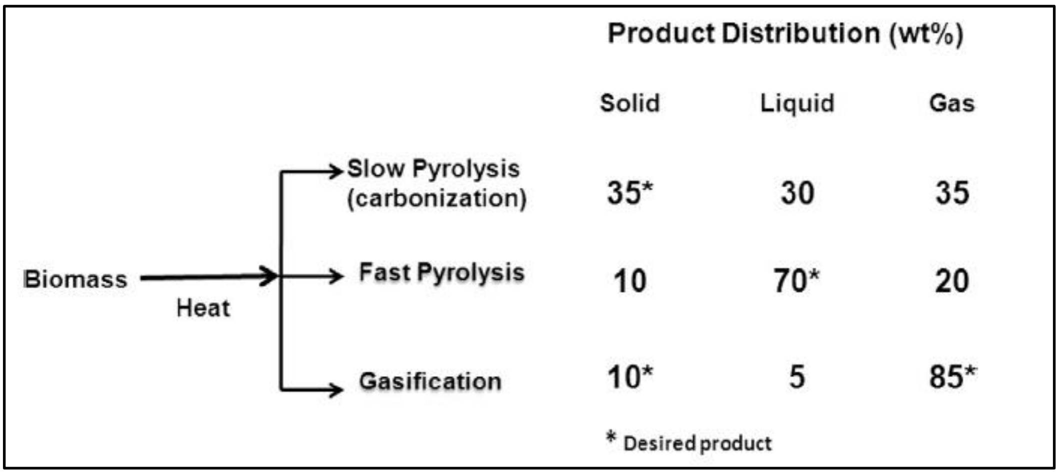

Figure 1.1 Thermochemical conversion of biomass into bio-oil, biochar, and gases (Mohan et al., 2014).

Subsequently, the production of biochar from POME sludge is a great idea to convert the waste into useful products. With this, we can reduce the amount of waste and utilise the waste into biochar that bring benefits to socio-economic development in the country and world. Besides, it also helps to alleviate environmental concerns such as climate change by lowering greenhouse gas emissions while also earning money by converting wastes into dollar-and-cent. This will fulfil the requirement towards a more sustainable and greener future.

1.1 Problem Statement

The rapid development of Malaysia’s palm oil industry contributes to an increasing trend of the POME production in Malaysia. Consequently, POME sludge is one of the principal wastes produced during POME treatment, and the growing amount of this waste requires immediate care. Unlike other wastes from palm oil mills, POME sludge cannot be used as a fuel for most renewable energy processes due to its high moisture content (Baharuddin *et al.*, 2010). Moreover, the POME sludge is often disposed of in oil palm plantations, which can result in hygiene difficulties as well as environmental pollution (Thangalazhy-Gopakumar *et al.*, 2015). The high BOD and COD level of the POME sludge making it becomes a potential source of greenhouse gases emission. Without proper treatments of the POME sludge before dumping it, greenhouse gases such as methane (CH_4) and carbon dioxide (CO_2) are emitted through natural biological processes, i.e. anaerobic respiration. Besides, the accumulation of these palm oil mill wastes created a major disposal problem of the Malaysia palm oil industry, thus, affect the environmental. To get the optimal solution for utilising these oil palm wastes, a balance of technological, economic, energy, and environmental factors must be maintained (Abdullah and Sulaim, 2013). Therefore, utilization of the POME sludge for the biochar production by pyrolysis process plays a vital role to reduce the POME sludge. Besides, the production of biochar from POME sludge reduces the emission of greenhouses gases to preserve the environment yet produces useful products, turning wastes into money. The pyrolyzed POME sludge-based biochar is then can be used in various applications, such as wastewater treatment for removing heavy metals from wastewater and soil remediation to decontaminate soil for better vegetation growth.

There are several parameters of the pyrolysis process in the production of biochar affecting the products’ yield and characteristics of the biochar, which are operating temperature, temperature rising rate or heating rate, and vapor residence time. It is important to study the effect of each of the parameters on the biochar yield and its characteristics.

1.2 Objectives

i. To produce biochar from Palm Oil Mill Effluent (POME) sludge using microwave pyrolysis process.
ii. To study the effect of power, and radiation time on the biochar yield and its characteristics.
iii. To evaluate the feasibility of using biochar to reduce turbidity of POME.

CHAPTER 2

LITERATURE REVIEW

Chapter 2 summarises past findings and reviews based on reputable scientific records and references that are relevant to the topic of this final year study. This chapter covers the overview of Palm Oil Mill Effluent (POME) and its sludge, the various types of thermochemical processes for biochar production, the pyrolysis process parameters, and the applications of biochar.

2.1 Palm Oil Mill Effluent (POME) and POME sludge

2.1.1 Production of POME from palm oil mills

Biomass is a green energy source and is abundantly available in Malaysia, typically the oil palm biomass. The Malaysia’s palm oil industries exported around 17.4 million metric tons of palm oil and palm-based products in the year of 2019 (Raudhah, 2021). The extraction of palm oil in the production of palm oil and palm-based products involves several processing stages which are sterilization, stripping, digestion, clarification, purification and vacuum drying. Large amount of water and steam are required for washing and sterilizing. As a result, a large volume of wastewater from palm oil mills, commanly known as POME, has been generated. According to Lam and Lee, (2011), for each tonne (1.13 m^3) of crude palm oil processed, approximately 0.9, 1.5, and 0.1 m^3 of POME will be created from steriliser condensate, sludge separator, and hydrocyclone waste. Figure 2.1 shows a simplified palm oil production process in a typical palm oil mill.

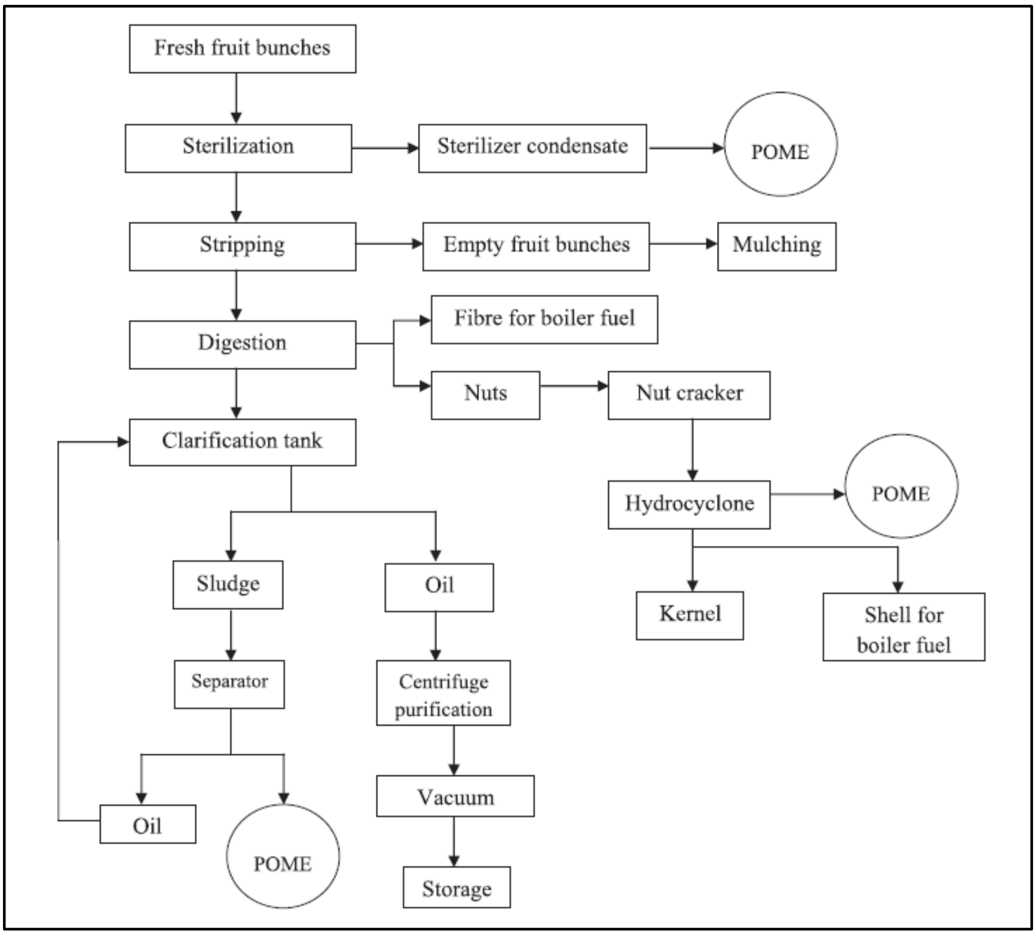

Figure 2.1 Simplified flow diagram of palm oil production (Lam and Lee, 2011).

In fact, the palm oil industry has been classified as one of Malaysia's agricultural industries that contributes the most pollution to the country's rivers due to the large amount of the raw POME produced from the mills (Lam and Lee, 2011). Yacob et al., (2005) estimated that for every tonne of fresh fruit bunch used, around 0.5 to 0.75 tonnes of POME will be discharged from palm oil mills. Table 2.1 shows the physicochemical characteristics of raw POME.

Table 2.1 Physicochemical characteristics of raw POME (Aziz and Hanafiah, 2017).

Parameter	Unit	Raw POME
pH	-	4.3
Temperature	°C	68.2
Ammonia Nitrogen (NH_3N)	mg/L	290
Chemical Oxygen Demand (COD)	mg/L	40667
Carbon to Nitrogen (C/N) ratio	-	49000
Heavy Metals		
Magnesium, Mg	mg/L	622.092
Calcium, Ca	mg/L	57.533
Phosphorus, P	mg/L	124.12
Potassium, K	mg/L	3553.085
Nutrient		
Protein	g/100g	0.83
Fat	g/100g	0.71
Carbohydrate	g/100g	1.5
Ash	g/100g	0.65
Moisture	g/100g	96.32
Energy	kcal/100g	16

Raw POME is hot with a temperature of 68.2 ºC and pH 4.3. Even though POME is a non-toxic liquid waste with an unpleasant odour, its COD (40667 mg/L) values are high enough to pollute rivers and affect the aquatic ecology by depleting the dissolved oxygen (Aziz and Hanafiah, 2017). Besides, POME also contains a considerable amount of important nutrient components such as Mg, Ca, P, K for plant growth. The content of dissolved elements such as high protein, fat, carbohydrate, and mineral concentrations can be converted into usable compounds by using anaerobic digestion (Aziz and Hanafiah, 2017). Anaerobic digestion is the process where the degradation of complex organic matters occurs in the absence of oxygen (Poh and Chong, 2009). There are four steps involved in the anaerobic digestion. Hydrolysis is the initial phase in the anaerobic digestion process, in which microbes secrete enzymes that break down organic materials such as carbohydrates, lipids, and nucleic acids into smaller units such as glucose, glycerol, and purines pyridines. The products of hydrolysis are then processed by fermentative bacteria into acetate, carbon dioxide, hydrogen, and volatile fatty acids during acidogenesis. Volatile fatty acids and alcohols are then oxidised into acetate, hydrogen, and carbon dioxide before being transformed into methane during the acetogenesis process. The final step, methanogenesis, in which specialised single-celled microbes (archaea) convert acetate, hydrogen, and carbon dioxide into methane (Aziz and Hanafiah, 2018). The biodegradation of the organic matters in POME produces residues, which will be accumulated in the wastewater treatment open pond and form a layer sludge.

2.1.2 Palm Oil Mill Effluent (POME) sludge

After the anaerobic digestion of the high suspended solids and dissolves solids content of POME, the remaining solid residue after treatment is called as the Palm Oil Mill Effluent (POME) sludge. As a result of the huge volume of POME produced each year, the POME sludge production also grows. Table 2.2 shows the physicochemical characteristics of raw POME sludge.

Table 2.2 Physicochemical characteristics of raw POME sludge (Baharuddin et al., 2010).

Parameter	Unit	Raw POME sludge
Moisture	%	94.03 ± 2.3
pH	-	7.41 ± 0.2
Carbon content	%	37.51 ± 5.1
Nitrogen content	%	4.68 ± 0.7
Carbon to Nitrogen (C/N) ratio		8.0
Oil and grease	mg/L	183.0 ± 10.1
Chemical Oxygen Demand (COD)	mg/L	40563.0
Biological Oxygen Demand (BOD)	mg/L	15180.0
Volatile suspended solid	mg/L	21110.0
Total suspended solids	mg/L	34720.0
Total solid	mg/L	55884.0
Cellulose	%	10.45 ± 5.1
Hemicellulose	%	6.01 ± 1.8
Lignin	%	48.13 ± 9.2
Composition of nutrients and metal elements		
Phosphorus, P	%	1.25 ± 0.1
Potassium, K	%	5.16 ± 2.2
Calcium, Ca	%	2.55 ± 0.1
Sulphur, S	%	1.21 ± 0.3
Ferrum, Fe	%	1.09 ± 0.4
Magnesium, Mg	%	1.41 ± 0.2
Zinc. Zn	mg/kg	151.0 ± 14.5
Manganese, Mn	mg/kg	495.24 ± 48.3

***Table 2.2** Continued*.

Copper, Cu	mg/kg	174.9 ± 20.3
Boron, B	mg/kg	65.0 ± 10.1
Molibdenum, Mo	mg/kg	5.0 ± 1.0
Cadmium, Cd	mg/kg	-
Nickel, Ni	mg/kg	14.0 ± 2.2

The nutritional value of POME sludge is higher than that of the slurry. It contains a significant level of moisture (94.03 ± 2.3 %), has a pH of 7.41 ± 0.2, and enriched with nutrients as it has high composition of phosphorus (1.25 ± 0.1%), potassium (5.16 ± 2.2%), calcium (2.55 ± 0.1%), and magnesium (1.41 ± 0.2%). Besides, it contains high BOD and COD level, high carbon (37.51 ± 5.1%) and nitrogen (4.68 ± 0.7%) content, indicating to high organic matter content in POME sludge (Baharuddin *et al.*, 2010). As a result, the POME sludge without further treatment has a high microbiological activity, leads to anaerobic respiration of bacteria which producing greenhouse gases and polluting the ground. (Esa *et al.*, 2010).

2.2 Biochar

Biochar is a carbon-rich solid material obtained from the carbonization of biomass. It can be derived from biomass via thermochemical route, such as pyrolysis, gasification, and hydrothermal carbonization (Cha *et al.*, 2016). Biochar is gaining popularity due to its unique characteristics, which include a high carbon content, a larger specific surface area, cation exchange ability, nutrient retention capacity, and a stable structure (Sakhiya *et al.*, 2020).

2.3 Thermochemical processes for biochar production

There are various thermochemical processes to convert biomass into biochar together with other products such as bio-oil and non-condensable gases (Duku *et al.*, 2011). The thermochemical processes include fast pyrolysis, slow pyrolysis, microwave pyrolysis, and gasification.

2.3.1 Fast pyrolysis

Fast pyrolysis process is where the biomass is heated very rapidly (heating rate up to 1000°C/s) in oxygen-free condition and short residence time (0.5 to 2 s) (Brewer *et al.*, 2009). Pyrolysis vapour (oil and gases) and solid residue (char) are produced by the polymerization and fragmentation of biomass. The pyrolysis vapour mentioned are aerosol, non-condensable gases, and condensable gases. Then, the condensation of condensable gases yields 65 to 80 percent of bio-oil on a dry basis, making bio-oil as the principal yield of the fast pyrolysis (Jones and Snowden-Swan, 2013).

2.3.2 Slow pyrolysis

Slow pyrolysis employs slow heating rate (1–20°C/min) in the absence of oxygen, and long residence times. Generally, when 1 kilogramme of wood is subjected to slow pyrolysis with a low heating rate at a temperature of 400 to 500 °C, there are 30 to 35 percent biochar, 45 to 50 percent bio-oil, and 20 to 25 percent pyrolysis gas produced (Jahirul *et al.*, 2012). In contrast to fast pyrolysis, vapours in traditional pyrolysis do not escape quickly. According to Kong et al., (2014), slow pyrolysis yields more biochar than fast pyrolysis. The biochar yield for slow pyrolysis is about 35% of the feedstock mass, while for fast pyrolysis is about 15% of the feedstock mass. However, fast pyrolysis produces more bio-oil than slow pyrolysis. Table 2.3 shows the mode of pyrolysis and their distribution of product yield. Solid product refers to biochar, liquid product refers to bio-oil, and gas product refers to non-condensable syngas.

Table 2.3 Mode of pyrolysis and their distribution of product yield (Kong et al., 2014).

Mode	**Conditions**	**Solid (%)**	**Liquid (%)**	**Gas (%)**
Fast	Reactor temperature 500 °C Very high heating rate > 1000 °C s^{-1} Short hot vapor residence ~ 1 s	12	75	13
Intermediate	Reactor temperature 400 - 500 °C Heating rate range 1 - 1000 °C s^{-1} Hot vapor residence ~ 10 - 30 s	25	50	25
Slow-torrefaction	Reactor temperature ~290 °C Heating rate up to 1 °C s^{-1} Solid residence time ~ 30 min	77	0 - 5	23
Slow-carbonization	Reactor temperature 400 - 500 °C Heating rate up to 1 °C s^{-1} Long solid residence time from hours to days	33	30	35

2.3.3 Microwave pyrolysis

Microwave pyrolysis is a promising technique over a conventional pyrolysis process because it has various advantages over conventional pyrolysis, including high safety and automation, rapid heating rate, volumetric heating, no physical contact with heat, selective space heating, and ease of operation with high safety and automation (Yu *et al.*, 2014). Jones *et al.*, 2002b states that the heating of biomass through microwave energy is more efficient than conventional pyrolysis as there is no wastage of energy to the surrounding. Besides, microwave heating has also a number of advantages that result in a higher production rate and reduced cost. Microwave pyrolysis, unlike traditional heating, includes the transmission of energy to the biomass through the interaction of molecules within the biomass. Microwaves force dipolar molecules to try to rotate in phase with the microwaves' alternating field, which heats the biomass. Microwave heating offers the advantage of generating heat within the material rather than from an external source, resulting in rapid and efficient heating (Wu *et al.*, 2014).

According to the study conducted by Salema and Ani, (2011), the biochar produced from microwave-assisted pyrolysis has a different surface structure compared to conventional electrical furnace. Figure 2.2 depicts the difference in surface image analysis. The surface structure of both the chars showed a considerable difference. As demonstrated in, large and deep cracks were discovered in standard pyrolyzed oil palm shell (OPS) char. Microwave pyrolyzed char, on the other hand, was found to have pores but no cracks.

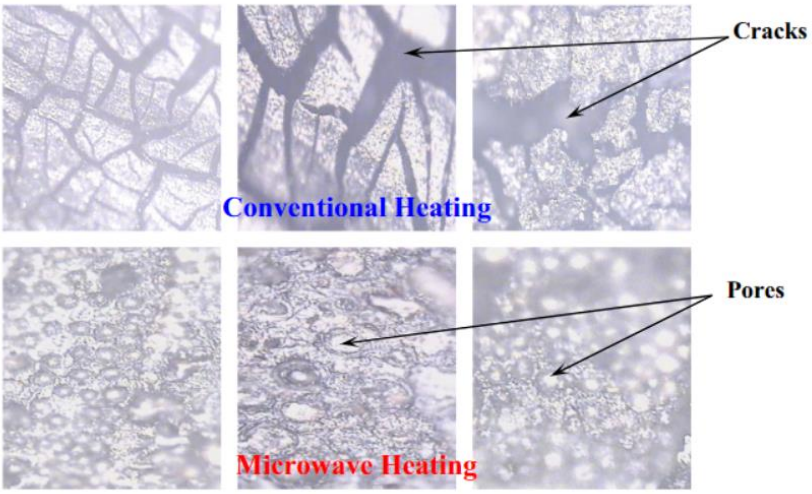

Figure 2.2 Surface image analysis of OPS chars after conventional pyrolysis and microwave pyrolysis (Salema and Ani, 2011)

According to Salema and Ani, (2011), the microwave produces volumetric heating. Unlike conventional pyrolysis, which transfers heat from the outer surface to the interior part of the material, microwave heat is generated throughout the full volume of the surface, and more specifically from the core of the materials to the surface of the materials. As a result, in conventional OPS pyrolysis, the outside surface is hotter than the inner core. By the time the heat reaches the inner surface, the outside surface has overheated, resulting in fractures or fissures. This degrades the biochar quality and makes it more fragile. In contrast, as described by Miura et al., (2004), during microwave pyrolysis of wood blocks, microwaves radiation penetrates and may have generated heat in the inner core of the OPS. As a result, during microwave pyrolysis of OPS, the temperature profile revealed a decreased surface temperature and minimal fracture on the biochar’s surface (Salema and Ani, 2011).

According to the study conducted by Wang et al., (2009), the biochar yield from microwave pyrolysis is lower than that of conventional pyrolysis in a temperature range of 400 to 700 °C. It is mainly due to microwave pyrolysis has a faster heating rate than conventional pyrolysis. Following that, microwave heat was absorbed by pyrolysis char, which increased the pyrolysis process and resulted in a decreased biochar production. During microwave pyrolysis, there was also a strong self-gasification interaction between CO_2 and the pyrolysis char, resulting in a drop in biochar production. Figure 2.3 shows the comparison of biochar yield between microwave and conventional pyrolysis.

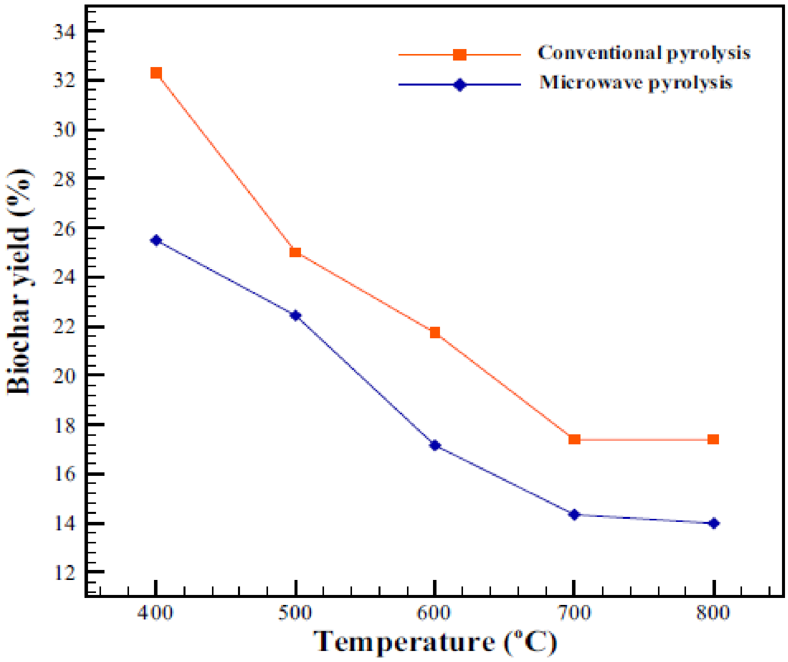

Figure 2.3 Comparison of biochar yield between microwave and conventional pyrolysis (Wang et al., 2009).

2.3.4 Gasification

Gasification is known as the partial combustion of solid biomass and produces a gas fuel that can be utilised to generate direct heat or electricity. It uses higher temperatures and some oxygen (less than the stoichiometric ratio) to produce non-condensable gas as fuel rather than biochar. The resultant gases, primarily H_2, CO, CO_2, and CH_4, can be utilised as fuel or as a synthesis gas (syngas) in downstream catalytic conversion processes to produce synthetic natural gas (SNG), methanol, Fischer-Tropsch fuels, and a variety of other products (Libra *et al.*, 2011). Brewer *et al.*, (2009) states that both fast pyrolysis and gasification produces small amount of biochar, usually 15 to 20% and 5 to 10% of the feedstock mass, respectively.

2.3.5 Hydrothermal carbonization (HTC)

Hydrothermal carbonization (HTC) of biomass at a high temperature and pressure in water, producing a slurry consisting of char and water, as known as the hydrochar (Libra *et al.*, 2011). In a hydrothermal process, biomass is mixed with water in a closed reactor, and the temperature is raised after a set period of time to achieve stability. To keep water in a liquid state above 100 °C, the pressure is also increased. Dry or wet pyrolysis is employed to carbonise the biomass, resulting in increased carbon-content products. The relative compositions of products in the gas/ liquid/ solid phases and the process energy requirements are depending on the input material and the process conditions (Libra *et al.*, 2011). Hydrothermal carbonization (HTC), hydrothermal liquefaction (HTL), and hydrothermal gasification (HTG) are the terms used to describe the hydrothermal processes at different temperature ranges. The carbon content of char produced by the HTC technique is higher than that of char produced by dry processes. The primary parameters controlling the properties of the products are reaction temperature, pressure, residence duration, and water-to-biomass ratio (Cha *et al.*, 2016).

2.4 Pyrolysis process parameters

2.4.1 Pyrolysis operating temperature

In comparison to residence time, particle size, and heating rate, reaction temperature is a critical parameter that controls biochar yield and properties. Increasing the pyrolysis temperature has a negative impact on biochar yield. This is due to high temperatures can cause thermal cracking of heavy hydrocarbons, which results in an increase in liquid and gas product and a decrease in solid product (Sakhiya *et al.*, 2020).

At high temperatures, the amount of energy given to biomass may exceed the bond breaking point, favouring the release of a volatile component from the biomass. The liquid and gas components of this volatile component are separated, resulting in a limited (less) biochar yield. As a result, it can be concluded that producing biochar at a low temperature is preferable (Sakhiya *et al.*, 2020).

2.4.2 Temperature rising rate or heating rate

The heating rate is a crucial factor in pyrolysis classification, which includes fast, flash, slow, and intermediate. The heating rate has an impact on the biochar's physicochemical properties as well as its yield. Higher bio-oil and gas production is achieved by increasing the heating rate and reaction temperature, whereas higher biochar yield is achieved by slowing down the heating rate and lowering the reaction temperature. The morphological properties of biochar, such as surface area and pore volume, are also affected by the heating rate. During the volatilization of organic matter from biomass, the process temperature and heating rate have a significant impact on the formation of pores in the biochar matrix (Sakhiya *et al.*, 2020).

Angın (2013) carried out a study of the pyrolysis of safflower. When the reaction temperature was increased from 400 to 600 °C at a rate of 10–15 °C/min, the specific surface area of biochar was reduced. It is due to the high heating rate and high reaction temperatures cause the cell structure to melt, resulting in a decrease in specific surface area and porosity.

For the effect of the variation of heating rate and reactor peak temperature, Tarelho et al. (2020) carried out a study to determine the biochar yield in bench-scale fixed-bed reactor using distinct operating conditions of heating rate and peak temperature. This study shows the biochar yield decreases with increasing peak temperature and heating rate. The increase of both temperature and heating rate promotes the decrease of biochar volatile matter content. The biochar ash content increases with peak temperature and heating rate. The corresponding fixed carbon content increases with an increase in the peak temperature. The carbon concentration increases with increasing peak temperature, and the general trend in the carbon concentration decreases with increasing heating rate.

2.4.3 Vapor residence time

Typically, longer vapour residence time favours biochar production because organic matter is removed at a slower rate, triggering the secondary reaction. Low temperature and a long residence time are ideal for maximizing tar decomposition and coking (Olukcu *et al.*, 2002). To achieve optimum biochar yield, a vapour residence time of a few minutes to a few hours is frequently recommended. Heat transfer and reaction time on the surface of the particles increase with increased residence time, resulting in increased biochar yield. To achieve high biomass conversion and yield, the vapour residence time must be shorter than the residence time for biomass decomposition (Sakhiya *et al.*, 2020).

Scott et al. (1999) studied the effect of vapor residence time on the biochar, bio-oil and gas yield during the pyrolysis of raw bagasse at a temperature of 525 °C. The results showed biochar and gas yield increase, whereas bio-oil yield decrease when there is an increase in vapor residence time from 0.2 to 0.9 s. Hence, optimization of residence time, taking into account a variety of factors, may aid in the production of high-quality and high yield of biochar.

2.5 Applications of biochar in water remediation

2.5.1 Removal of metal ions

Water pollution by heavy metals is a huge concern to the environment and human health. Metal pollutants such as Cu, Cd, Zn, Pb, Hg, As, Ag, Cr, Fe and Pt, which are commonly found in wastewater (Zamora-Ledezma *et al.*, 2021) threatening marine life and are introduced to human food chain by water and food consumption. Exposure to heavy metals at low concentrations may not lead to immediate fatal of an organism though, if ones exposed to heavy metals for a long period of time, these heavy metals would become cumulative poisons and lead to health complications (Jan *et al.*, 2015). Since the past few decades, the application of activated carbon is commonly used to remove metal ions. However, the low adsorption rate and regenerative ability of activated carbon, making it expensive in wastewater treatment. In contrast, biochar with comparable adsorption capacities and of lower cost compared to the activated carbon, has become an alternative approach to remove metal pollutants from wastewater (Mohan *et al.*, 2014).

A study by Pellera et al., (2012) revealed that the slow pyrolysis lignocellulose chars removed more Cu^{2+} ions than the hydrothermal chars. Nonetheless, modified peanut, canola, and soybean straw biochars were also proved to be able to adsorb Cu^{2+} ions, but the high phosphate contents of soybean and canola straw chars lead to the formation of insoluble Cu-phosphate salts. Report also shows that the leguminous straw (eg. Peanut and soybean straw) possessed higher adsorption capacities than the non-leguminous straw (e.g. Canola straw) (Mohan *et al.*, 2014; Tong *et al.*, 2011). To date, there are many biochars with metal ions adsorption capabilities have been discovered (Table 2.4). These biochars adapt different mechanisms to remove metal ions, including the chemisorption, electrostatic attractions, physisorption and ion exchange. In addition, several conditions have to be considered in wastewater treatment to ensure high metal adsorption by biochars, these include the temperature, pH, biochar dosage and initial solute concentration (Senthilkumar and Prasad, 2020).

Table 2.4 Biochar adsorption of heavy metals in water (Xiang et al., 2020).

Biochar feedstock	Heavy metals	Adsorption capacity (mg/g)	Removal mechanisms
Bamboo wood	Ag^+	1217	Innersphere complexation and electrostatic attraction by outer-layer Fe oxides
Pomelo peel	Ag^+	137.4	Chemical adsorption with oxygenic functional groups
Paper mill sludge	As^+	34.1	Chemisorption or chemical reaction process between available adsorption sites and adsorbate
Pine wood	As^+	4.38	Electrostatic attraction and surface complexation with hydroxyl groups
Rice husk	Cr^{6+}	435.7	Introduction of amino group facilitate chemical reduction of Cr^{6+} and increase sorption capacity
Peanut shell	Cu^{2+}	10	Nonspecific outersphere surface complexation provided by oxygen-containing groups, specific innersphere complexation offered by the impregnated HMO

Table 2.4 *Continued*

Marine macroalgal	Cu^{2+}	69.37	Oxygen-containing functional groups as potential adsorption sites
Banana peels	Pb^{2+}	247.1	Electrostatic attraction, partial of physisorption, ion exchange and precipitation
Cauliflower leaves	Pb^{2+}	177.8	Electrostatic attraction, partial of physisorption, ion exchange and precipitation

2.5.2 Removal of organic contaminants

Organic contaminants including herbicides, pesticides and antibiotics are also one of the major pollutants in the environment due to excessive human activities. These organic pollutants are toxic to the ecosystem and may lead to the emergence of organisms which gain resistances over these compounds. There are several biochars which can be used to remove organic compounds. One example is the application of switchgrass biochars (Pristine and magnetized) for metribuzin herbicide removal, which their adsorption capacities were favoured by low pH value and high temperature (Essandoh *et al.*, 2017). Research by (Klasson *et al.*, 2013) also reveals that the slow pyrolysis almond shells was able to adsorb dibromochloropropane, a pesticide that used to control nematodes. Additionally, digested bagasse biochars, and Fe- and Zn- doped sawdust biochars were able to remove sulfonamides and tetracyclines respectively (Peiris *et al.*, 2017; Yao *et al.*, 2018). Table 2.5 demonstrates more biochars which have been studied for organic contaminants removal. The adsorption of organic compounds by biochars can be govern