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Comparing Characteristics of Oil Palm Biochar Using Conventional and Microwave Heating

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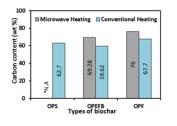
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Abstract

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Graphical abstract



Microwave heating technique is one of the most attractive alternative applications in the thermal conversion process. In addition, microwave pyrolysis is one of the thermochemical technologies using microwave irradiation heating in order to obtain biofuels and materials from biomass. Microwave pyrolysis not only overcomes the disadvantages of conventional pyrolysis methods such as slow heating, but also improves the quality of final pyrolysis products. Recently, the biomass from oil palm wastes (empty fruit bunch, oil palm shell and oil palm fiber) has been gaining more attention in order to produce the biochar. In addition, biochar is important for sequestering carbon and as an effectively additive to improve soil fertility, aid sustainable production, reduce contamination of water streams. This paper focused on the comparison of biochar characteristics produced from oil palm biomass via microwave heating and conventional heating. Analysis on the characteristics of the biochar includes its physical properties, proximate and elemental analysis, the Brunauer- Emmet- Teller (BET) surface area and Scanning Electron Microscopy (SEM).

Keywords: Microwave pyrolysis; biochar; thermochemical; conventional pyrolysis

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1.0 INTRODUCTION

1.1 Oil Palm Biomass

In the past ten years, biomass has been identified as an alternative sustainable source of material [1]. Based on a study by Serdar Yaman (2004), the biomass generally defined as an organic matter derived directly from living organism and any hydrocarbon material which mainly consists of carbon, hydrogen, oxygen, nitrogen an insignificant amount of sulfur [2]. In addition, according to Adrados et al., (2013), biomass means the biodegradable fraction of products, waste and residues from various biological origin of agriculture, forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste. Generally, most of the biomass was pyrolysed into bio-oil, biochar as well as syngas [3]. Biomass which is considered as socio-environmental liabilities is now scrutinized to be contributor of wealth from waste and establishment of carbon credit business [4]. Indeed, due to the widely abundant and cheap feedstocks, biomass is highly attractive and beneficial in a broad sense [5]. In the last four decades, Malaysian oil palm plantation has seen unprecedented growth to emerge as the largest producer of oil palm in the world, generates a significant amount of oil palm waste [6]. Oil palm biomass is the most important product of Malaysia that has helped to change the scenario of its agriculture and economy. Conversion of oil palm biomass into value added products has been previously investigated by many researchers [4, 7, 8, 9, and 10]. This conversion into beneficial value added products not only save the overall cost, but also helping in economic returns [11].

1.2 Biochar in General

Simply said, biochar is the carbon rich product obtained when biomasses such as wood, oil palm fiber, pine sawdust, manure or baggase is heated in a closed container with little or the absence of air [12 and 13]. As well, biochar is a fine-grained charcoal high in organic carbon, largely resistant to decomposition and depending on properties which can remain in the soil for greater than 1000 years [12]. The long term persistence of this carbon form is due to slow microbial degradation and chemical oxidation rates. Therefore, biochar addition to soils could provide a potential sink for carbon [14]. In addition, Sohi (2009), reported that the relative stability of biochar determines the length of its contribution to the mitigation of greenhouse gas (GHG) emissions [15]. There are actually a lot of benefits can be gained by using biochar such as increase in water holding capacity [16], increase soil microbial biomass and support other beneficial organism like earthworms [17], enhance plant growth, raise and sustain crop yields and help in improving the good and problematic nutrientpoor soils including acidic tropical humid and drier environment soil [15]. In addition, biochar may also improve soil moisture retention, increasing agricultural resilience against climatic change effects like increased drought and floods [18] as well as it can reduce methane and N2O (nitrous oxide gas) emission from cultivated soil and leaching of nitrates into water [19]. However, application of biochar in soil has been observed in decreasing efficacy of pesticides and it has been concerned that the toxicity of biochar produced from feedstock could contain chlorinated organic compounds [20].

Technically, biochar is produced by so-called thermal decomposition of organic material which is known as pyrolysis with limited oxygen supply and at relatively low temperatures <700 °C in order to capture combustible gas [12 and 21]. According to Xu Gang *et al.*, (2012) the elemental composition of biochar included carbon (> 60%), nitrogen, hydrogen and some lower nutrient element such as K, Ca, Na, Mg, Si. These contained nutrient elements were important for plant growth where the bulk composition of biochar is dominated by condensed aromatic rings and a few functional groups making it resistant to decay [22]. There are two techniques pyrolysis available in order to produce biochar which includes by using conventional heating as well as microwave heating system and increased crop production.

1.3 Conventional Heating

Conventional pyrolysis is defined as the thermal decomposition of biomass occurring in the absence of oxygen which is operating at medium temperature range normally from 350–550°C [2 and 23]. Initial decomposition of waste material is around 120°C–200°C. Under this pyrolysis condition, the long chains of carbon, hydrogen and oxygen compounds in biomass break down into smaller molecules in the combination of condensable vapours (tars and oils), solid charcoal and non-condensable gases, which of each has a potential economic values [24].

According to Bahng *et al.*, (2009), this conventional pyrolysis can be categorized as a slow pyrolysis that occurred under slow heating rate, low temperature and long gas and solid residence time [25]. Normally, the heating rates are about 0.1 to 2° C per second and prevailing temperatures are around 500°C. In addition, the biomass slowly devolatilized during conventional pyrolysis which resulted into the production of tar and char as a main product [26]. However, this conventional pyrolysis has some limitation which is lack of rapid heating occurred in conventional reactor can cause the long heating duration. This long heating resulted into the undesired secondary reaction which made it not suitable to produce high quality of bio oil where the primary product was cracking in slow pyrolysis due to high residence time which at the same time could unfavorably affect the quality and yield of bio oil [4 and 23].

1.4 Microwave Heating

Microwave pyrolysis is classified as an electric volumetric heating method which generally performed at frequencies of 915 MHz ($\lambda = ~33$ cm) and 2.45 GHz ($\lambda = ~12$ cm) as specified by international agreement [27]. According to Abubakar *et al.* (2013), the materials are classified into conductor, insulator, absorber and mixed absorber of microwave heating (MW) based on the dielectric properties. An activated carbon is one of the good MW absorber [28]. Microwave synthesis whereas is an alternative technique that overcomes the problems of conventional fast firing because microwave pyrolysis is a non-contact technique where the heat is transferred to the product via

electromagnetic waves, and large amounts of heat can be transferred to the interior of the material, minimizing the effects of differential synthesis [29].

Microwave pyrolysis (MP) heating combined with the use of carbon materials has recently attracted many researchers around the world to explore about it and has gained tremendous recognition in the thermo-chemical treatment of waste materials which includes waste cooking oil, scrap tires, biomass and coal [9, 30 and 31]. In fact, the microwave radiation which acts as an indirect heat source combined with the use of carbon materials as the microwave receptor involved in this microwave pyrolysis in order to directly heat and pyrolyse the materials [27]. It is a relatively new technique applied for pyrolysis process which has a series of advantages over conventional pyrolysis which include having high efficiency, energy saving, selective, no pollution, easier control [4, 27 and 32]. This is due to the feedstock of microwave pyrolysis normally require fewer pretreatment and conditioning steps such as grinding, chipping compared to the conventional pyrolysis process. As a result, it can be advantageous in term of time and energy savings for crushing, grinding and related process [5, 27 and 33]. Furthermore, the unique internal heating phenomenon of this technology associated with microwave energy can enhance the overall production quality, allowing for the development of new products and process that cannot be realized using conventional methods [34].

In addition, microwave pyrolysis as a rapid pyrolysis prevents the formation of secondary reaction which results in improving the quality of product produced unlike the conventional heating method [4]. As reported by Luque et al., (2012), it is also possible to obtain mainly the organic volatiles as well as gas at the same low temperatures under microwave heating compared to conventional heating which required higher temperature to achieve the gas products [5]. Likewise, the microwave pyrolysis also allows a careful control of pyrolysis parameters to maximize gas, char or yield production taking into account that operating parameters can induce and alter the particular chemical reactions, resulting in different chemical profiles of the produced volatiles/oils [5]. Besides, by using microwaves heating, it is not only provides a rapid and energyefficient heating process, but also offers a reliable, low cost as well as powerful heat source with modern equipment operating at over 90% conversion efficiencies of electricity into thermal energy [35]. Therefore, this present paper reviewed on the comparison of biochar characteristics produced from oil palm biomass using microwave heating versus conventional heating. The characterization of biochar is important in order to evaluate and match its requirement for related application.

2.0 CHARACTERISTIC OF OIL PALM BIOCHAR USING CONVENTIONAL VERSUS MICROWAVE HEATING

The efficiency of microwave pyrolysis for different biomasses has been proved in a number of publications including oil palm biomass [4, 36, 37 and 38], wheat straw [5] as well as corn stover and aspen [32]. The comparison of biochar characteristic which includes SEM, BET surface area, elemental analysis, proximate analysis and calorific value produced via microwave heating pyrolysis and conventional pyrolysis has been reviewed in this present study. The review of the biochar produced in the present study mostly from the oil palm wastes includes oil palm empty fruit bunch (OPEFB), oil palm fiber (OPF) and oil palm shell (OPS) as a biomass.

2.1 Basic Analysis of Elemental and Proximate Analysis

The proximate analysis is important in order to know the percentage of moisture content, volatile matter, fixed carbon as well as ash content in each oil palm waste biochar meanwhile the elemental analysis is normally used to determine the percentage of carbon, hydrogen and oxygen content in biochar by using elemental analyzer. Figures 1 and 2 show the comparison of carbon and fixed carbon content respectively for different types of oil palm biomasses via microwave and conventional heating. In Figure 1, the carbon content of EFB biochar using microwave heating shows much higher compared to conventional heating which was correspondingly are 69.28% [38] and 59.62% [39]. Meanwhile, almost 62.7 wt % of carbon content was detected via conventional heating by Abnisa et al. (2013). Moreover, the carbon content in biochar from OPF was detected around 76 wt % [38] by using microwave heating compared to 67.7 wt % [37] as detected in conventional. Carbon content is really important to ensure the carbon sequestration in soil. To date, there is no investigation has been carried out for elemental analysis on OPS biochar via microwave heating, thus the comparison of carbon content between both heating techniques could not be described.

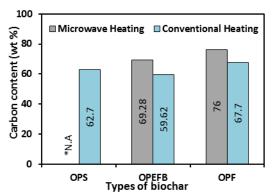


Figure 1 Carbon contents for all types of biomasses via microwave and Conventional heating (*N.A is not available)

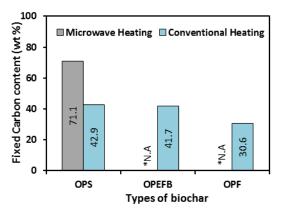


Figure 2 Fixed carbon contents for different types of biomasses via microwave and Conventional heating (*N.A is not available)

In addition, according to Figure 2, the fixed carbon in EFB and OPF biochar produced via microwave heating has not been investigated yet unlike in conventional heating where 41.7 wt % [37] of fixed carbon was detected in OPEFB and 30.6% [39] in OPF. Likewise, there was almost 71.1 wt % [31 and 36] of fixed carbon from OPS biochar was noticeable via microwave heating compared to 42.9 wt % [40] of fixed carbon in OPS biochar produced via conventional heating. Whereas, fixed carbon is a vital element in order to determine the quality of biochar since the highest fixed carbon content show the best quality of biochar.

On the other hand, the comparison of calorific value between microwave and conventional heating was presented in Figure 3. This calorific value is a measure of energy that is chemically available in the fuel per unit mass. According to the figure, the highest calorific value was detected in OPS biochar produced via microwave heating compared to conventional heating which respectively were 29.5 MJ/kg [28] and 28.85 MJ/kg [37]. Likewise, Salema and Ani, (2012) reported that the calorific value of EFB biochar via microwave heating was 25.16 MJ/kg [9] higher than observed in conventional heating which only gave 21.34 MJ/kg [37]. Meanwhile, almost 29.1 MJ/kg [37] of the calorific value for OPF biochar was detected in conventional heating but not yet investigated for microwave heating. Indeed, the highest calorific value of biochar can be potentially used for any application that uses coal as well as fuel. The low calorific value could be due to excessive pyrolysis of oil palm waste pellets, which might have pyrolysed the fixed carbon in the biochar [9].

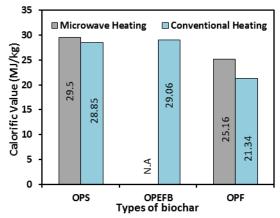


Figure 3 Calorific value for different types of biomasses via microwave and conventional heating (*N.A is not available)

The volatile content between microwave and conventional heating has also been observed. From the observation, microwave heating pyrolysis produced lower volatile content of biochar which was 21.4 wt % [36] as compared to conventional heating 45.5 wt % [40]. Higher volatile content in biochar is not favorable for activated carbon and not classified as a good biochar. Thus, it shows that, biochar produced via microwave heating has better quality than conventional heating.

2.2 BET Surface Area Analysis

Generally, BET method is important to measure the surface area of biochar. The surface area and pore size distribution of biochar were determined by using BET equation which calculated from N₂ adsorption isotherms. Most of the researchers such as Hussein and Ani, (2006), Sukiran *et al.* (2011), Abnisa *et. al.* (2013), and Lua and Guo, (1998) has characterized the BET surface of biochar produced via conventional heating [37-42]. The comparison of BET surface area between microwave and conventional heating was presented in Figure 4. According to Lua and Guo, (1998) the highest surface area of biochar was found in OPF which was 521 m²/g with micropore area was 366 m²/g. In addition, the surface area of biochar that produced from OPS respectively were 318 m²/g [43], 253.6 m²/g [44], and 58.3 m²/g [40] which are more

lower than OPF. Meanwhile the biochar from EFB gave the lowest of surface area which is $4.54 \text{ m}^2/\text{g}$ [39]. All these results were observed in conventional heating system.

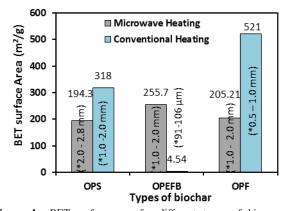


Figure 4 BET surface area for different types of biomasses via microwave and conventional heating at optimum condition (*initial size of raw biomass)

The observation of BET surface area of biochar produced by using microwave heating system was also investigated by Guo and Lua, (2000), Salema and Ani (2012) and Foo and Hameed, (2011). The highest surface area (255.7 m^2/g) with average pore size of 2.23 nm was detected in OPEFB biochar [38]. It should be noted that, the surface area of biochar produced from OPF using microwave heating was 205.21 m²/g lower than surface area of 521 m²/g by using conventional heating [38] and it was observed that the lowest surface area of 194.3 m²/g was detected in biochar from OPS [36]. Meanwhile the biochar from EFB gave the lowest of surface area of 4.54 m²/g by conventional heating [39]. The heating rate in pyrolysis significantly affects the BET surface area where when heating rate was increasing; the BET surface area was decreasing as observed by Lua and Guo, (1998). Furthermore, the heating temperature also affects the surface area, pore diameter as well as total pore volume where all of them will increase with the increasing of heating temperature [45]. The comparison of BET surface area between microwave and conventional heating could not be clearly described due to the dissimilar in initial size of biomass as well as heating rate and final temperature used in their experiment.

2.3 SEM Characterization

The characterization of SEM micrograph has been investigated for both heating techniques and it was noticed most of the researchers characterized the biochar from oil palm shell by using conventional heating. Scanning electron microscopy (SEM) is required in order to study the surface morphology and pore size of biochar produced as well as to verify the presence of porosities [4 and 41]. In addition, the microstructure of porous solid can be reviewed by using SEM in order to give the real picture of pore structure which include meso and macropores [45]. The study on SEM characterization of biochar from oil palm waste using microwave heating has been carried out by a few researchers including Guo and Lua (2000), Salema and Ani (2011) as well as Foo and Hameed, (2011). Foo and Hameed (2011) found that the pore size of EFB and OPF biochar produced via microwave heating respectively were about 2.23 nm as well as 2.39 nm but both pore size of biochar produced via conventional heating has not been reported. Meanwhile, the pore size produced from OPS via conventional heating respectively were 2.32 nm [30] and 0.8 μ m [44]. The difference of pore size produced might be due to the differences of initial size of raw biomass used as well as the heating temperature during pyrolysis. Recently, Abnisa *et al.* (2013) has also carried out the SEM characterization on OPF and OPS as well as EFB biochar via conventional heating but the pore size produced has not been reported [37].

According to Salema and Ani, (2011), biochar produced from conventional heating favor to have a deep cracking surface as observed in their study, unlike biochar produced via microwave heating which the pores were clearly uniform without any cracks. This is due to the heat was transferred from the outer surface of the material to the inner part in conventional heating meanwhile the microwave heating was generated in entire volume of surface. Hence, in conventional heating pyrolysis, the outer surface is at higher temperature than inner core. Thus, the outer surface undergoes overheating when the inner surface gets the heat and it will create the deep cracks on the biochar SEM image. Due to this problem, it makes the biochar more fragile and diminishes the quality of biochar itself as well as defeat of porous nature [4]. Similarly to the previous study done by Guo and Lua, (1998) where they observed a cracking on the biochar surface that was heated at 800°C and 900°C for 3 hour in conventional heating. This is due to the sintering effect and shrinkage of the char which consequently reduced the pore area. It can be said that there are detrimental effects on the development of micropore areas when biochar was pyrolyzed at highest temperature via conventional heating [43].

Guo and Lua, (2000) performed the SEM analysis in order to differentiate the OPS biochar with OPS activated carbon via microwave heating and they found the pores on biochar surface could be clearly seen and after it was carbonized to an activated carbon there were many orderly pores with round shape and in uniform sizes all over the surface. For the meantime, Arami-Niya *et al.* (2012) and Faisal Abnisa *et al.* (2013) compared the SEM image of oil palm biomass towards the oil palm biochar. They observed that there were very small and not much pores present on the OPS biomass surface compared to after carbonization process, the number of pores increased on the surface of OPS biochar.

3.0 CONCLUSSION

Microwave heating pyrolysis has been proved to be a promising alternative to conventional pyrolysis for biomass and waste processing. Based on the result observed from this review, it shows that biochar produced via microwave heating technique can increase the value of oil palm biochar as well as produced a better quality of biochar. This was agreed by Rafael Luque and his colleagues, (2012) where the biochar produced under microwave heating pyrolysis has higher quality as compared to conventional heating pyrolysis in which significant cracks and fissure due to convective heating profiles and differences in temperature of outer and inner surface [5]. Thus, it leads to more fragile biochar produced. It ascertained that microwave heating pyrolysis has huge potential as a means of recovering commercially valuable products from oil palm waste compared to conventional heating. In addition, the pores surface oil palm biochar produced via microwave heating were clearly seen without suffering any cracking compared to biochar produced via conventional heating. Therefore, microwave heating can be significantly approved as an economical heating technique and could be worthwhile in order to produce the high quality of biochar since it has better heat transfer to the waste material, good control over the heating process as well as offering a very reducing chemical environment.

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