Synergistic Effect of Co-combustion of EFB Char with Coal Using BET Analyzer

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***Abstract* - This study is to identify the synergistic effect during co-combustion between EFB char with MB coal blends by using Brunauer-Emmett-Teller (BET) analyser. The pore specific volume and surface area of EFB char and MB coal blends were investigated over a range of different weight ratio and temperature. In this research, the weight ratio of EFB char/MB coal blends are from 100:0, 60:40, 20:80, and 0:100 and the temperature for co-combustion will be conducted at 400, 600, and 700°C. Raw EFB were pyrolyzed in microwave pyrolysis condition at 300 W exposed for 35 minutes. The resulting solid char was mixed with MB coal at different blending ratio prior undergoing co-combustion in furnace. A BET analyser was used to analyse the BET surface area of the co-combusted product. The results revealed that the surface area is inversely proportional to temperature of combustion. The higher the combustion temperature, the lower the BET surface area. Besides that, as the mass fraction of EFB char increase, the surface area of pores decreases. Overall, the actual BET surface area obtain experimentally does not synchronize with the predicted BET surface area. Therefore, there is a synergistic effect occur on the co-combustion of EFB char with MB coal.**

***Keywords* – BET analysis; Coal; Empty Fruit Bunch Char; Synergistic effect.**

INTRODUCTION

Renewable energy is becoming more popular worldwide due to critical source of current fuel and economic crisis. Fossil fuel such as coal is decreasing from time to time and eventually will run out in the future (Council, 2016). Hence it is vital to look for alternative energy to overcome the problems.

Malaysia is the second largest crude palm oil producer in the world thus leading to a high amount of palm oil waste from the industry. Palm oil waste can be classified into three kinds; mesocarp fibres (PMF), palm kernel shell (PKS) and empty fruit bunches (EFB). Currently, the waste products mainly EFB were sent back to plantation as mulching (Yusoff, 2006). Over the past few years, EFB have attracted increasing attention and have been considered for application such as fuel to generate steam and power.

Coal-biomass co-combustion is introduced as a short-term alternative for the use of renewable fuels with the reason to reduce the emission of carbon dioxide and reduce the consumption of coal as the main source of fuel. One of the advantages of co-combustion is fuel flexibility due to wide range of usable fuels and high efficiency for power generation from biomass/coal blends compared to the use of biomass standalone (Powertech, 2008). However, co-combustion of biomass/coal blends emits high production of volatile matters which leads to environmental issue. Therefore, biomass need to be converted into biomass char where volatile matter is removed earlier before undergo combustion process (Jamaluddin et al., 2011). This volatile has other potential uses, such as biofuel and biochemical. A study has been made on comparison of raw EFB and EFB char and it is proven that the EFB char have more suitable characteristic for combustion as compared to raw EFB (Rahman, Sulaiman, & Abdullah, 2015).

A study has been made on combustion and gas emission characteristic of coal, biomass char and their blends. The result showed that combustion of chars gives only little impact on the atmosphere. The alkali and alkaline earth metal contained in ash from the combustion can act as catalyst in burning of coal. Biomass char blends with coal gives positive result where NOx emission decreased when the biomass char ratio increased. Addition of biomass char into coal blends can improve the efficiency of co-combustion and reduce air pollution (P. Zhang et al., 2017).

Most of the previous study on synergistic effect of co-combustion of biomass/ coal blend was conducted by using TGA analysis. A research on TGA analysis has been made on co-combustion of palm kernel shell char with coal. The results show that raw PKS and coal underwent individual thermal degradation with no synergistic interaction. However, combustion of PKS char blends with coal results in single evolution profile. This means that there is a synergistic interaction between PKS char/coal blends and it is feasible to be used as alternative fuel in future (Jamaluddin et al., 2011).

Until now, there is still no research has been done on analysing the synergistic interaction of blending biomass char with coal by using Brunauer-Emmett-Teller (BET) analysis especially the development of the pore structure of the co-combusted coal/biochar blend. It is crucial to study the pore volume and surface area of the biomass char and coal blends in studying in new area. Rashidi et. al. (2018) stated that porous material contains energy conversion and storage that can be used for various process in energy system such as adsorption process, thermal energy saving system, evaporation system, insulation system, and geothermal system (Rashidi, Esfahani, & Karimi, 2018). Therefore, the objective of this study is to identify the synergistic effect of co-combustion between EFB char with MB coal blends by using BET analyser. The BET analyser was used to determine the pore surface area of the EFB char blends with MB coal at certain weight ratio and different combustion temperature. In this case, the co-combustion process was conducted at temperature of 400, 600 and 700°C and the weight ratio of EFB char/MB coal blends are from 100:0, 60:40, 20:80, and 0:100.

METHODOLOGY

A) Materials

Empty Fruit Bunch is taken from palm oil mill at Sime Darby plantation located at Labu, Negeri Sembilan Malaysia while Mukah Balingian cola is obtain from Mukah, Sarawak. Both samples were air dried for 3-4 days to remove moisture and then ground and sieved until the particle size less than 212 µm. Some portion of the samples were dried in vacuum oven at 80 °C for 24 hours. The dried sample were stored in a sample bottle and placed in desiccator to prevent moisture taped in the sample. The dried sample are ready for ultimate and proximate analysis for the characterisation of the EFB and MB coal.

B) Microwave Irradiation of EFB

EFB char was done by using microwave irradiation system operated at 300 Watt for 35 minutes. 20 g of EFB was compacted into the reactor without any void and continuous nitrogen gas was supplied with flow of 150 mL/min to remove oxygen contain in the reactor. After 35 minutes of irradiation process, EFB char is produced and ready for co-combustion process with MB coal.

C) Co-combustion EFB char with MB coal

Sample of EFB char and MB coal were blended together to undergo co-combustion process. The blending weight ratio of EFB char/MB coal are 100:0, 60:40, 20:80, 0:100. The co-combustion was done at 600, and 700 °C with constant heating rates of air, 10 °C/min. Weight loss of the sample were recorded before and after combustion process.

D) BET analysis

Brunauer-Emmett-Teller (BET) analyser is used to measure the specific surface areas and pore volume. Product obtained from the combustion process were send to BET analyser. BET method was conducted at temperature 100 °C with a supply of nitrogen gas at 10 °C/min for 300 minutes. After 300 minutes, the result of specific surface areas and pore volume were obtained.

RESULTS AND DISCUSSION

A) Characteristic of biomass and MB coal

Table 1 shows the characteristic of raw EFB, EFB char and MB coal in terms of ultimate and proximate analysis. From table 1, it can be seen clearly that EFB char consist lesser moisture content and volatile matter compared to raw EFB. This is because the moisture and volatile matter has released during the microwave irradiation process from raw EFB to EFB char which results in a lower content of moisture and volatile matter (Rahman et al., 2015). Besides that, the carbon content of MB coal and EFB char are higher than in raw EFB. High value of carbon leads to high heating value (Idris, Rahman, & Ismail, 2012). Referring to the

Table 1: Characterisation of MB coal and Biomass material

Analyses	MB coal	Oil Palm Biomass	
		EFB Char	EFB
Proximate Analysis (%)			
Moisture Content	10.00	0.95	3.46
Volatile Matter	25.61	19.27	60.76
Fixed Carbon	31.34	35.43	13.22
Ash	33.05	44.35	22.56
Ultimate Analysis (%)			
Carbon	55.60	69.92	46.36
Hydrogen	4.27	3.74	6.22
Nitrogen	0.09	0.00	0.00
Sulphur	0.00	0.00	0.00
Oxygen*	40.04	26.34	47.42

* Calculated by difference

nitrogen content, according to Idris et. al. (2012), having a nitrogen more than 0.6% would emits nitrogen oxides which cause hazardous emission. In this case, there is no nitrogen found in the biomass and only 0.09% of nitrogen contain in MB coal. Also, there is no sulphur contain in these three sample. This means that MB coal and EFB char are suitable for combustion process and does not contribute air pollution.

B) Effect of combustion temperature on ash yield

Ash yield is the mass of residue left from the combustion process. Table 2 shows the effect of co-combustion of EFB char with MB coal at different combustion temperature and weight ratio of blending resulted in form of ash yield. The yield exhibits the same trend. By comparing the effects of various temperature of co-combustion, the higher the combustion temperature, the lower the ash yield present as the product of combustion. For example, at ratio 20:80 of EFB char: MB coal, when the combustion process occur at 400 °C, the ash yield presented are 2.21 g. As the combustion increases to 600 and 700 °C, the ash yield reduces to 1.09 and 0.88 g, respectively. This may be due to different combustion reaction at different temperature. Chen et. al (2018) stated that the combustion reaction is depends on the intensity and duration of heating the sample. By reducing the temperature, the time for interaction is reduced. Lack of time for the consecutive reaction occurrence leads to inefficient heat transfer from the surface to the core of the sample. This will result an in-complete decomposition and more final product produced (Chen, Chan, Medwell, & Heng Yeoh, 2018).

Another comparison can be made by looking at the combustion of pure EFB char and pure MB coal. Both having the same trend where the ash yield decrease as the temperature increase but the ash yield for EFB char is less than MB coal. When the temperature increase, volatile matter in EFB char and MB coal precipitated out more thoroughly results in decreasing char yield (Y. Zhang et al., 2015). From the result of proximate analysis in table 1, the volatile matter in MB coal is higher than EFB char. That is why the ash yield of MB coal is higher than EFB char.

C) Effect of blending of EFB char with MB coal on ash yield

From table 2, the co-combustion of EFB char with MB coal resulted in different ash yield for each of the ratio study. From the result obtain, the trends are nearly similar for different combustion temperature, the higher the mass fraction of MB coal, the higher the mass of residue after combustion. However, when the weight percent of EFB char is 60%, the mass of ash yield drop significantly, and then rise as the EFB char reduced to 20%. This may be due to the interaction of EFB char and MB coal during the combustion process at that blending ratio

Table 2: Ash yield of co-combustion EFB char with MB coal

Ratio (%) EFB Char: MB Coal	Ash yield (g)		
	400°C	600°C	700°C
100:0	1.90	0.95	0.87
60:40	1.73	0.83	0.55
20:80	2.21	1.09	0.88
0:100	2.68	1.45	1.14

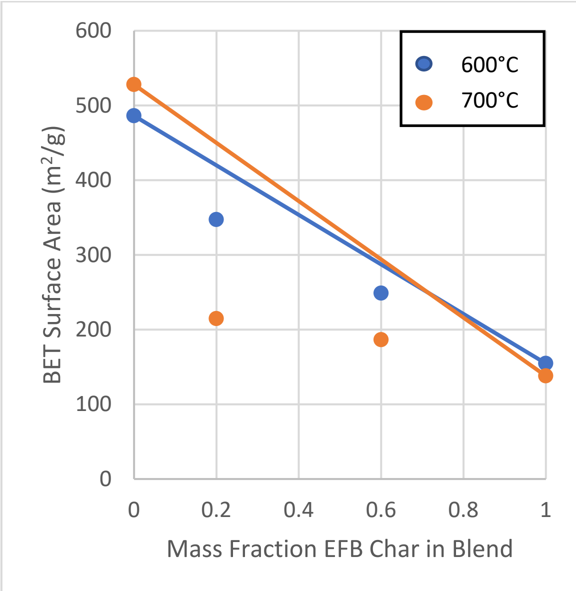

Fig. 1: BET surface area as a function of mass fraction biomass in blend at each combustion temperature with solid lines showing predicted surface area and dotted point showing experimental data.

D) Effect of combustion temperature on BET surface area

Figure 1 shows the result of BET surface area of EFB char co-combust with MB coal at different combustion temperature and mass fraction of EFB char. Generally, high temperature resulted in high BET surface area. High temperature was conductive to open the inner pore structure which promoting the expansion of the pore structure (Y. Zhang et al., 2015). However, in this study, the BET surface area at 600 °C was significantly higher than 700 °C. Similar result are observed in Angin and Sensoz (2014) data where the BET surface area slightly increases while increasing pyrolysis temperature up to 550 °C and decrease thereafter. Increasing the combustion temperature does not improve the textual properties of the blends. This can be due to a sintering effect followed by shrinkage and realignment of the structure of biochar/coal blends which leads to a decrease of the mean size and surface of the pores (Angin & Sensoz, 2014). When combustion occur at high temperature, the structure of porous material cracked, and pores might be partially blocked due to the melting and softening the elements inside the pores which results in a lower surface area (Liu, Zhang, & Wu, 2010).

E) Effect of blending of EFB char with MB coal on BET surface area.

Combustion at temperature 600 °C is selected to study the effect of blending of EFB char with MB coal on BET surface area. Based on figure 1, at temperature 600°C, the measured BET surface area decreases as the mass fraction of EFB char increases. Initially at 0 wt.% of EFB char, the BET surface area is 486.18 m^2/g. As the mass fraction of EFB increase to 0.2, 0.6, and 1.0 wt.%, the BET surface area decreases to 347.25, 248.64, and 154.62 m^2/g, respectively. This is because the surface area of material is depending on the amount of inorganic material such as ash content. The combination of the molten ash covered up pores hence reducing the accessibility surface area. It can be inferred that the higher the amount of ash content, the smaller the surface area presented (Ahmad, Alias, Talib, Rashid, & Ghani, 2018). From the proximate analysis presented earlier, the ash content of EFB char is higher than MB coal. That is why the BET surface area decreases when the mass fraction of EFB char increases. The ash content increases as the mass fraction of EFB char increases.

F) Synergistic Effect of co-combustion of EFB char with MB coal.

The synergistic effect of co-combustion of EFB char with MB coal were determined by constructing a plot of predicted BET surface area and actual BET surface area at different temperature and mass fraction of EFB char as shown in figure 1. The lines in figure 1 represent what might expect in terms of surface area development if the EFB char blends with MB coal as a function of mass fraction, x whereby the predicted surface area, $SA_{predicted}$ would be equal to (Vyasa, Chellappa, & Goldfarb, 2017):

$$SA_{predict} = x_{EFBc}SA_{EFBc} + x_{MBc}SA_{MBc} \quad (1)$$

By comparing the predicted surface area with actual surface area, the result shows the actual surface area does not intercept with the predicted surface area line. At temperature 600 °C, the predicted surface area at 20% and 60% of EFB char blends are 419.87 and 287.24 m^2/g respectively. However, the measured surface area obtained from experimental are 347.25 and 248.64 m^2/g for 20% and 60% of EFB char blends. This shows that there is a synergistic effect of co-combust of different blending ratio at temperature 600

°C. Similar with 700 °C, the actual surface area does not lie on the predicted surface area whereas the distance between these two points are much larger compared to 600 °C. This means that the synergistic interaction is much higher at temperature 700 °C. Similar trend was reported in Vyasa et al. (2017). They stated that there is no generalizable linear trend between the percent of biomass in a blend and the BET surface area. There is a potential synergistic reaction between biomass-coal blends pyrolysis where different compounds develop as a function of temperature and blending ratio (Yangali, Celaya, & Goldfarb, 2014). Thus, this means that it is possible for such chemical synergies shown in physical ways such as surface area.

CONCLUSION

The aim for this study is to investigate the synergistic effect of co-combustion of EFB char with MB coal at different combustion temperature and different weight ratio of the blends. It was found that EFB char and coal blends does create an impact in terms of ash yield and surface area of the pores. As the temperature of combustion decrease, the ash yield and BET surface area increases. For the effect of blending, the surface area decreases as the mass fraction of EFB char increases. The result obtain for BET surface area does not follow the predicted surface area calculated. This can be concluded that there is a synergistic effect on the co-combustion of EFB char with MB coal. Further studies need to be conducted in order to study the interaction happen in the pores of the blends during combustion.

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