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CHARACTERISTICS OF RICE HUSK BIOCHAR BLENDED WITH COAL FLY ASH FOR POTENTIAL SORPTION MATERIAL

(Ciri-Ciri Gabungan Biochar dari Sekam Padi dengan Abu Terbang Arang Batu Sebagai Potensi Bahan Penjerab)

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Abstract

Biochar has received a great attention recently due to abundant biomass left in Malaysia. Besides that, the application of biochar in environmental aspects widely used in the world to improvise soil fertility and water quality. In this research, biochar is produced from rice husk (RH) by pyrolysis at 500 °C using fixed-bed tube reactor. Then the biochar will be blended with coal fly ash (CFA) using the ratio of rice husk biochar (RHB) to CFA (0.2:0.8, 0.5:0.5, and 0.8:0.2) to be further analyzed on their characteristics. From proximate analysis, the ash content is increasing while moisture content, volatile matter, and fixed carbon decrease as the ratio are decrease. For determination of carbon, hydrogen, oxygen, nitrogen and sulphur, the result from ultimate analysis indicates that hydrogen, carbon and nitrogen increase as the ratio increases. Based on the BET result, the surface area is increase proportionally to the ratio (0.2:0.8, 0.5:0.5, 0.8:0.2). Based on this research, RHB has a great potential to be applied as an adsorbent. However, blended RH with CFA are not giving desire result to be used an adsorbent. It is believed that introduction of CFA will offer some magnetic effect to the sorbant to attract pollutants.

Keywords: biochar, biomass, coal fly ash, pyrolysis, rice husk

Abstrak

Biochar telah diberi perhatian besar baru-baru ini disebabkan kuantiti biojisim terbuang ini yang amat banyak di Malaysia. Selain itu, biochar ini banyak digunakan di dalam aspek alam sekitar iaitu secara meluas untuk penambahbaikkan kesuburan tanah dan kualiti air. Dalam penyelidikan ini, biochar dihasilkan dari sekam padi (RH) oleh proses pirolisis pada 500 °C menggunakan reaktor tiub lapisan tetap. Kemudian biochar akan dicampurkan dengan abu terbang (CFA) batu arang menggunakan nisbah sekam padi biochar (RHB) kepada CFA (0.2:0.8, 0.5:0.5 dan 0.8:0.2) seterusnya dianalisis ciri-ciri mereka. Dari analisis proksimat, kandungan abu bertambah manakala kandungan lembapan, jirim meruap dan karbon tetap berkurang dengan pengurangan nisbah RHB kepada CFA. Untuk nilai karbon, hidrogen, oksigen, nitrogen dan sulfur, keputusan dari analisis muktamad menunjukkan kadar hidrogen, karbon dan nitrogen dan sulfur meningkat dengan peningkatan nisbah RHB kepada CFA. Berdasarkan keputusan BET, luas permukaan meningkat secara berkadaran kepada nisbah (0.2:0.8, 0.5:0.5, 0.8:0.2) RHB kepada CFA. Berdasarkan penyelidikan ini, RHB mempunyai potensi besar untuk digunakan sebagai satu bahan penjerap. Walaubagaimanapun, dengan mencampurkan RH dengan CFA tidak memberi keputusan positif untuk diguna pakai sebagai bahan penjerap. Penambahan CFA dipercayai akan memberi kesan magnet kepada bahan penjerab bagi menarik bahan pencemar.

Kata kunci: biochar, biojisim, abu terbang arang batu, pirolisis, sekam padi

Introduction

Biomass can be defined as a biological material derived from living thing or organisms. Biomass is a renewable resource since it often comes from plant-based material but can be applied to animal source as well [1]. Biomass can be categorized into five main groups which are virgin wood, energy crops, agricultural residues, food waste and industrial waste and co-products [2]. Scope of biomass as renewable energy can be derived into a new product by undergoes a few processes. Biomass will undergo some processes to turn as bio-product, bio-fuel and bio-power.

Biochar is applicable to control the environment pollution. Biochar acted as adsorbent to filter all the contaminants in the polluted water. Adsorption is a process whereby the surface interaction between dissolved materials and char. The difference between adsorption and absorption is based on the concept "to soak up" or "to take into". The contaminants will diffuse into char pores (absorption) where they bind to char surfaces (adsorption). A large area of porosity content in the char provides many reactive sites for the attachment of dissolved compounds. Hence, heavy metal content can be removed by using biochar during water treatment [3]. Bio-fuel or known as biochar needs to be excess in order to maintain forest and agricultural cropland health. Biomass turns to biochar by thermal conversion process. Biochar is produced during pyrolysis and gasification whereby superheating of the biomass with limited oxygen and presence of nitrogen gas. By pyrolysis, all the volatile gases such as methane and carbon monoxide are burned and only carbon-enriched biochar left.

Pyrolysis is a thermal decomposition of materials in the absence or less presence of oxygen as compared to complete combustion. From the ancient philosophy, the product from pyrolysis is a carbonization of biomass or called as char. Nowadays, the pyrolysis will produce different product according to the principal of pyrolysis (temperature, heating rate and vapor residence time).

Rice husk (RH) is a waste product from paddy field after the harvesting season. The disposal of RH can cause a problem due to bulky volume because of its lower density. RH contains approximately 38% of cellulose, 18% of hemicellulose and 22% of lignin [4]. The application of RHB comes in many ways such construction material to produce concrete and adsorbent of organic dye and inorganic metal in wastewater treatment.

Coal fly ash (CFA) is a waste product from coal combustion from anthracite to lignite. In Malaysia, coal is widely used in generating electricity of power plant. CFA can be considered as high contamination since it is by-product from coal combustion and consist of toxic trace element condenses from the flue gas. Most of CFA is disposed as a landfill or became a source in cement industry as a raw material for concrete production. CFA has a spherical size within range 0.5 to 300 µm and pozzolanic properties. Pozzolans can be defined as a siliceous and aluminous material stick together and form as cementations products when it react with water and calcium hydroxide at ambient temperature. Common fly ash consists of SiO_2 (57.82%), Al_2O_3 (22.10%), Fe_2O_3 (8.33%) [4].

The RHB and CFA have potential to be used in environmental aspect as an adsorbent to save the environment. Therefore, this study is to determine the characteristics of single RHB and blend biochar with CFA.

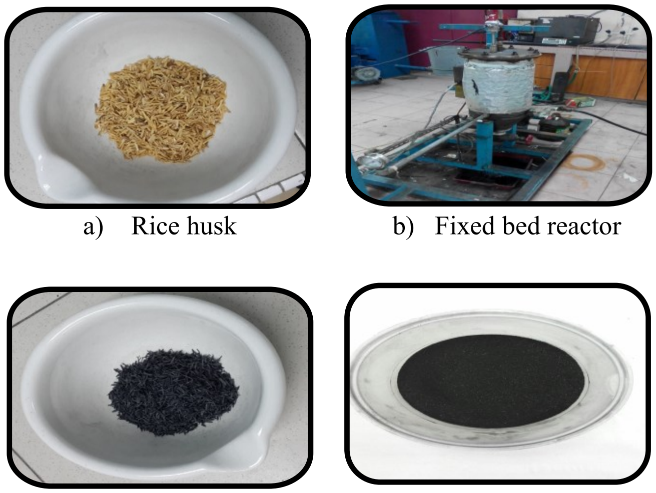
Materials and Method

Materials

RH samples were collected from BERNAS Rice Factory, Sekinchan and CFA samples originated from low rank coal (Mukah Balingian), Sarawak Biomass are crushed and leave them dry for 24 hours at 100^{o}C.

Production of biochar

A laboratory scale fixed-bed tube reactor slow pyrolysis was developed to pyrolyse the feedstock. The dried biomass is placed in cylindrical stainless steel fixed bed reactor. The sample placed in crucible and covered with aluminum foil. Pyrolysis was undergoing at constant temperature at 500^{o}C for 60 minutes. The nitrogen as carrier gas was fed at flowrate 30 mL/min into the reactor. Biochar was collected and weighed after cooling session for 3 hours [5]. The production steps of biochar are illustrated in Figure 1.



a) Rice husk b) Fixed bed reactor

c) Rice husk biochar d) Grinded rice husk biochar

Figure 1. Preparation of biochar

Preparation of sample single and blended biochar

RHB undergo leaching process with 0.1 mol/L of until pH 6 is obtained to remove ash increase the porosity. Then RHB will be neutralized and dried for 1 day at 40 ^oC. Then, the samples were prepared by 4 sample by the blended ratio RHB to CFA are 1.0:0.0, 0.2:0.8, 0.5:0.5, 0.8:0.2 and 0.0:1.0 by wt%.

Characterization of RHB and blended RHB

To analyze proximate analysis, the samples were measured by Thermogravimentric Analyzer (Model: Thermobalance TGA/SDRA51e, Mettler Toledo). Ultimate analysis was performed by Elemental Analyzer CHNO-S (Model: Thermo Finnigan FlashEA 1112 Series). Proximate and ultimate analysis of the samples is shown in Table 1 and Table 2, respectively. Scanning Electron Microscope was performed to observe the surface morphology changes in the RHB and blended RHB. To measure the surface area, pore volume and porosity size samples, Brunauer-Emmett-Teller (BET) with nitrogen was performed.

Table 1. Proximate analysis

Proximate (db) (wt.%)	**Sample Ratio (RHB: CFA)**				
	1.0:0	**0.8:0.2**	**0.5:0.5**	**0.2:0.8**	**0.0:1.0**
Moisture	3.9	4.8	2.6	0.9	0.3
Volatile matter	10.8	10.0	9.6	3.4	1.4
Fixed carbon	62.1	52.4	41.2	11.3	3.7
Ash	23.3	23.3	46.6	84.4	94.6

Table 2. Ultimate analysis

Ultimate (daf) (wt.%)	Sample Ratio (RHB: CFA)				
	1.0:0	0.8:0.2	0.5:0.5	0.2:0.8	0.0:1.0
Nitrogen	0.2	0.18	0.10	0.08	0.05
Carbon	18.32	21.99	15.13	13.65	21.34
Hydrogen	1.35	1.22	0.62	0.27	0.18
Sulphur	0.00	0.00	0.00	0.00	0.00
Oxygen[a]	80.09	76.61	84.15	86.00	78.43

*a = Calculate by differences (100-N-C-H-S)

Results and Discussion

Proximate analysis

Proximate analysis is performed to measure the moisture content, volatile matter, ash content and fixed carbon of the blended biochar. The moisture content of single RHB and CFA is 3.9 and 0.3. While the moisture content of blended biochar of 0.8:0.2, 0.5:0.5 and 0.2:0.8 is 4.8, 2.6 and 0.9 respectively according to the increment of ratio. The percentage of ash in CFA is seem to be the highest which is 94.6% since it is already in ash form. The percentage of ash for single biochar is the lowest compared to the blended RHB with CFA. The percentage of ash is increasing from 23% to 84% which from single biochar to the blended biochar from low to high ratio biochar to CFA. Effect of cellulose and silicon content give difference result on char. If the char contains high cellulose and hemicellulose, therefore the components will reduce to carbon which forms as a fixed carbon. Meanwhile, for silicon and mineral factor, the higher silicon contents, the higher the ash content. The RH contained high silicon and mineral concentration and convert it to ash composition during pyrolysis [7]. Besides, the temperature also affected the composition of ash. The higher the temperature during pyrolysis, the higher the ash composition due to the releasing of volatile matter is increases [6]. Therefore, the increment of composition ash can be varying by ratio of biochar to blended biochar due to the chemical composition of RHB: CFA at constant temperature of 500 ^{o}C in this study.

Ultimate analysis

Determination the amount of nitrogen, carbon, hydrogen, sulphur and oxygen is performed by ultimate analysis. Nitrogen is an inert gas and it does not give any significance usage and generally found as low as 1%. Composition of carbon and hydrogen is related which means the greater the percentage, the higher the quality and calorific value. However, the hydrogen is related to the volatile matter which when it combines with oxygen (O) and form as water, the calorific value reduces. Therefore, a less amount of hydrogen is more preferable. Meanwhile, the lesser the sulphur is the best. This is because oxidation from sulphur form sulphur dioxide or sulphur trioxide which may lead to acid rain and environmental pollution [7]. From the result, it can be inferred that the composition of nitrogen, hydrogen and carbon increase when the ratio of RHB to the CFA increases. Composition of nitrogen of single biochar is 0.24% and increase from 0.08% to 0.18% from the ratio 0.2:0.8. For carbon composition of single biochar is 18.32%. The same trending is shown by carbon which the compositions raise proportionally to the ratio. The composition of carbon is increase from 13.65% to 21.99% by 0.2:0.8. In this study, there is no sulphur content either in single biochar or blended biochar. According to the result, these materials have no impact on sulphur oxidation.

Surface morphology

Figure 2 to 5 show the scanning electron microscopy (SEM) images of CFA, RHB by the ratio 0.2, 0.5 and 0.8 of RHD to CFA. The result for surface morphology will be varies due to the evaporation of volatile matter of biochar. From Figure 2, it depicts that the particles are comes from various sized and shapes. The sizes are varying from smaller to larger sizes of particle. Moreover, the shape comes in varies from regular spherical shapes to completely irregular shape. Figure 2 shows the image of CFA from SEM.

From Figure 3, the SEM image showed the micro porous structure. The shape is honeycomb-like with formation of porosity cylindrically. It shows that the RHB has various size of porosity on the tip side while on the body the porosity is hardly to form as viewed from 600 magnifications. Based on the size of porosity, it has the potential to act as an absorbent. The formation of pores is due to creation of numerous micropores when de-volatilization [8]. A similar observation is also reported in literature [9].

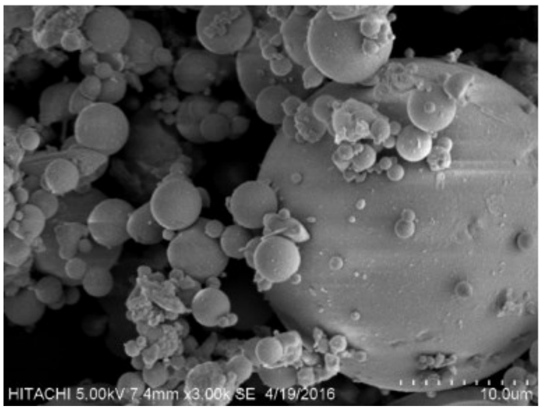


Figure 2. SEM image of CFA (0.0:1.0)

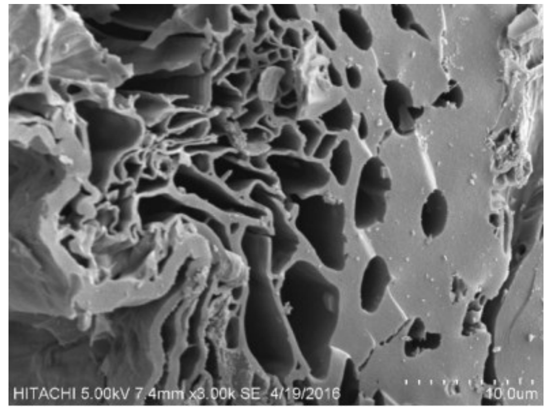


Figure 3. SEM image of RHB (1.0:0.0)

Figure 4, 5 and 6 are the images for blended biochar with coal fly ash by different ration. From the result, it can be observed that the particle of coal fly ash is attached over the biochar surface. For the ratio 0.2:0.8 from Figure 4, the pores and surface are mostly covered by the coal fly ash. Ratio of 0.5:0.5 that shown in Figure 5, the particles of coal fly ash is less cover the pores and surface area of biochar. Figure 6 shown the result for the ratio 0.8:0.2 the pores have more surface and most of the coal fly ash are attached on body's surface area.

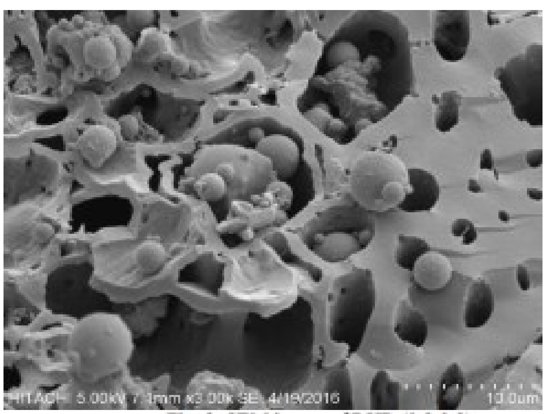


Figure 4. SEM image of RHB (0.2:0.8)

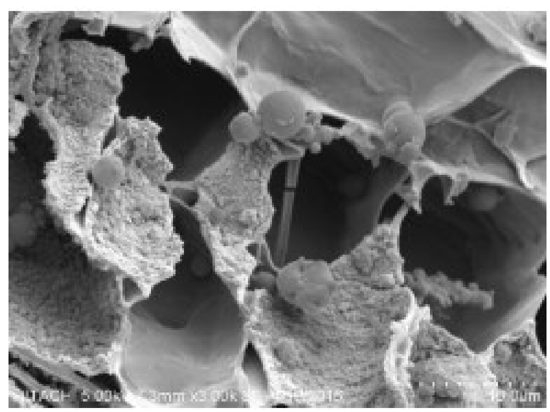


Figure 5. SEM image of RHB (0.5:0.5)

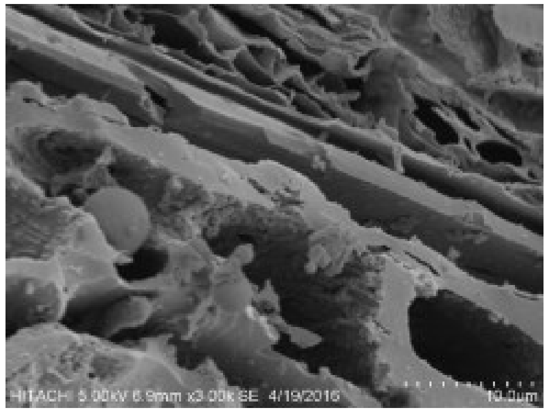


Figure 6. SEM image of RHB (0.8:0.2)

Surface area, pore volume and pore size

From the SEM image above, it can be related to the BET result to discuss about the BET surface area, pore volume and pore size. The result of BET surface area, pore volume and pore size shown in Table 3. Based on the result, the surface area is decreasing from 3.8661 to 3.3769 m^2/g as well as pore volume and pore size. For the pore volume, the volume reduced from 0.00908 to 0.00726 cm^3/g. While for the pore size, the size is decreasing from 93.9042 to 79.0427 Å. This is because the surface area of biochar is depending on the amount of inorganic material which is CFA (ash content) due to the fusion of the molten ash covered up pores in the biochar hence reducing the accessible surface area, [10]. It can be inferred that the higher the amount of ash content, the smaller the surface area of biochar as resulting from proximate analysis. By referring to Table 1, the ash content of samples is increasing from ratio 1.0:0.0 to 0.0:1.0 (RHB: CFA)

Table 3. BET surface area, pore volume and pore size

Sample Ratio (RHB: CFA)	**BET Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Pore Size (Å)**
1.0:0.0	3.866	0.0090	93.904
0.8:0.2	3.539	0.0084	90.566
0.5:0.5	3.430	0.0079	85.593
0.2:0.8	3.376	0.0072	79.042
0.0:1.0	4.301	0.0064	60.116

Even though the results seem not giving a desire result however based on the pozzolanic criteria on coal fly ash, it has high potential to adsorb heavy metal. As mentioned, pozzolans can be defined as siliceous or aluminous material stick together and form as cementitious products when it reacts with water at ambient temperature [8]. Therefore, by adding coal fly ash it may become as a medium to aid biochar in adsorbing contaminant in wastewater.

Conclusion

Blended ratio of RHB and CFA resulting different data and observation. From proximate analysis, the ash content is increasing while moisture content, volatile matter and fixed carbon decrease. For determination of C, H, O, N and S the result from ultimate analysis indicates that hydrogen, carbon and nitrogen increase as the ratio increases. Referring to surface morphology, the shape and pore size is varying by difference ratio. Based on the BET result, the surface area is increase proportionally to the ratio of RHB: CFA 0.2:0.8, 0.5:0.5, 0.8:0.2.

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