Characterization the potential of biochar from cow and pig manure for geoecology application

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Abstract. Biochar is a solid product generated from the carbonization of biomass with various potential benefits. The utilisation of biochar should be adapted to its characteristic which is mainly influenced by its feedstock. In this study, cow and pig manure biochar generated by a conventional process, were characterized by its physical and chemical analysis and its potential to be used as soil amendment. For this purpose, several main parameters were analyzed: organic carbon, Nutrient (total-N, available P and K) status, Cation Exchange Capacity (CEC), proximate data analysis (moisture content, ash, volatile matter and fixed carbon) and its ash composition. The comparison between biochar and feedstock will be based on these parameters. The results of this study show that the organic carbon, available P, ash, and fixed carbon content of pig-manure biochar is higher than cow manure-derived biochar; while total-N, available K, CEC and volatile matter is lower. On its ash composition, the pig manure-derived biochar is dominated by SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, P$_2$O$_5$, and CaO while the cow manure-derived biochar is dominated by SiO$_2$, CaO, Al$_2$O$_3$, K$_2$O, and P$_2$O$_5$. However, both biochar show potential for improving soil quality and reducing carbon emission from animal manure.

1. Introduction

Biochar, in scientific literature, is known by many names such as black carbon, pyrogenic carbon, and charcoal [1]. Biochar is a co-product of the bio-energy pyrolysis (carbonization) process during which biomass is heated in a low-oxygen to zero-oxygen state which results in carbon-rich and recalcitrant carbon-burning ingredients [1-3]. In other words, biochar is the result of combustion or carbonization process from carbonized lignocellulosic material at 350-700°C [4-5] and its activity is still low and contains solid and porous carbon [6-7]. Therefore, the biochar is not produced with the same characteristics and depends on the pyrolysis condition and the source of the feedstock [8-10].

Prior studies indicate that the greatest importance of biochar properties is the feedstock used for biochar production [11-13], which has a substantial impact on the compositional constituents of the biochar [10, 14, 15]. According to Shalini et al. [13], before and after production, biochar differed in physical, chemical, and nutrient characteristics. Feedstock was a better predictor of biochar ash content and C/N ratio [15]. In Zhao et al. [10], the biochar parameters most affected by feedstock properties were for e.g. total organic carbon, fixed carbon, and mineral elements of biochar. Thus, biochar is not pure carbon but a mixture of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), and ash in various proportions [16]. This properties are required in the soil amendment materials.
In previous studies, biochar’s feedstock usually consisted of material from plants and very limited animal manure. In this present study, the cow and pig manure feedstock and their derived biochar were characterized by organic C, total-N, K and P available, CEC, and ash mineral composition. The abundant availability of this type of manure, especially in Bali, makes them good feedstock for biochar production and an excellent resource for waste management.

2. Materials and Methods

2.1. Biochar preparation

Cow and pig manure were used and converted into biochar. These materials were obtained from individual farms in Buleleng, Bali. For this biochar research we used a carbonizer made from a clay pot and its lid (2.5 L traditional beverage container), obtained from the local market. As for the pyrolysis process we used an LPG stove. During the carbonization process, the temperature was not controlled. The manure was dried in the sun for two weeks and then placed in the carbonizer. Once the fire started burning, the lid was put on the stove. Twenty minutes later, the smoke exuding from the small crevices of the lid was somewhat black and was subsequently replaced by white smoke, which acted as a sign that the manure was burnt. After 4 hours, the manure was completely combusted indicated by the depletion of smoke. Prior to testing, the resulting biochar was then crushed and sieved into a 2 mm mesh sieve to acquire a more homogenous substrate [17].

2.2. Biochar chemical analysis

Feedstock and the biochar were analyzed for organic carbon, available P and K, N-Total, Cation Exchange Capacity (CEC), proximate analysis data, and the ash composition. The organic carbon was determined by Walkley-Black procedure, available P by Bray I method, available K by titrisol method, N-total by Kjeldahl method, and CEC using the percolation method with ammonium acetate [18]. The proximate analysis and ash composite determination were conducted at the Centre for Mineral and Coal Technology (tekMIRA), Bandung. A typical proximate analysis includes the moisture, volatile matter, ash content, and fixed carbon [19, 20]. ASTM D.3173 was used to determine the moisture content, ISO 562 to determine volatile matter (VM), ASTM D.3174 to determine ash content, and ASTM D.3172 to determine fixed carbon. The moisture content was determined by the weight loss after the sample was heated at 105°C for an hour. The volatile matter was thus determined by measuring the weight loss following the combustion of approximately 1 g sample in a crucible at 900°C. Following the same procedure, the ash content was determined at 750°C. The fixed carbon (FC) derived by subtracting from 100 the percentage value of moisture content, VM and ash. The ash compositions were determined by the gravimetric method for SiO₂, LOI, and SO₃; spectrofotometry for TiO₂ and P₂O₅; and atomic absorption spectroscopy (AAS) for Al₂O₃, Fe₂O₃, K₂O, Na₂O, CaO, MgO, and MnO. Hence, all acquired elements were translated into oxides.

3. Results and Discussion

3.1. Organic carbon of biochar

As is the raw material, organic carbon in pig manure-derived biochar (18.88%) was lower than in cow manure-derived biochar (27.31%). These results were much lower than in wood-derived biochar (71.47%), coconut shell-derived biochar (60.07%) and in organic waste-derived biochar (31.41%); as reported by Widowati et al. [21] and Widowati and Asnah [22]. According to Verheijen et al. [3], in addition to the operating conditions of pyrolysis, the composition and chemical structure of biomass feedstocks is closely related to the composition and chemical structure of the biochar produced. Cellulose and lignin, for example, had thermal degradation in a range between 240-350°C and 280-500°C [23]. Therefore, the relative proportions of these components will affect the carbon content of biomass where higher lignin content biomass will provide higher carbon content in biochar compared with that produced from biomass with lower lignin content [3]. In Winter et al. [24], the lignin content is 16 - 30% in cow manure and <5% in pig manure. However, the results taken from this study show that organic carbon content in cow manure-derived biochar is lower than in pig manure-derived
biochar. This is possible because the content of protein and fat in pig manure is higher than that of in cow manure. According to Winter et al. [24], protein content in pig manure ranges from 16 - 40% and fat 10% while in cow manure the protein content ranges from 17-20% and fat between 4 - 7%. As discussed above, organic-C in cow and pig manure-derived biochar are relatively high when measuring against International Biochar Initiative (IBI) Standard which required 10% minimum organic-C in biochar [25].

3.2. Nutrient of biochar

According to Piash et al. [26], the content of N, P and K is generally not determined by its concentration in the feedstock. The result observed in this study suggested that 0.5% nitrogen concentration in cow manure and 0.75% in its biochar, while 1.075% in pig manure and 0.74% in its biochar. Thus, the nitrogen conversion efficiency for biochar obtained from cow and pig manure is 150% and 70.48%, respectively. This data indicates that converting livestock manure into biochar does not reduce its role as a nitrogen provider. Although the nitrogen content of pig manure is higher, the conversion efficiency of N in pig manure is less than half the efficiency of N conversion in cow manure. The loss of N on the carbonization of pig manure may be caused by organic compounds in pig manure dominated by more labile organic compounds than those available in cow manure. This is understandable because pig feed is much softer than cow feed.

Unlike the conversion efficiency of nitrogen, the conversion efficiency of P on the carbonization of pig manure (104%) is greater than that of cow manure (71%). However, the conversion is relatively small. This is because the fraction P in feedstock is converted into stable P during biomass carbonization thereby reducing P mobility [27]. The results observed from this study show that the content of P available in cow manure and its biochar are 0.746g/kg and 0.529g/kg while for pig manure and its biochar are 0.620g/kg and 0.646g/kg. The P available content of both biochars are higher than in wheat straw-derived biochar (0.21 g/kg) and corn cobs-derived biochar (0.45 g/kg), but lower than in corn stalk-derived biochar (2.10 g/kg) as reported by Chan and Xu [28]. However, consistent with Dai et al. [27], the results observed in this study indicate that P in livestock manure can be recycled into biochar as source P to reduce the need for chemical fertilizers.

As is the case with total-N and available P, the data found in this study also showed that the content of available K in the biochar was not consistent with the concentration in its feedstock. The content of available K in cow manure is lower than in pig manure, but in their biochar available K content in cow manure-derived biochar is much higher than in pig manure-derived biochar. The results observed in this study show available K in cow manure and its biochar are 15.96g/kg and 21.26g/kg while for pig manure and its biochar are 16.22g/kg and 15.28g/kg. These are higher than in biochar which are reported by Chan and Xu [28], where the available K for wheat straw-derived biochar is 2.90 g/kg, corn cobs-derived biochar is 9.40 g/kg, and corn stalks-derived biochar is 0.03 g/kg. The data also indicated that the K conversion efficiency of cow and pig manure was 133.22% and 94.19%, respectively. This indicates that the volatility of these elements during the carbonization process is very low. In other words, there was 33.22% increase of available K in cow manure-derived biochar and a slight decrease of 5.81% in the biochar obtained from pig manure.

3.3. Cation exchange capacity

Another factor that determines the quality of biochar is the CEC values. CEC is the measure of the number of cations (positively charged ions) that can be retained by biochar. The results from this research show that CEC decreased in both biochars when compared to its feedstock. However, when comparing results between the two biochars and feedstock, CEC in cow manure-derived biochar (2.11 me/100g) is slightly higher than in pig manure-derived biochar (2.06 me/100g) even though CEC in cow manure (5.37 me/100g) is much higher than in pig manure (3.19 me/100g). According to Montecillo [29], the presence of organic matter contributes to CEC. However, when viewed from the content of organic-C, both cow manure (30.32%) and its biochar (27.31%) are much higher than pig manure (22.51%) and its biochar (18.88%). As mentioned in the previous section, the content of lignin
in cow manure is higher than that of pig manure, in contrast to fat and protein. In comparison to Zhao et al. [10], CEC biochar produced in this study are much less. This is consistent with relatively low readings in organic-C content and volatile matter.

3.4. Proximate analysis

Except for moisture content, all values of proximate analysis were reported on a dry weight basis. VM is a measure of gas, oil, and tar that is released when the biomass is heated above 300°C. The major constituents of feedstock (C, H, and O) evaporate during dehydration and pyrolysis with H and O are lost in much greater quantities than C. O and H were initially lost as water and then as hydrocarbons, slowly evaporating agents, H2, CO, and CO2 [30]. Thus, the biochar contains a lower VM when compared with its feedstock. Based on the dry weight it was founded that VM of both feedstock was 51.54% and 39.96% respectively for cow and pig manure. The VM decreased to 51.16% in cow manure and 38.94% in pig manure. VM of cow manure-derived biochar (19.36%) was higher than that of pig manure-derived biochar (13.62%). The results of this study are very close to those reported by Zhao et al. [10] but lower than VM of biochar obtained from various types of grass [31]. A study conducted by Spoka [32] showed that VM in biochar may affect overall microbial activity when added to the soil and in some case result in increased mineralization due to stimuli in microbial respiration. Theoretically, biochar with high VM content is less stable and has a higher proportion of labile carbon that provides energy for microbial growth and limits the nitrogen availability necessary for plant growth so it will suppress plant growth. A study by Deenik et al. [33] consider that VM materials above 35% are high (causing nitrogen deficiency) and VM below 10% is low, therefore, both biochars in this study are not expected to limit plant growth.

Organic material in the feedstock is not released as the remaining VM as Fixed carbon (FC). FC in cow and pig manure were founded in this study to be 14.05% and 6.46%, respectively. Generally, the fixed carbon in biochar increases relative to the FC content of the raw material with increasing pyrolysis temperature even up to 500% [18]. However, in this study the increase occurred only by 53.74% for the carbonization of cow manure and 120.43% for pig manure. The FC for each cow and pig manure-derived biochar is 21.60% and 14.24% and in their feedstock it is 14.05% and 6.46% respectively.

According to Dume et al. [18] the fixed carbon content of biochar will be lower than 30% if the ash content is more than 35%. Ash is the remaining mineral material after complete combustion has occurred in feedstock. The results observed in this present study showed that the ash content of cow manure-derived biochar reached 59.04% and pig manure-derived biochar reached 72.14%, this is consistent with its feedstock that ash content of pig manure (53.58%) is higher than cow manure (34.41%). They are determined by the ash content of its feedstock. In this present research, for both biochars, the ash composition was rich in Si oxide (SiO2) and to a lesser extent in Mn oxide (MnO). The ash of cow manure-derived biochar showed considerably higher concentration of CaO than the ash in pig manure-derived biochar. It is important to note that the percentage of CaO in the former was about 13.73%, while that of Al2O3 in the ash of pig manure-derived biochar was 13.65%. In Brewer et al. [34] it is also reported that SiO2 was predominate in the ash composition of switchgrass (61.86%) and cast stover-derived biochar (47.06%), but not so in the composition of hardwood-derived biochar which CaO (22.37%) is the oxide predominant. In more detail, the order of metal oxides in ash composition of cow manure-derived biochar from the highest to the lowest are SiO2 (50.10%), CaO (13.73%), P2O5 (7.75%), Al2O3 (7.28%), K2O (5.54%), Fe2O3 (4.71%), MgO (4.09%), Na2O (1.95%), LOI (1.32%), SO3 (1.05%), TiO2 (0.39%), and MnO (0.15%). A slightly different order on ash composition of pig manure-derived biochar; SiO2 (48.09%) followed by Al2O3 (13.65%), Fe2O3 (9.54%), P2O5 (7.67%), CaO (7.22%), K2O (5.59%), MgO (4.17%), Na2O (2.48%), SO3 (1.05%), LOI (0.92%), TiO2 (0.87%), and MnO (0.26%). The findings further confirm that the application of both biochar into agricultural soil, in addition to reducing carbon emissions by increasing the fixed carbon content from their initial conditions, may have a vital effect due to their mineral content.
4. Conclusion
Biochar are chemically different in cow and pig manure feedstocks. Biochar from cow manure has a higher concentration of C-organic, P-available, ash, and fixed carbon content when compared with pig manure. While, on the other hand, biochar from pig manure has a higher concentration of N, K, CEC, and volatile matter than cow manure. But all of these were not consistent with their feedstock. Si, Al, and Ca are the most widely available minerals in both biochars, whereas Mn is the least available component.

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