Indonesian Journal of Environmental Management and Sustainability
e-ISSN:2598-6279 p-ISSN:2598-6260

Research Paper

The Advantages and Disadvantages of Livestock Manure and its Biochar as a Solid Fuel and Soil Amendment

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Abstract
The aim of this study is to elucidate some of the basic characteristics of manure and its biochar and to explore its potential as a solid fuel and soil amendment. Cow, pig, chicken, and duck manure were selected and collected in the farmer's pen. Furthermore, composite sampling was applied to obtain a representative sample of each manure. Each of them was dried in the sun for four to seven days, and each sample was divided into two parts. The first part was not further processed, while the rest were carbonized. Carbonization was carried out within a temperature range of 300 to 400°C and 4 h residence time. C-organic, N-total, available P and K, CEC, volatile matters, fixed carbon, ash content, Carbon (C), Hydrogen (H), Oxygen (O), Nitrogen (N), Sulfur (S) content), higher heating value, and the chemical composition of their ash in both original and carbonized manure were identified. In addition, the nutritional content was relatively comparable and the H/C and O/C ratio in biochar were lower than in its original state. Both the original and carbonized manure indicated low calorific value, while the ash content and fouling index were high. The results showed that livestock manure in both forms has more potential as a soil amendment than solid fuel.

Keywords
Manure, Biochar, Solid Fuel, Soil Amendment

Received: 7 September 2022, Accepted: 1 December 2022
https://doi.org/10.26554/ijems.2022.6.4.119-129

1. INTRODUCTION

Animal waste could be divided into two main categories, namely solid and liquid livestock (Barker et al., 2002). The solid livestock waste is mainly collected by drying livestock manure, while the liquid mainly comes from watering (or treated waste) and livestock manure (wet manure) or from washing livestock and their pens with water after the manure is dry. In addition, the solid form of this waste is generally used as manure.

The use of manure as a fertilizer supplement has widely been used in various agricultural sectors. Before the advent of cheap inorganic fertilizers after World War II, farmers routinely used manure to increase soil fertility (Barker et al., 2002). Currently, due to the increasing cost of commercial fertilizers and the pressure on proper fertilizer management to protect environmental quality, attention is being focused on maximizing the use of manure as organic fertilizers.

According to Barker et al. (2002), the decomposition and mineralization of manure in soil could release large amounts of nutrients essential for plant growth. The byproducts of the decomposition process also have the potential to release gas emissions into the atmosphere, which could lead to increased environmental problems. However, increasing demand for food leads to an intensification of livestock production, which causes serious environmental problems whenever animal waste is not properly managed. Proper management of livestock waste is necessary for common environmental problems associated with it, such as chemical emissions, methane (CH_4), nitrous oxide (N_2O), ammonia (NH_3), and nitrate (NO_3) to air and water could be prevented (Gerber et al., 2007). Therefore, advanced technology for converting waste to energy is highly recommended.

According to Rosillo-Calle (2016), there are two types of processing technologies that are involved, namely thermochemistry (e.g. pyrolysis, carbonization, gasification, and liquefaction) and biochemical (e.g. aerobic and anaerobic digestion). Thermochemical and biochemical conversion produces value-added bioenergy products, which could be categorized into three forms which are not solid, liquid or gas and charcoal, biochar, bio-oil, and biogas (Rosillo-Calle, 2016).

Biochar obtained from carbonization could be used both as an energy source and as a soil amendment. However, research related to the carbonization of livestock manure is very rare. Most of them have focused on biochar obtained from certain biomass and also there has been no research that has produced biochar from a combination of several types of plant-derived biomass. The biomass from plant derivatives generally has a high mineral content but relatively low N, P, and K content. However, livestock manure generally contains high N, P, and K content.

Characteristics of the quality of biochar also need to be adjusted according to its use. According to Gusmailina and Pari (2019), the use of biochar really depends on the type and quality. Like carbon nanomedicine, it is physically useful, among others to absorb solar radiation, electromagnetic wave insulators, electrodes, carbon filaments, and battery water. Biochar morphology has a porosity which is useful for water purification, air purification, gas suction, soil fertilization, filters, anti-moisture, microorganism growth, and others. Furthermore, they are chemically reactive, as shown in the process of ignition, carbon sulfate production, gasification, pharmaceuticals, and steelmaking. Biochar is also a source of energy for household, cooking and power supply, and as a non-organic component, it is used as a glaze, microelement, ceramics, and to build soil fertility (Gusmailina and Pari, 2019).

The physical and chemical characteristics of biochar are often associated with interest in applications for agricultural soils, which include proximate analysis structure, ultimate analysis, pH, cation exchange capacity, macro and microelements, ash composition, porosity, surface morphology, structure and functional groups, and aromatics (Liang et al., 2006; Spokas, 2013; Jindo et al., 2014; Pituello et al., 2015; Xie et al., 2016). The physical and chemical characteristics of biochar associated with its application to energy include proximate and ultimate analysis, energy content, and ash composition. Furthermore, there are some characteristics that are required for the purpose of both applications, namely proximate, ultimate analysis, and the composition of the ashes. The proximate analysis data includes moisture content, volatile matter, fixed carbon, and ash content. In comparison, volatile matter and fixed carbon are the combustible parts that release their chemically bound energy when oxidized. The volatile matter consists of carbon (C), hydrogen (H), sulfur (S), oxygen (O), and nitrogen (N), and these elements are called ultimate analysis data. Ash comprises mineral substances that are found in solid fuel and consist mainly of a mixture of oxides of inorganic elements K_2O, Na_2O, CaO, MgO, FeO_3, Al_2O_3, SiO_2, and P_2O_5.

Based on the above information, the knowledge of the properties both in origin and biochar manure is very important when used effectively. This study focused on both the origin and biochar of cow, pig, chicken and duck manure properties in view of soil amendment and fuel solid. Therefore, an overview of the suitability of its utilization and further development need to be obtained.

2. METHODS

2.1 Manure Collection and Preparation

The livestock manure used in this study includes cow, pig, chicken and duck manure, and they were all collected from the farm. The samples were dried under the sun for 7 days up to the combustible.

2.2 Carbonization Procedure

Biochar was produced and used in this study, according to Gunamantha and Widana (2018). The carbonization was carried out in 2.5-L cylindrical clay containers filled with manure samples and placed in a stove. The containers were loaded with 500 g of manure before tightly securing the lid allowing only the evolved volatiles to escape through small vents on the lid and a thin gap between the cover and the container was allowed to occur. Furthermore, the evolved volatiles was neither collected nor quantified. Carbonization was conducted within a temperature range of 300 to 400°C and in four-hours residence times. After the stove was turned off, the containers were left closed and cooled in order to prevent char oxidation. The resulting biochar was then crushed and sieved in 2 mm mesh sieve prior to testing.

2.3 Manure and Biochar Characterization

The organic carbon was determined using Walkley-Black procedure, in which the sample was digested with potassium dichromate ($K_2Cr_2O_7$) and concentrated sulfuric acid. Furthermore, available P was determined using the Bray I method. Available K was determined by titrisol method and N-total using Kjeldahl method. In addition, the Cation Exchange Capacity (CEC) was determined using the percolation method with ammonium acetate.

The proximate analysis of raw biomass was based on the ASTM standards methods (ASTM E871-82, ASTM E1755-01, and ASTM E872-82). The moisture content was determined by the weight loss after the samples were heated at 105°C for an hour. The volatile matter was also determined by measuring the weight loss that follows the combustion of about 1 g of biochar in a crucible at 950°C. Following the same procedure, the ash content was determined at 750°C, while the fixed carbon was determined by subtracting the percentages of moisture, volatile matter, and ash from 100%. The C, H, N, and O were performed using CHON analyzer according to ASTM D.5373 for carbon-hydrogen, and nitrogen and ASTM D.3176 for oxygen. Furthermore, total sulfur was determined using a high-temperature combustion test method according to ASTM standard D.4239. The ash composition was conducted by using the gravimetric method for SiO_2, LOI, and SO_3, spectrophotometry for TiO_2 and P_2O_5, and AAS for Al_2O_3, Fe_2O_3, K_2O, Na_2O, CaO, MgO, and MnO. In addition, all the obtained elements were translated into oxides. The energy content was determined according to ASTM D.5865 using a bomb calorimeter. The determination of proximate, ultimate, calorific value and ash composition were conducted at the Centre for Mineral and Coal Technology (tekMIRA), Bandung, Indonesia.

3. RESULTS AND DISCUSSION

3.1 Characteristics of Livestock Manure and its Biochar

Like other biomass, livestock manure has the potential to be used as a soil amendment and an alternative energy source. It could be used directly by converting it first into other forms, for example, as biochar. The basic characteristics of livestock manure, both in its original condition and carbonized for any purpose, need to be considered before its being used. Table 1 shows the main characteristics of manure and biochar and the potential to be used as soil amendments. Pig manure had the highest content of C-organic in dry manure, which was followed by that of cow, duck, and chicken. Furthermore, the highest total nitrogen content was found in pig manure, followed by chicken, duck, and cow manure. However, in biochar, the highest total nitrogen composition was found in cow manure, followed by pig, chicken, and duck manure. In all types of manure, there was a decrease in the composition of the P-available content in the biochar from its original condition. This study found that the highest available P content was shown by chicken manure, followed by duck, cow, and pig manure. While in the biochar form, the highest available P content was found in chicken manure, followed by pig, duck, and cow manure. This result was relatively consistent with the P_2O_5 content in the ash composition (Table 3), whereby the chicken manure and biochar showed the highest P_2O_5 content. Furthermore, it was found that the K-available content in pig, cow, chicken, and duck manure was 16.224, 15.961, 1.1881, and 1.026 g/kg, respectively. While biochar was 15.282, 21.263, 1.257, and 0.830 g/kg biochar from cow, pig, chicken, and duck manure. Another parameter that is also related to bio-drug fertility characteristics is CEC. This is a measure of the number of cations (positively charged ions) that biochar particles could have. In this study, there were materials that had increased CEC, while some decreased after carbonization (Table 1). The highest CEC was shown by duck manure, followed by chicken, cow, and pig manure. While in its biochar form, the highest CEC was shown by the biochar from chicken manure (56.10 me/100g) followed by CEC biochar from duck manure (42.71 me/100g), cow, and pig manure.

Proximate analysis of moisture content (Mc), ash (A), volatile matter (VM), and original fixed carbon (FC) and impurities are presented in Table 2. Furthermore, the moisture content for the bioagents produced varied from 1.55 to 4.82%. Based on the dry weight, it was found that the VM of biochar raw material varied from 30.43 to 45.93% and 12.97 to 21.48%.

Livestock manure and biochar were composed of main elements such as carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), and ash in various proportions. Furthermore, elemental carbon (C) is different from organic carbon (OC). C is released directly from the incomplete combustion of fossil fuels and biomass, while OC an aggregate of hundreds of individual compounds spanning a wide range of chemical and thermodynamic properties, is formed by a variety of processes, including combustion and secondary organic carbon formation. Elemental carbon is particles of graphite or amorphous carbon. While "Organic carbon" is the content of organic molecules, which contain carbon, hydrogen, and oxygen, and often with nitrogen or sulfur bonded in as well. Table 2 illustrates the variation of C manure from 14.59 to 30.32%, H from 2.52 to 4.83%, N from 1.51 to 2.51%, O from 21.00 to 32.36%, and S from 0.21 to 0.50%. In biochar, C from 17.39 to 27.31%, H from 1.52 to 2.28%, O from 9.17 to 13.21%, N from 1.5 to 1.97%, and S from 0.17 to 0.46%.

Table 3 shows the ash composition of manure and its biochar. Furthermore, the ash minerals, both in their original state and biochar, are silica and the next sequence component is different for each ingredient.

Table 3 shows that ash in cow manure contains 52.73% (SiO_2), 13.67% (CaO), 7.75% (P_2O_5), 7.28% (Al_2O_3), 5.24% (K_2O), 4.71% (Fe_2O_3), 4.11% (MgO), 2.03% (N_2O) and 0.45 % (TiO_2). High concentrations of CaO, P_2O_5, and Al_2O_3 are found in this material. Pig manure contains 49.80% (SiO_2), 13.65% (Al_2O_3), 9.54% (Fe_2O_3), 7.22% (CaO), 6.82% (P_2O_5), 4.67% (K_2O), 3.42% (MgO), 2.08% (Na_2O), and 0.84% (TiO). After SiO_2, the concentration of Fe_2O_3, CaO, P_2O_5, and K_2O, which are quite high, are also found in this material. Chicken manure contains 35.21% (SiO_2), 22.44% (CaO), 17.18% (P_2O_5), 8.15% (K_2O), 6.05% (MgO), 1.98% (Al_2O_3), 1.45% (Fe_2O_3), 0.52% (Na_2O), and 0.08% (TiO_2). In this material, CaO is also available, P_2O_5 and K_2O in high concentration. Duck manure contains 46.75% (SiO_2), 20.00% (CaO), 9.27% (Al_2O_3), 5.43% (Fe_2O_3), 3.58% (P_2O_5), 3.42% (K_2O), 2.90% (MgO), 0.9% (Na_2O) and 0.27% (TiO_2). Apart from SiO_2, the dominant components in the ash from this material were CaO and Al_2O_3.

Table 3 shows that ash in biochar from cow manure contains 50.10% (SiO_2), 13.73% (CaO), 9.23% (Al_2O_3), 6.51% (K_2O), 6.44% (P_2O_5), 5.08% (Fe_2O_3), 4.09% (MgO), 1.95% (Na_2O), and 0.39% (TiO_2). Apart from SiO_2, the dominant components in the ash from this material were Al_2O_3, K_2O, and P_2O_5. Furthermore, biochar from pig manure contains 48.09 (SiO_2), 13.23 (Al_2O_3), 8.76 (Fe_2O_3), 7.67 (P_2O_5), 7.44 (CaO), 5.59 (K_2O), 4.17 (MgO), 2.48 (Na_2O) and 0.87% (TiO). The dominant component other than SiO_2 is Al_2O_3, Fe_2O_3, P_2O_5, and CaO. Biochar from chicken manure contains 38.45% (SiO_2), 20.47% (CaO), 15.64% (P_2O_5), 7.68% (K_2O), 5.45% (MgO), 2.69% (Al_2O_3), 1.71% (Fe_2O), 0.64% (Na_2O) and 0.11% (TiO_2). The dominant component other than SiO_2 is CaO, P_2O_5, and K_2O. Biochar from duck manure contains 49.28% (SiO_2), 18.74% (CaO), 8.88% (Al_2O_3), 5.21% (Fe_2O_3), 3.76% (K_2O), 3.49% (P_2O_5), 3.03% (MgO) and 0.27% (TiO_2). The dominant components be-

Table 1. Fertile Properties of the Origin and Manure of Biochar

Feedstock and Biochar Manure	Chemical Properties				
	C-organic (%)	N-total (%)	Available P (g/kg)	Available K (g/kg)	CEC (me/100gr)
Cow manure	41.82	0.50	0.74584	15.96101	5.37
Pig manure	53.82	1.05	0.61990	16.22437	3.19
Chicken manure	33.78	0.89	0.97739	1.18143	4.28
Duck manure	37.23	0.79	0.91440	1.25695	3.96
Cow manure biochar	36.98	0.75	0.52911	21.26275	2.11
Pig manure biochar	40.13	0.74	0.64556	15.28223	2.06
Chicken manure biochar	56.10	0.26	0.87260	1.02698	14.86
Duck manure biochar	42.71	0.21	0.61004	0.83086	13.89

Table 2. Proximate and Ultimate Analysis Data from Manure and its Biochar

Feedstock and Biochar Manure	Chemical Properties								
	Proximate (%)				Ultimate (%)				
	Mc	VM	FC	Ash	C	H	N	O	S
Cow manure	10.89	45.93	12.52	30.66	30.32	4.83	1.72	32.26	0.21
Pig manure	9.52	36.16	5.84	48.48	22.51	3.99	1.71	23.13	0.18
Chicken manure	13.86	41.16	8.38	36.60	23.78	4.61	2.15	32.36	0.50
Duck manure	7.22	30.43	2.41	59.94	14.59	2.52	1.51	21.00	0.44
Cow manure biochar	1.55	19.06	21.27	58.12	27.31	1.91	1.87	10.62	0.17
Pig manure biochar	4.82	12.97	13.55	68.66	18.88	1.61	1.50	9.17	0.18
Chicken manure biochar	3.64	21.48	19.24	55.64	26.44	2.28	1.97	13.21	0.46
Duck manure biochar	2.86	18.76	10.37	68.01	17.39	1.52	1.17	11.48	0.43

sides SiO2 were CaO and Al_2O_3, and both were in their original form and bio-substances. Apart from SiO_2, the dominant components are CaO and Al_2O_3, while the relatively few components include MgO, Na_2O, and TiO_2.

3.2 The Potential of Livestock Manure and its Biochar as a Solid Fuel and Soil Amendment

Carbonization of livestock manure also increases the composition of C-organic content in the obtained biochar. This means that at the same weight, biochar has higher C-organic compared to its origin and is also more stable (Jindo et al., 2014; Stella Mary et al., 2016). According to Stella Mary et al. (2016), the carbon in biochar comes from organic carbon compounds that are easily biodegradable into a very stable polycondensed aromatic carbon structure (carbon black). This stable carbon condition is desirable because it reduces the potential for carbon emissions without reducing its absorption by plants.

Table 1 also illustrates that there is a fairly wide difference between organic C in cow and pig manure and chicken and duck manure. This is possible because chicken and duck feed are generally in the form of concentrate, while cows and pigs still use feed from plants. Furthermore, organic carbon is the amount of carbon bound in an organic compound. Important characteristics of organic compounds include their ability to form water-soluble and insoluble complexes with metal and hydro oxide ions, interact with clay minerals and bind particles together, adsorbing and desorb organic compounds both natural and anthropogenic (Schumacher, 2002). In this perspective, biochar from cow and pig manure is more beneficial than from chicken and duck manure.

In terms of total nitrogen content, the loss of N in the carbonization of pig, chicken, and duck manure is probably caused by organic compounds which are more labile than those available in cow manure. According to Winter et al. (1992), the fiber content in cow manure is about 50%, fat (20-27%), protein (17-22%), and lignin (16-30%), while in pig manure the fiber content is about 20%, 10% fat, 16 to 40% protein, and $<5\%$ lignin. The fiber content in chicken manure is around 15%, 5% fat, protein (20-40%), and lignin 10 to 14%, while no information was available for duck manure. Furthermore, the high fiber and lignin content in cow manure confirm that it is tougher than other livestock manure.

In comparison with the various types of biochar reported by Chan and Xu (2012), the total N content found in this study was lower than in biochar produced from wood (1.09%), poultry manure (2.00%), urban waste sludge

Table 3. Ash Composition of Manure and its Biochar

Components	Feedstock and Biochar Manure							
	Cow manure	Pig manure	Chicken manure	Duck manure	Cow manure biochar	Pig manure biochar	Chicken manure biochar	Duck manure biochar
SiO_2	52.73	49.8	35.21	46.75	50.1	48.09	38.45	49.28
Al_2O_3	7.28	13.65	1.98	9.27	9.23	13.23	2.69	8.88
Fe_2O_3	4.71	9.54	1.45	5.43	5.08	8.76	1.71	5.21
K_2O	5.54	4.67	8.15	3.42	6.51	5.59	7.68	3.76
Na_2O	2.03	2.08	0.52	0.90	1.95	2.48	0.64	0.83
CaO	13.67	7.22	22.44	20	13.73	7.44	20.47	18.74
MgO	4.11	3.42	6.05	2.90	4.09	4.17	5.45	3.03
P_2O_5	7.75	6.82	17.18	3.58	6.44	7.67	15.64	3.49
TiO_2	0.45	0.84	0.08	0.27	0.39	0.87	0.11	0.27
LOI	1.02	1.09	2.85	5.00	1.32	0.92	3.29	4.17
MnO	0.15	0.26	0.33	0.21	0.15	0.26	0.30	0.20
SO_3	0.86	1.01	2.90	1.91	1.05	1.05	2.77	1.91
H_2O	0.11	0.33	<0.001	<0.001	0.14	0.29	<0.001	<0.001
MJ/kg	12.05	8.43	4.60	8.97	9.91	6.59	5.74	9.94

(6.4%), rice straw (1.32%), bagasse (1.77%), and coconut shells (0.94%). Meanwhile, Jassal et al. (2015) reported that the total N content in biochar from ungag manure ranged from 3.27 to 4.48%. However, both (Chan and Xu, 2012; Jassal et al., 2015) reported that its application could change the dynamics of soil nitrogen and biochar from livestock manure as a fertilizer. Biochar has also been shown to reduce N leaching (Laird et al., 2010), N_2O gas emissions (Spokas and Reicosky, 2009), ammonia volatilization (Steiner et al., 2010), and increase biological nitrogen fixation (Rondon et al., 2007). However, there is no report that states the minimum limit for the total N content of biochar to fulfill this role.

For the available P content both in manure and its biochar it showed a higher quantity than the ones from wheat straw 0.21 g/kg and corn cobs 0.45 g/kg as reported by Chan and Xu (2012). However, it was lower than the P available in bio-products produced from corn stalks (2.10 g/kg) as also reported by Chan and Xu (2012). When compared with biochar from 12 types of biomass (including pig and cow manure), it was found that for cow manure, the results of this study were lower than those reported by Zhao et al. (2013), which is 0.646 g/kg. Furthermore, the biochar content of pig manure was 4.386 g/kg, which was much lower than those reported by Zhao et al. (2013). The P-available found in this study was also lower when compared with biochar from shrimp shells (2.585 g/kg), bone pulp (10.86 g/kg), and wastewater sludge (1.702 g/kg). How it was higher when compared to biochar from paper waste (0.124 g/kg), sawdust (0.061 g/kg), grass (0.590 g/kg), wheat straw (0.074 g/kg), peanut shells (0.166 g/kg), chlorella (0.717 g/kg), and waterweeds (0.514 g/kg).

The data found in this study also showed that the K-available content in biochar was not in line with the concentration in the raw material. The highest K content was available in pig manure, followed by the cow, duck, and chicken manure, while in biochar, the highest K content was found in biochar from cow manure, followed by pig, chicken, and duck manure. Based on the data from the analysis of the ash composition of each material (Table 3), the highest K_2O content was actually found in chicken manure and biosubstances. This indicates that the chicken manure is more dominated by inorganic K, while the others are by organic K.

This value of K-available is much lower than in biochar made from wheat straw 2.90 g/kg and corn cobs 9.40 g/kg. However, it was higher than the biochar made from corn stalks of 0.03 g/kg (Chan and Xu, 2012). In other studies Zhao et al. (2013) it was reported that K available was found in biochar from cow (1.021 g/kg) and pig manure (3.506 g/kg), shrimp skin (1.896 g/kg), bone pulp (0.444 g/kg), wastewater sludge (0.525 g/kg), waste paper (0.079 g/kg), sawdust (1.189 g/kg), grass (5.151 g/kg), wheat straw (5.182 g/kg), peanut shells (1.733 g/kg), chlorella (13.67 g/kg), and waterweeds (3.244 g/kg). Furthermore, both (Chan and Xu, 2012; Zhao et al., 2013) provided a variety of available K. These data indicate that the carbonization of livestock manure would change a lot of available K content. Therefore, the application of biochar from livestock manure to agricultural soil would help increase the efficiency of using K fertilizer.

In terms of its CEC content, it was found that the CEC of cow and pig manure was much smaller than in chicken and duck manure, and this contradicts the existence of organic C. According to Montecillo (1983), the presence of organic matter contributes to CEC and when viewed from the C-organic content, both chicken and duck manure and biochar are much lower than that of cow and pig manure and biochar. The increase in CEC in chicken and duck manure removal showed that the release of –OH, aliphatic CO, and C=O ester groups was less from the surface of the manure compared to cattle and pigs or in a larger surface area (Chan et al., 2007). In addition, the negative functional groups on the surface of the biochar particles hold the cations.

When compared with the results obtained by (Dume et al., 2015), CEC biochar produced from coffee husks was 64.75 ± 0.76 to 79.23 ± 0.33 me/100g and those produced from corn cobs (Corncob) were 47.52 ± 0.66 to 62.03 ± 0.8 me/100g. In comparison with Zhao et al. (2013), CEC biochar from cow manure was 149 me/100g and pig manure ranged from 23.6 to 132 me/100g. Furthermore, the following contents were also reported in the same study, namely CEC biochar from shrimp shell (389 me/100g), bone pulp (87.9 me/100g), wastewater sludge (168 me/100g), waste paper (516 me/100g), sawdust (41.7 me/100g), grass (84.0 me/100g), wheat straw (95.5 me/100g), peanut shell (44.5 me/100g), chlorella (562 me/100g), and waterweeds (509 me/100g). This indicates that the CEC of biochar produced in this study was lower than those reported by previous researchers.

Another impact of the carbonization of livestock manure was the decrease in the volatile matter content. According to Antal and Grønli (2003), biomass with its main constituents C, H, and O undergoes evaporation during the dehydration and pyrolysis phases with H and O lost in much greater amounts as water and then as hydrocarbons compared to C. Furthermore, materials that are slow to evaporate include H, CO, and CO_2. The VM results shown in this study are very close to those reported by Zhao et al. (2013) namely 17.2% cow manure for biochar and 11.0% pig manure. However, it was still lower when compared to biochar made from chicken manure (30.6-36.9%), eclapitus sawdust (28.5-36.9%), coffee skin (26.2-34.6%), bagasse (33.2-35%), and tree bark and pine (29.3-38.5%) (Domingues et al., 2017). In Oram et al. (2014) it was reported that VM biochar produced from various types of grass ranged from 32.10 ± 1.89%. The low VM found in this study was made possible by the difference in temperature and the length of time carbonization. In addition, it was also possible by the quantity and quality of volatile organic materials in the original material.

Research conducted by Spokas (2010) shows that VM in biochar affects the overall microbial activity when added to the soil and in some cases result in increased mineralization due to stimulation of microbial respiration. In theory, biochar with high VM content are less stable and have a higher proportion of labile carbon which provides energy for microbial growth and limits the availability of nitrogen required for plant growth in order to suppress it. In addition, high levels of VM (e.g. aldehydes, alcohols and carboxylic acids) in biochar could create a fire hazard during handling, transportation and storage (Brown, 2012; Werther et al., 2000). A study by Deenik et al. (2009) stated that VM material above 20% is classified as being high (causing nitrogen deficiency), and below 10% is classified as being low. Therefore, the VM manure found in this study was classified as high, while in the biochar as moderate. The application of the four biochar as a soil amendment does not have the potential to limit plant growth.

From a fuel perspective, fuel with low VM has a low heating value, but when the VM becomes too high it produces a lot of smoke during its combustion. Furthermore, it is an index of the gases present in the fuel. A high VM would increase the length of the light and help ease fuel ignition. When compared with coal that has VMs ranging from 2 to 45 (wt.%) (from anthracite to lignite) (Speight, 2015), biochar produced in this study are in this range. Therefore, judging from the VM content, biochar produced from livestock manure has the potential to act as an amendment to both soil and solid fuel.

The presence of VM in a material is related to its ash composition. The higher the ash composition, the lower the VM. The results obtained showed that the ash content varied from 30.66 to 48.48 and 55.64 to 68.66 for the origin and bio-substances, respectively (Table 2). In line with (Novak et al., 2009; Singh et al., 2010) it was stated that biochar from livestock manure has a higher ash content compared to the ones from wood, due to the high nutrient content in livestock manure. Furthermore, animal manure has a high content of unstable organic and inorganic compounds in order to produce biochar with high ash content which is positively related to its nutritional and mineral composition. In (Xie et al., 2016; Wang et al., 2016) it was stated that the ash content is also influenced by temperature and residence time during curing. Therefore, the higher the temperature and residence time, the higher the ash content in the biochar is produced because more and more unstable organic and inorganic compounds are released.

Ash contain minerals needed by plants (Domingues et al., 2017). However, Joseph et al. (2009) there is limited understanding of the high role of minerals in biochar ash due to limited data available on their long-term effects on soil properties. Based on Brewer et al. (2009) study, biochar produced from raw materials such as switch grass and corn residue had an ash content of 26 to 54% of which was mostly silica, while hardwood ash mainly contains alkali metals. Other studies Verheijen et al. (2010) stated that various elements have been measured in bioorganic ash such as boron, copper and zinc. However, the most common include potassium, calcium, silicon and to a lesser extent aluminum, iron, magnesium, phosphorus, sodium, and manganese. These elements are all in oxidized forms such as Na_2O, CaO, K_2O, and could be reactive or water soluble to varying degrees.

In the ash components, a high P_2O_5 (available P) content was also found, especially in chicken manure, followed by biochar ash from chicken, pig, cow, and duck manure. Furthermore, for K_2O (K available) the highest was found in the ash from chicken manure, followed by biochar ash from chicken manure, biochar from cow and pig manure, pig and cow manure, biochar from duck manure. This shows that both in its original and bio-organic conditions, chicken manure is very useful because it provides P and K for plants. However, this value is in contrast to the available P and K content (Table 1) which is determined directly from the state of origin and biochar (not ignored). This difference is made possible by the P and K in cow and pig manure and the biochar are dominated by organic P and unstable inorganic P. Therefore, from the point of view of the need for P and K availability, it would be more profitable by utilizing cow and pig manure and biochar compared to chicken and duck manure and their biochar, and to chicken and duck manure and its biochar. However, utilizing ash from chicken and duck manure and their respective biochar would be more profitable compared to ash from cow and pig manure and bio-products.

P_2O_5 is the dominant component besides SiO_2. Therefore, the phosphates do not change significantly as a result of the carbonation and these ingredients could be considered as phosphate supplements. Apart from phosphate, calcium is also a dominant element in almost all materials. However, the role of calcium is only as a micro element needed by plants. The presence of calcium would actually contribute more as a liming agent.

From a fuel perspective, the high ash content in the biochar produced indicates that it is not good for fuel. Besides that, high ash could also cause slagging/fouling (Yao et al., 2017). According to Yao et al. (2017), there are five important parameters, namely alkali index (AI), the base-to-acid ratio (Rb/a), silica ratio (G), silica to alumina ratio (S/A), and slagging/fouling (Hw) of ash. The alkali index (AI) expresses the percentage of alkali metal (K_2O + Na_2O) in biomass. Furthermore, the Rb/a expresses the base (Fe_2O_3, CaO, MgO, K_2O, Na_2O) to acid (SiO_2, TiO_2, Al_2O_3) ratio. Silica ratio (G) expresses (SiO_2 x 100)/(SiO_2 + Fe_2O_3 + CaO + MgO). The silica-alumina index (S/A) expresses SiO_2/Al_2O_3. The slugging/fouling index expressed as Rb/a x Na_2O, when Fe_2O_3/(CaO + MgO) > 1 or as Na_2O and Fe_2O_3/(CaO + MgO) < 1 and CaO + MgO > 2. The results of slagging and fouling indices of different manure and its biochar are shown in Table 4.

Rb/a ratio may be determined from where the lower range of the slag is defined at Rb/a less than 0.2. Values between 0.2 to 1.0 indicate medium deposition tendency and those greater than 1.0 indicate high potential (Pintana et al., 2014). Furthermore, the silica ratio value in the range of 72-80 is expected to show slight deposition tendency. A value between 65 and 72 may show moderate slag tendency, and when in the range of 50 to 65 it indicates the possibility of a severe slagging problem (Niu et al., 2014). Ash fusion temperatures (AFTs) increase with increase of S/A (Song et al., 2010). In addition, the biomass materials that have high S/A ratio and Na_2O appeared to have high fouling tendency (Pintana et al., 2014). It was also found that the higher the ash content, the smaller the HHV value (Table 3). However, for certain components such as SiO_2, the higher the content, the higher the HHV value. While, for CaO and P_2O_5, the higher the content, the lower the HHV value.

Another important property of the fuel is fixed carbon. It is the remains of the water, VM and ash content. Fixed carbon is not pure carbon but dry period which is not VM and ash and is therefore dominated by the combined aromatic structures. Table 2 also shows fixed carbon (dry basis) varying from 2.41 to 12.52% and 10.37 to 21.27% on the origin and biochar of impurities, respectively. In general, the fixed carbon content of biochar increases relative to that of the raw material with increasing pyrolysis temperature and could even reach 500% (Dume et al., 2015). However, in this study the increase was 69.89, 132.03, 129.59 and 330.29% for cow, pig, chicken, and duck manure respectively. The highest increase occurred in duck manure removal, where the lowest VM decreased. The fixed carbon content of biochar produced from cow and pig manure, respectively was 21.60 and 14.24%, while for the raw material was 14.05 and 6.46%. According to Enders et al. (2012) this changes are much larger than the ones that occur in the organic C content. It also stated that the fixed carbon content of biochar would be lower than 30% when the ash content is more than 35%. In line with Enders et al. (2012), the value of fixed carbon for all materials in this study was lower than 30% with ash content ranging from 30.66 to 68.66%.

When compared with the fixed carbon biochar reported by Dume et al. (2015), fixed carbon obtained from this study was much lower than eucalyptus sawdust (62.2 - 78.8%), coffee skin (52.4 - 60.9%), bagasse (63.0 – 73.9%), and pine bark (53.2 - 62.8%) when compared to the results from Antal and Grønli (2003). Furthermore, based on Zhao et al. (2013), it was found out that the fixed carbon content of cow, pig and chicken manure was 14.7%, 34.7 to 40.2%, and 11.1 to 14.1%, respectively. Fixed carbon content is an indication of recalcitrance carbon sequestration potential of the biochar (Enders et al., 2012). The low fixed carbon shown by the biochar produced in this study shows its low recalcitrant compound and this means that its potential as a carbon sequestration is also low. Furthermore, this is consistent with the value of its C-organic content. Therefore, both the results reported by Zhao et al. (2013) and the results of this study indicate that the potential of biochar carbon sequestration from cow manure is higher than the ones from chicken, pig, and duck manure.

From the perspective of fuels, fixed carbon is also positively correlated with the heating value and acts as a primary heat generator during combustion. It is the remaining solid in the pyrolysis after the VM is evaporated. Fixed carbon mainly consists of carbon, therefore, it is very appropriate to use it to estimate the calorific value of fuel. Furthermore,

Table 4. Slagging and Fouling Indices of Different Manure and its Biochar

No.	Feedstock and Biochar Manure	Slagging and Fouling Indices				
		AI	Rb/a	G	S/A	Hw
1	Cow manure	7.57	0.50	70.10	7.24	2.03
2	Pig manure	2.25	0.42	71.16	3.65	2.08
3	Chicken manure	15.67	1.04	54.04	17.78	0.52
4	Duck manure	3.80	0.58	62.27	5.04	0.90
5	Cow manure biochar	3.34	0.53	68.63	5.43	1.95
6	Pig manure biochar	2.25	0.46	70.25	3.63	2.48
7	Chicken manure biochar	12.00	0.87	58.19	14.29	0.64
8	Duck manure biochar	4.53	0.45	64.62	5.55	0.83

AI, alkali index; Rb/a, base to acid ratio; G, silica ratio; S/A, SiO_2/Al_2O_3; Hw, fouling index

it is a carbon in its free state and does not combine with other elements. Based on Table 3, the heating value was also low in line with the fixed carbon.

Table 2 indicates the H:C and O:C ratios for each ingredient. The H:C ratios of various manure were 0.159, 0.173, 0.177, and 0.194 for cow, duck, pig, and chicken manure, respectively. Furthermore, the H:C ratios for biochar from various livestock manure were 0.070, 0.085, 0.086, and 0.087 for biochar from cow, pig, chicken, and duck manure, respectively. The hydrogen to carbon ratio (H:C) is a term often used to measure the degree of aromaticity and maturation of the biochar, which is linked to their long-term stability in the environment (Stella Mary et al., 2016). Therefore, the higher the C ratio the higher the degree of aromaticity and maturation of a material. In this study, there was a decrease in the H:C ratio of biochar to the original material. This shows that biochar from livestock manure are also more stable than their raw materials. Therefore, this means that its ability to be minimized decreases.

The O:C ratio is an indication of weathering (oxidation) of the biochar (Spokas, 2010). It is also related to the number and composition of the substituted functional groups (Spokas, 2010), and to cation exchange capacity and presence of oxygenated groups on the biochar(Lee et al., 2016). Oxygen content also plays a major role in determining the overall biochar surface chemistry behavior, particularly for surface pH (Cheng et al., 2008), which could be an important driver for chemical reactions and degradation potential (Spokas, 2010). In this study, the O:C ratios of various livestock manure were 1.028, 1.064, 1.361, and 1,439 for pig, cow, chicken, and duck manure respectively and the O:C ratios for biochar were 0.389, 0.486, 0.500, and 0.660 for cow, pig, chicken, and duck manure, respectively. This indicates that in its biochar form, manure is more difficult to degrade than in its original state. Decreasing the ratio of O/C also indicates the decreasing functional group thereby reducing the capacity of the cation exchange. However, this is not entirely consistent with the CEC generated in this study as shown in Table 1. This inconsistency mainly occurs in chicken and duck manure with biochar. Therefore, the decrease in the O:C ratio of the biochar to its original state leads to an increase in the CEC of the biochar to its original state.

The C:N ratio is an indication of N mineralization (Clough et al., 2013). According to Clough et al. (2013), its decrease was due to a higher C:N ratio of the biochar. Furthermore, N mineralization or immobilization occurs with organic amendments to soil depending on the C:N ratio of the amendment. Whenever the C:N ratio is high enough (generally more than 25:1), the N tends to be immobilized (Brassard et al., 2017). Brassard et al. (2017) discovered that, biochar with a lower N content (C/N ratio> 2 30) were more suitable for mitigation of N_2O emissions from soils. The C:N ratio of masters depends on the microbial processes involved in N dynamics. Moreover, the rate of N and C mineralization and magnitude of CO_2 and N_2O emission depends on it (Baggs et al., 2000). Furthermore, the C:N ratio in general determines whether microorganisms would immobilize mineral N or release it into the soil (Henriksen and Breland, 1999). Biomass with low C:N ratio are expected to decompose rapidly and cause little immobilization (Willson et al., 2001). According to De Neve et al. (2004), N are successfully immobilized by increasing the C:N ratio of organic materials. In this study, the C:N ratio that were obtained include 9.66 (duck manure), 11.06 (chicken manure), 13.16 (pig manure), and 17.63 (cow manure) and 12.59 (biochar from pig manure), 13.42 (biochar from chicken manure), 14.60 (biochar from cow manure), and 14.86 (biochar from duck manure). Furthermore, there was a decrease in C:N ratio of both cows and pigs manure. While an increase in C:N ratio occurred by calculating chicken and duck manure. However, the C:N ratio for all materials was lower than 25:1. This means that there is a potential for N mineralization in all materials and this is beneficial for its use as a land amendment. The increased C/N ratio, N_2O generation from both nitrification and denitrification process was decreased

(Yan et al., 2017).

Ultimate analysis is also one of the important factors when studying biomass fuel properties. It helps in accessing the percentage of N, S, and Cl to study the environmental impact of biomass. Moreover, it helps in calculating the percentage of C, H, and O in order to estimate the heating value. These elements are converted to CO_2, H_2O, and SO_2 for C, H, and S, respectively, which release heat. Therefore, the ratio of hydrogen to carbon and oxygen to carbon atoms of hydrocarbon fuels is also one of the important parameters affecting its energy content. The lower the hydrogen per carbon, the lower the oxidation state and the more energy that would be released during the oxidation reaction. Therefore, the lower H/C and O/C ratios are desirable for the use of char to energy (Pereira et al., 2013). The biochar samples in this study had H:C ratio in the range of 0.839 to 1.049 and O:C ratio in the range of 0.292 to 0.495 both of which are higher than graphite. This means all biochars is undesirable for the use of char to energy.

4. CONCLUSIONS

Animal manure is widely recognized due to its nutritional content. Furthermore, by converting it into bio-products, it provides value to livestock manure in terms of the potential for reducing carbon emissions produced. This is indicated by the lower H/C and O/C ratios in the form of biochar compared to the origin. Moreover, the C/N ratio was relatively small which indicates nitrogen rich conditions, and also the content of P and K-available was relatively stable. The reduced odor emission is also another advantage of animal manure compared to its original condition. Livestock manure, both in its original form and bio-products also contains combustible materials. However, its energy content is very low due to high ash content. Several other characteristics that also do not support livestock manure as fuel include the H/C and O/C ratios which are still much higher than graphite and have a high slag potential.

5. ACKNOWLEDGMENT

The authors are grateful to the Institute for Research and Community Service of Ganesha University of Education for their support to the research programs in this study.

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