

Carbonization Characteristics of Municipal Solid Waste/Cow Manure Blend

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Abstract— The goal of this research was to elucidate the characteristics of organic fraction of municipal solid waste or cow manure blend biochar produced in a batch-type carbonization reactor at range temperature, ranging from 300 to 350 degrees Celcius. The OFMSW composition to cow manure in feedstock were varied through five different levels (0, 25, 50, 75, 100 wt percent). The biochar properties of soil quality support were determined. The results of this study revealed that the pH was relatively stable. The EC, N total, and K available increased with increasing proportion of cow manure. Meanwhile, C-organic, P available, and ash, decreased with increase OFMSW proportion. The O/C and H/C ratio decreased with increasing proportion of OFMSW. The resulted composite biochar showed potential advantages such as stability and nutrient content.

Keywords—organic fraction of municipal solid waste; cow manure; carbonization; biochar.

I. INTRODUCTION

A large amount of organic waste including animal manure and urban organic waste continues to increase. Population growth has driven an increase in the need for food and the resulting waste. Because the land areas for growing crops are decreasing, poultry and livestock production can be the solution to meet the need of human consumption. This has an impact on increasing cow manure and the resulting garbage.

Both cow manure and the Organic Fraction of Municipal Solid Waste (OFMSW) are materials that are rich in nutrients needed by plants. Cow dung has been used extensively as manure. However, this direct use contributes to increasing greenhouse gas emissions as a result of the decomposition process. Likewise, the organic waste. This waste component has also been used extensively as a soil conditioner in its form as compost. The compost content, which is still dominated by labile organic matter, is easily decomposed which also releases carbon emissions. Thus, innovative efforts are needed in its use that can minimize carbon emissions without ignoring its potential as a soil enhancer. Coining or converting it into a form of biochar is one way to that end.

Biochar is an organic carbon material that is predominantly recalcitrant, produced by heating biomass to the temperature between 300°C and 600°C under the conditions of low or no oxygen [1]. Since the organic carbon which is produced in biochar is very stable, adding biochar to the soil has the potential to improve the quality and absorption of soil carbon which is also important for reducing carbon dioxide in the atmosphere. According to [2], soil with biochar will increase the soil fertility so that it will provide benefits for land productivity. Conceptually, there are three mechanisms related to these benefits: (1) biochar will modify the soil directly through its intrinsic and compositional elements; (2) biochar provides an active surface that modifies the dynamics of soil nutrients or, if not, a catalyst that is useful for reactions in the soil; and (3) modifying soil characteristics in a beneficial way that affects root and/or nutrients growth and retains and acquires water [2]. However, the role of this biochar will be greatly influenced by its properties, and their properties are mainly influenced by their raw materials [3,4,5].

Raw materials of biochar have an impact that is substantial for the elements composition in biochar. Those raw materials are good predictor of the biochar ash content and the C/N ratio [6]. Such as [7] reported, biochar parameters such as mineral elements, fixed carbon, and organic carbon are most affected by the nature of raw materials. Thus, biochar is a mixture of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), potassium (K), phosphorus (P), sulfur (S) and ash content which contains various types the metal oxides. It makes biochar is not a pure carbon [8]. It means that each biochar shows specific characteristics that will make it suitable as a soil enhancer [8].

Biochar of pea leaves and cauliflower leaves showed higher organic carbon value and mineral content and showed the best soil amendment compared to biochar from orange peels [9]. There were significant differences in ash content (grass and manure > wood) and C/N ratio (softwood > grass and manure) [6]. In another study [7], reported that the total N, K-available and CEC in cow manure biochar were greater than in pig manure biochar, while P available in biochar from cow manure (0.529 g/kg) was lower than the biochar produced from pig

manure (0.646 g/kg). These shows that biochar raw material is very important to be used as a basis for consideration as soil enhancers and has the potential to be combined between different raw materials.

Previously, most of the research has focused on biochar obtained from certain biomass. There are no studies conducted to investigate the production of biochar from a combination of several types of biomass. Biomass from plant derivatives generally has a high mineral content but relatively low N, P, K content. On the other hand, cow manure generally has high N, P, and K content. Combination to produce composite biochar has the potential to obtain the best biochar quality. This study aims to develop and apply a composite biochar obtained from a mixture of cow manure with organic components of urban waste. This is intended to produce the best biochar quality as well as to reduce the volume of organic waste piled up in cell landfills. In addition, the availability of these two wastes is quite abundant and has not been handled well.

TABLE I. NATIONAL WASTE GENERATION AND SERVICE DATA

Region	Population	Total Waste Generation	Waste Gen per person	Population being served	Actual waste Collection	Non collected Waste Gen
	Million	Mtons/yr	kg/day	Million	Mtons/yr	Mtons/yr
Sumatra	49,3	8,7	0,48	23,4	4,13	4,57
Jawa	137,2	21,2	0,42	80,8	12,49	8,71
Bali	12,6	1,3	0,28	6	0,82	0,68
Kalimantan	12,9	2,3	0,49	6	1,07	1,23
Sumapapua	20,8	5	0,66	14,2	3,41	1,59
Total	232,8	38,5	0,45	130,4	21,72	16,78

Table 1 reports the result of survey about the national waste generation and service data according to [10]. The data revealed that around 38.5 million tons of urban waste are produced annually by 232 million people in Indonesia (450 grams per person per day), of which 21.2 million tons in Java as a whole. 26 The largest city in Indonesia with a total population of 40.1 million people, produces a total of 14.1 million tons per year (around 1 kg per person per day). Municipal waste consists of 62 percent organic waste, 14 percent plastic, 9 percent paper, 2 percent glass, 2 percent rubber and leather, 2 percent metal and 13 percent other types of waste. This data shows that the main component of waste in Indonesia is organic waste. To convert of both waste into biochar will decreasing thei contamination to environment. According to the 2017 Animal Husbandry and Animal Health Statistics [11], the total cattle population in Indonesia is 16,599. 247 head and one cow produce dung 10-30 kg/day on average.

The main objective of this study was to determine the physical and chemical characteristics of biochar from a mixture of cow dung and organic waste and its effect on soil quality. In more detail, the objectives are to: 1) determine the nutritional

chemical properties of the composite biochar produced, 2) find out the elementary composition of the composite biochar produced.

II. METHOD

A. Research Subjects and Objects

The subject of this research was the confined biochar and soil from agricultural land, while the object was the chemical properties of biochar and soil including: bulk density, pH, C-organic, N-total, P-available, K- available, and their electrical conductivity (EC). The ultimate analysis was only conducted on biochar.

B. Sample Collection

This research used cow dungs, organic waste and soil and then divided them into five samples. Cow dung samples were collected from community farm areas. Since Bali has a considerable amount of cow livestock, it was easy to collect the samples. The texture of cow dung that was used as a sample is relatively dry, means that they are not fresh.

Organic waste samples were collected from the composting facility (compost material) at Jagaraga composting facility. Each of about 25 kg of samples was taken randomly from dirt mounds and compost material. The sample then was dried in the sun until conditions allowed it to be fabricated.

The soil followed three steps to be considered as the sample for this research. First, the soil samples were taken on horizons 0-20 cm from agricultural land. Second, the soil samples were cleaned of impurities such as garbage from plants and rocks. Third, the soil sample was dried for about 1 week for further smoothing and sifting with a 2 mm sieve.

C. Biochar Chemical Analysis

Biochar pH was measured by preparing a mixture of biochar with water in a ratio of 10: 1 (mL: g). Before measurement was conducted, the mixture was stirred for 1 hour to ensure the biochar particles were evenly distributed. Then the pH of the supernatant was measured using a pH meter. Organic C was determined using the Walkley-Black method. Potassium was determined as available K (K₂O) by the titrisol method according to SNI-2803-2010. The phosphate was determined as available P (P₂O₅) by the Bray I method in accordance with SNI-2803-2010. Determination of N was done by the Kjeldahl method. Electrical conductivity (EC) determination was done by placing two electrodes into the sample, and measuring the difference in electrical potential. The measurement results were the conversion of electrical resistivity into electrical conductance in units of mmhos/cm.

The ultimate analysis included carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S). These elemental analysis were conducted using CHNS-O Analyser (Perkin-Elmer 2400 Series). The content of carbon (C) was determined by the standard ASTM D 5373, hydrogen (H) by the standard ASTM D 5373, nitrogen (N) by the standard ASTM D 5373, oxygen (O) by standard ASTM D 3176, and sulfur (S) by standard ASTM D 4239.

III. RESULT AND DISCUSSION

The findings of this study can be described as follows. The chemical composition such as carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S) were analyzed using CHNS-O Analyser. The results of analysis for chemical composition of organic fraction of waste and cow dung biochar were summarized in Table II.

TABLE II. CHEMICAL PROPERTIES OF COMPOSITE BIOCHAR

Properties	Biochar					Soil
	S1	S2	S3	S4	S5	
pH	7.20	7.50	7.78	7.67	8.70	7.01
EC (mmhos/cm)	11.55	11.31	12.20	14.20	17.10	0.21
C-Organic (%)	32.19	32.75	28.57	24.73	16.35	0.88
N Total (%)	0.22	0.21	0.22	0.25	0.23	0.03
P-available (ppm)	419.69	385.69	339.59	275.68	215.07	5.11
K-available (ppm)	448.00	410.67	468.83	503.02	498.22	192.00
Moisture content (%)	5.79	5.07	4.76	3.29	4.89	13.40

Note: S1 = 100% organic waste; S2 = 75% organic waste; S3 = 50% organic waste; S4 = 25% organic waste; and S5 = 0% organic waste (100% cow dung).

The pH varies from 7.2 to 8.7 and tends to get higher with the increasing composition of cow dung in the biochar raw material. The value of DHL biochar is much higher than that of land. Because the portion of lignin biomass is greater in waste, fixed carbon is also greater in charcoal with a greater composition of waste in raw materials and thus lower ash content. Biochar which is produced from pure cow dung has a low fixed carbon level and high ash content. The superior quality of this biochar is also associated with the presence of N, P, K.

In more detail, each composition was divided into several tables. The tables and the descriptions can be seen as follows:

TABLE III. PH PRODUCTION OF IN BIOCHAR

Biochar	Property	
		pH
Biochar	S1	7.20
	S2	7.50
	S3	7.78
	S4	7.67
	S5	8.70
Soil		7.01

Note: S1 = 100% organic waste; S2 = 75% organic waste; S3 = 50% organic waste; S4 = 25% organic waste; and S5 = 0% organic waste (100% cow dung).

Table III represents the pH production in biochar. In accordance with changes in the composition of raw materials, the pH of the biochar produced varies from 7.20 to 8.70. In this case, all biochars reach a neutral to alkaline pH range or tend to have alkaline properties. Table II shows that the higher the content of cow dung, the higher the biochar pH produced. Biochar with raw material 100% cow dung (0% organic waste) has the highest pH of 8.70. The alkaline nature of biochar has been reported to be beneficial for increasing the pH of acidic soils. This is in line with [12], that most of the biochar used for land amendments is alkaline. This is possible, as long as the carbonization of the acid functional groups is released and the

alkaline earth salts become enriched. These salts include (i) soluble salts, (ii) carbonates, (iii) thrifty metal oxides and hydroxides and (iv) silicates, the latter especially when raw materials contain soil particles [12]. Most of this salt will provide a considerable alkalinity to biochar, although it depends on the raw material and its production process [13]. As a result, biochar with low ash content, such as those produced using 100% raw organic waste (S1), has a lower pH value than biochar with higher ash content, such as those produced using 100% (S5) cow manure. These results are in line with those reported by [14]. However, the pH of the biochar is also determined by the temperature of carbonization. Biochar produced under high temperatures (> 400°C) tends to have a pH value greater than low temperatures (< 400°C) from the same raw material [14]. In this study, carbonization was carried out at 300 - 400°C.

Similar to pH, the EC of biochar samples also depends on the raw material. EC is an indication of the amount of electrolytes dissolved in the soil, meaning that the higher the electrolyte value, the more the amount of salt contained in the solution. EC is proportional to the amount and nature of salt, and is the most used soil salinity test [12]. Based on the EC value, the level of soil alkalinity can be classified [15]. Land with a value of EC 0 - 2 is classified as non-salinity soil, 2-4 low salinity, 4 - 8, medium salinity, 8-16, high salinity, and > 16 classified as land with very high salinity. This shows that, biochar produced in this study belongs to the classification of high salinity. Biochar from organic waste has a lower EC compared to cow manure.

TABLE IV. ELECTRICAL CONDUCTIVITY (EC) AND CARBON PRODUCTION IN BIOCHAR

Properties	Biochar					Soil
	S1	S2	S3	S4	S5	
EC (mmhos/cm)	11.55	11.31	12.20	14.20	17.10	0.21
C-Organic (%)	32.19	32.75	28.57	24.73	16.35	0.88

Note: S1 = 100% organic waste; S2 = 75% organic waste; S3 = 50% organic waste; S4 = 25% organic waste; and S5 = 0% organic waste (100% cow dung).

In [12] was mentioned that adding biochar with a high EC value to soils with a low EC value would increase soil EC. From the analysis of Table IV, it can be interpreted as follows. In biochar production, it is considered that soil EC (0.21 mhos / cm) will increase with the addition of biochar. However, before adding biochar to the soil and to avoid problems related to salinization and nutrient imbalance of the soil, the use of biochar must be carefully investigated. The presence of salts and alkaline cations in biochar is responsible for high pH and EC values [12]. Soil that becomes more saline cannot absorb enough water from the soil. Salt will inhibit the flow of natural water from the soil to the roots of plants and will be pulled back into the soil so that plants cannot take enough water for the growth process. As a result, the plant will wither and die regardless of the amount of water supplied [12].

Conversion of biomass waste into biochar (charcoal from biological derivatives) is a source of carbon (C) that can be used to increase the level of organic C in soils in agricultural

soils. Biochar can contain 50 to 90% organic carbon [16]. Therefore the use of biochar can contribute to carbon storage (C) in the soil. Based on the result of the analysis in table III, the organic C produced from each biochar (16.35 - 32.75%) was far lower than the general condition. This is made possible by the high ash content of each biochar. Other findings are, the higher the proportion of cow manure, the lower the organic C biochar. This is consistent with the tendency of ash levels. However, this value is potential enough to increase organic C in the soil samples analyzed in this study (0.88%).

Soil carbon plays a role in regulating climate, water supply, and biodiversity, and provides ecosystem services that are important for human welfare. On the other hand, maintaining the threshold level of organic matter in the soil is very important to maintain the physical, chemical and biological integrity of the soil and also for the soil to carry out agricultural production and environmental functions [17].

TABLE V. NITROGEN CONTENTS IN FEEDSTOCK COMPOSITION

		Property
		Nitrogen Total (%)
Biochar	S1	0.22
	S2	0.21
	S3	0.22
	S4	0.25
	S5	0.23
Soil		0.03

Note: S1 = 100% organic waste; S2 = 75% organic waste; S3 = 50% organic waste; S4 = 25% organic waste; and S5 = 0% organic waste (100% cow dung).

Table V shows the nutrient content (NPK) identified in this research. It revealed that the nitrogen contents are varies in all feedstock composition. The highest content is in S4 (25% OFMSW and 75% cow manure). The lowest is in S2 (75% OFMSW and 25% cow manure). This fact shows that more nitrogen content in 100% OFMSW derived than in 100% cow manure biochar derived. This study found also, low nitrogen content in soil sample (0.03%). It indicates that the addition biochar into soil will improve their nitrogen capacity.

According to [18], the addition of biochar resulted in significant changes in N content (NH₄⁺-N and NO₃-N). Biochar can adsorb both NH₄⁺ and NH₃⁻ from soil solutions thereby reducing inorganic N solutions at least temporarily, but will be more concentrated to be utilized by plant [19]. Biochar is a process that reduces N content so biochar tends to have a high C/N ratio [5]. Another possibility is the occurrence of decomposition when fresh biochar is added to the soil [20], which can induce the net immobilization of inorganic N already present in the soil solution. The addition of biochar to the soil causes a decrease in ammonification thereby reducing the potential for NH₃ volatilization [18]. This decrease could be due to the high biochar C/N ratio and the potential for greater N immobilization [19]. The immobilization potential associated with the addition of biochar to this soil will be severely limited by the resistant nature of biochar [18].

TABLE VI. POTASSIUM (K) & PHOSPHORUS (P) CONTENT IN BIOCHAR

Properties	Biochar					Soil
	S1	S2	S3	S4	S5	
P-available (ppm)	419.69	385.69	339.59	275.68	215.07	5.11
K-available (ppm)	448.00	410.67	468.83	503.02	498.22	192.00
Moisture content (%)	5.79	5.07	4.76	3.29	4.89	13.40

Note: S1 = 100% organic waste; S2 = 75% organic waste; S3 = 50% organic waste; S4 = 25% organic waste; and S5 = 0% organic waste (100% cow dung).

According to the result shown in Table VI, it can be described as follows. In term P available, P decreases with increasing amount of cow dung in the raw material. The NPK content in the P element is lower than that in K, but both are higher than that in N. This means biochar has the potential to increase the P element in the soil. The amount of P leaching is relatively low on the ground, mainly due to low permeability [21].

For K, the amount of K tends to increase with the increasing amount of cow, dung in biochar. Both the P and K content in biochar are much higher than those available in soil samples. This also indicates that biochar is also a good source of land available. K function is known as an enzyme that increases metabolism in plants. In plants, K is needed in photosynthesis and protein synthesis, plants lacking K will have slow and stunted growth. While P deficiency in the soil affects plant growth, P technically assists in the activation of many enzymes related to plant growth, and therefore helps in proper plant growth.

TABLE VII. ELEMENTAL COMPOSITION OF BIOCHAR

Items	S1	S2	S3	S4	S5
C	35.80	35.75	32.24	28.99	20.57
N	1.65	1.92	1.95	1.78	1.75
S	0.34	0.34	0.34	0.34	0.38
H	2.09	3.26	2.73	2.70	2.24
O	14.95	19.51	18.37	16.53	13.18
Abu	45.17	39.22	44.37	49.66	61.88

Note: S1 = 100% organic waste; S2 = 75% organic waste; S3 = 50% organic waste; S4 = 25% organic waste; and S5 = 0% organic waste (100% cow dung).

The elementary compositions of C, O, H, S, and N from biochar are presented in Table VII. The content of C and O decreases with increasing pyrolysis, while % H, S, and N do not experience significant differences. This is consistent with the elementary control of each biochar produced from each ingredient (without mixing raw materials). Biochar from organic waste has higher % C and O and % H, S, and N lower than biochar from cow dung alone. So the higher the composition of cow dung in the composite raw material, the lower the content of C and H in biochar and vice versa for the content of H, S, and N.

TABLE VIII. H/C AND O/C RATIO

Biochar	Items	
	H/C	O/C
S1	0.70	0.31
S2	1.09	0.41
S3	1.02	0.43
S4	1.12	0.43
S5	1.31	0.48

Note: S1 = 100% organic waste; S2 = 75% organic waste; S3 = 50% organic waste; S4 = 25% organic waste; and S5 = 0% organic waste (100% cow dung).

Table VIII presents H/C and O/C ratios in all samples. It shows that the H/C and O/C ratios increase with increasing composition of cow manure in raw materials. These are molar ratios. The higher ratios indicate low aromaticity and stability [22]. Therefore, H/C and O/C ratios are the current most commonly used biochar stability indicators [22]. According to [22], stability of biochar is the most decisive factor that determines its carbon sequestration potential. In this study

IV. CONCLUSION

In this study, analysis of composite biochar from cow manure and OFMSW indicated that it contains variation and more nutrients than the soil sample. The P available of biochar decrease with increasing proportion of cow manure otherwise of K available. The high ash content in cow manure biochar alone, indicated its rich in minerals content. All biochar in the classification of high salinity. The O/C and H/C ratio decreased with increasing proportion of OFMSW. The resulted composite biochar shows advantages such as their stability and nutrient content. Its mean the composite biochar presents suitable properties for its use for agricultural applications. However, future researches should consider the effective changes in nutrient availability, plant growth, and its stability in soil.

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