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Increasing Anaerobic Digestion Efficiency Using Food-Waste-Based Biochar

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Abstract: The efficiency of methane production by anaerobic digestion (AD), during which energy is generated from organic waste, can be increased in various ways. Recent research developments have increased the volume of gas production during AD using biochar. Previous studies have used food waste itself in AD, or, added wood-biochar or sewage sludge charcoal as an accelerant of the AD process. The application of food-waste biochar in AD using activated sludge has not yet been studied and is considered a potential method of utilizing food waste. Therefore, this study investigated the use of biochar prepared by the thermal decomposition of food waste as an additive to AD tanks to increase methane production. The addition of food-waste biochar at 1% of the digestion tank volume increased the production of digestion gas by approximately 10% and methane by 4%. We found that food-waste biochar served as a medium with trace elements that promoted the proliferation of microorganisms and increased the efficiency of AD.

Keywords: anaerobic digestion; biochar; thermal decomposition; methane production; food waste

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1. Introduction

Anaerobic digestion (AD) is one of the best methods to utilize various organic waste materials for energy production [1]. Numerous methods have been applied to the process to increase bioenergy production from biomass waste [2].

The surplus sludge generated by sewage treatment produces biogas through AD. Therefore, energy can be recovered from the sludge, contributing to organic waste management—the production of biogas increases or decreases depending on the management of the AD tank. Accordingly, technologies are being developed to improve energy recovery and increase biogas production [3]. Most previous studies on increasing biogas production have focused on improving the microorganism activity or increasing the number of microorganisms [4].

Various AD studies have been conducted using food waste to produce biogas. When food waste is single-digested by AD, the accumulation of volatile fatty acids (VFAs) and the suppression of ammonia inhibit the digestion tank reactions [5,6]. The AD tank reactions are also inhibited by the salt concentrations of the food waste used in AD [7,8]. In addition, the high biodegradability of food waste inhibits reactions that produce methane [9].

Recent studies have focused on improving the yield of biogas by using various additives such as bio-based carbon materials including biochar, activated sludge, granulated activated carbon, and carbon cloth [2,10]. These additives improve the stability of active sludge in AD and increase biogas production [11,12]. Activated carbon increases sludge reduction and methane production [13], and biochar improves the rate of methane production [14,15].

Among these additives, biochar can negatively affect sludge production because of the composition of biomass in the AD, but positively affects methane production and can be used to recycle organic waste by biochar [16] Biochar, produced through pyrolysis of biomass, is an eco-friendly material with a high carbon content, porous structure, large specific surface area, and good biocompatibility. Biochar was reported to improve the efficiency of methane production by 32%, when added to the AD [17,18]. Wood-biochar or sewage sludge charcoal have been added to improve the methane production efficiency in AD [19,20].

However, in Korea, more than 50% of lignocellulosic waste is processed using paint, oil, and preservatives, and there is a limit in manufacturing biochar. In addition, sewage sludge contains heavy metals; therefore, continuous addition of sewage sludge to AD can lead to the accumulation of heavy metals [21].

To overcome these limitations, there is a need to use biochar using food waste. Because the generation of food waste is increasing, the production and use of biochar from food waste has been examined. The production of food-waste-based biochar has been studied to convert food waste into resources to be used as a soil conditioner or fuel [22,23]. The components of food-waste biochar can increase microorganism activity during the digestion process. Although the application of food-waste biochar in AD using activated sludge has not been evaluated, this method shows potential for utilizing food waste.

Therefore, in this study, we analyzed the physical properties of food-waste-based biochar to determine which trace elements are necessary for AD, and to evaluate whether it is useful as media in Brunauer, Emmett, Teller analysis. In addition, the biochemical methane potential (BMP) test confirmed that the amount of biogas generated was determined by the amount of biochar injected. The methane production potential confirmed the methane gas generation characteristics. We examined the effect of biochar produced by the thermal decomposition of food waste on the improvement of methane yield during AD.

2. Materials and Methods

2.1. Production of Biochar from Food Waste

The biochar used in the experiment was produced using primarily processed (screened, crushed, and dried) food waste at the resource recycling center in City Gimpo, Korea. The raw material contained 70.66% volatile matter, 9.35% ash, 10.74% fixed carbon, and 9.26% moisture.

Food waste usually has a high salt content. The food waste used in this study contained 1.2–1.8 $g \cdot L^{-1}$ salt (average 1.52 $g \cdot L^{-1}$). After thermal decomposition, the resulting biochar contained 0.3–1.0 $g \cdot L^{-1}$ salt (average 0.78 $g \cdot L^{-1}$). According to Gao et al. [24], the change in the digestion efficiency is insignificant when the salt content is below 5 $g \cdot L^{-1}$. Roberts et al. [25] reported that the effect of salt on microorganisms is not significant when the content is below 1 $g \cdot L^{-1}$. The salt tolerance of the microorganisms increased to 10 $g \cdot L^{-1}$ with adaption to salt. The current study did not consider the effect of salt on microorganisms in AD.

The biochar was prepared by slow pyrolysis by carbonizing the raw material at 500 °C for 10 min. The hopper of the pyrolizer was designed to minimize the inflow of external air. Nitrogen was used as a carrier gas to meet anoxic conditions and a "three-screw"-type internal system was created to facilitate heat transfer and mixing.

A proximate analysis was conducted to determine the composition of biochar, X-ray fluorescence spectrometry (XRF) was used to identify trace elements affecting digestion efficiency, and the Brunauer, Emmett, Teller (BET) analysis was used to examine porosity.

2.2. Operating Conditions for the BMP Test

The digestion efficiency was examined based on the volume of biogas produced and the methane content. For this, the BMP test was performed as suggested by Owen [26] and Shelton and Tiedje [27]. The microorganisms applied in the BMP test were seeded using sludge from the digestion tank operated in the field. The surplus and digested sludge used for the test were collected from the sewage treatment plant in City Ilsan, Korea. Table 1 shows the sludge properties.

Table 1. Sludge properties.

	COD (mg/L)	TSS (mg/L)	VSS (mg/L)	NH_4^+-N (mg/L)	VFA (mg/L)	Alkalinity (mg/L as $CaCO_3$)
Excess sludge	15,184	13,380	9170	8.1	22.5	110
Digested sludge	-	17,630	8870	-	198.5	4140

COD: chemical oxygen demand; TSS: total suspended solids; VSS: volatile suspended solids; VFA: volatile fatty acids.

Experiments were performed under six different conditions to examine the volume of gas produced based on the quantity of biochar used (0% control, 0.1%, 0.5%, 1.0%, 3.0%, and 5.0% of the volume ratio (v/v%), respectively). The ratio of conditions to microorganisms was the same in all conditions: 150 mL of surplus sludge and 200 mL of digested sludge (microorganisms). At this time, the organic material load for each case was 4.83 g COD/L, and the VS load was 3.21 g VS/L. To prevent a pH decrease due to acid production during AD, 1.2 g·L^{-1} sodium bicarbonate ($NaHCO_3$) was added. A 500-mL serum bottle was thoroughly purged with nitrogen gas to ensure that no oxygen remained in the headspace of the bottle and the bottle was sealed with a butyl rubber and aluminum cap. A BMP test was performed at 40 °C and 65 rpm until no gas was produced (60 days).

2.3. Analysis of Gas Production and Composition

The volume of digestion gas produced was measured simultaneously every day for the first seven days (24-h intervals), after which the time interval was adjusted according to the gas production rate. The volume of gas generated was measured using a gas syringe with capillary tube (capacity: 100 mL). The methane content was measured by analyzing the concentrations of N_2, CH_4, and CO_2 in the digestion gas. The gas chromatograph used in the gas analysis was a CTGC 1000 (Chemtekins Co. Ltd., Seoul, Korea). The maximum temperature of the oven inside the GC was 280 °C. A thermal conductivity detector with a minimum detection limit of 50 pg was used.

2.4. Analysis of Biochar before and after the Biochemical Methane Potential (BMP) Test

Surface and elemental analyses were performed to predict the change in biochar during the BMP test. A field emission scanning electron microscope (JEOL-7610F-Plus, JEOL Ltd., Tokyo, Japan) was used for surface analysis, and pre-treatment (lyophilization) was conducted before the analysis to consider the microorganisms that could be present in the biochar. Additionally, energy dispersive spectrometry (EDS) was used during the surface analysis to investigate changes in the biochar.

2.5. Analysis of Methane Production Potential

This study analyzed the effect of the addition of biochar on the methane generation potential using experimental data from the cumulative production curves of methane gas. The cumulative production curves obtained from the BMP test were applied to the modified Gompertz model [28], and the best-fit method by trial and error was used to estimate various parameters included in the model equation. Equation (1) is the modified Gompertz model [29].

$$M = P \times \exp\left[-\exp\left(\frac{R_m \times e}{P}(\lambda - t) + 1\right)\right] \tag{1}$$

where: M, cumulative methane production (mL); P, methane production potential (mL); R_m, methane production rate (mL·day^{-1}); e, exp(1); λ, lag growth phase time (days), and t, time (days).

2.6. Statistical Analyses

Experimental data were statistically analyzed using Microsoft Excel (2016). The means and standard deviations of the biogas production and methane content were calculated. The samples were analyzed thrice or more to ensure precision.

3. Results and Discussion

3.1. Biochar Composition

Proximate analysis revealed that the food-waste biochar contained 41.63% fixed carbon, 30.42% volatile matter, 26.82% ash, and 1.12% moisture. It consisted of 42.54% C, 7.28% H, and 3.46% N. Table 2 shows the component analysis results using XRF. Due to the characteristics of food waste, Ca was the highest, at approximately 60%, followed by Cl. Notably, it included trace elements such as Ti, Cu, Cr, and Zn, which are not found in wood-biochar [17].

Table 2. Food-waste-biochar composition.

Element	Ca	Cl	K	Fe	P	S	Sr
Fraction (%)	59.16	17.63	15.39	4.48	1.73	0.83	0.25
Element	Mn	Ti	Br	Cu	Cr	Rb	Zn
Fraction (%)	0.15	0.13	0.08	0.07	0.06	0.02	0.02

The trace elements in the biochar, including Ca, Fe, Cu, and Zn, exhibited the following characteristics with regard to AD microorganisms:

1. Ca is a key component for the growth of some methanogens and is critical for the formation of microbial aggregates [30];
2. Trace elements act as a cofactor for enzymes involved in methane formation [31];
3. Trace elements facilitate methane production [32];
4. Trace elements play an important role in the growth and metabolism of anaerobes [33];
5. Fe, Zn, and Ni are required for hydrogenase [34–37], and Fe is a key component for methane monooxygenase [38,39] and nitrogenase [40].

The BET analysis of the biochar indicated that the surface area was 1.2969 $m^2 \cdot g^{-1}$, the total pore volume was 0.004982 $cm^3 \cdot g^{-1}$, the adsorption average pore width was 153.6522 nm, and the adsorption average pore diameter was 179.996 nm. The graph of nitrogen isothermal adsorption (Figure 1) suggests Type II, according to the IUPAC classification [41]. According to Rouquerol et al. [42], biochar with such characteristics has mesopores, indicating that abundant pores were formed inside the biochar. As Yue [17] reported, the insides of the pores provide a beneficial environment for microbial growth [43,44].

3.2. Results of Digestion Gas Production

3.2.1. Trend in Gas Generation

Figure 2 shows the digestion gas generated with different quantities of biochar. The first two days were the stabilization phase, with little difference in the volume of gas produced in the control and experimental conditions. The 5% biochar condition produced 15 mL less digestion gas than the control condition due to increased trace elements and a high level of biochar, which suppressed microbial activity [45].

All conditions recorded the maximum volume of gas generation on day 4, which gradually decreased thereafter. The maximum volume of gas was higher in the added-biochar conditions than in the control condition. The less the biochar, the greater the maximum volume of gas generated on day 4 (133 mL at 0.1% biochar compared with 114 mL at 5.0%). In terms of the total amount of biogas generated during the period (Figure 3), however, increasing the amount of biochar increased the gas production (control condition: 1049 mL, 0.1%: 1084 mL, 0.5%: 1131 mL, 1.0%: 1155 mL, 3.0%: 1164 mL, and 5.0%: 1253 mL).

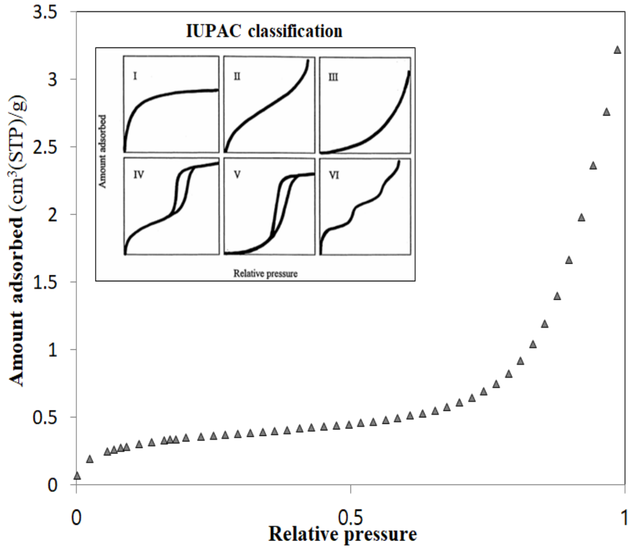

Figure 1. Adsorption-desorption isotherm curves of nitrogen.

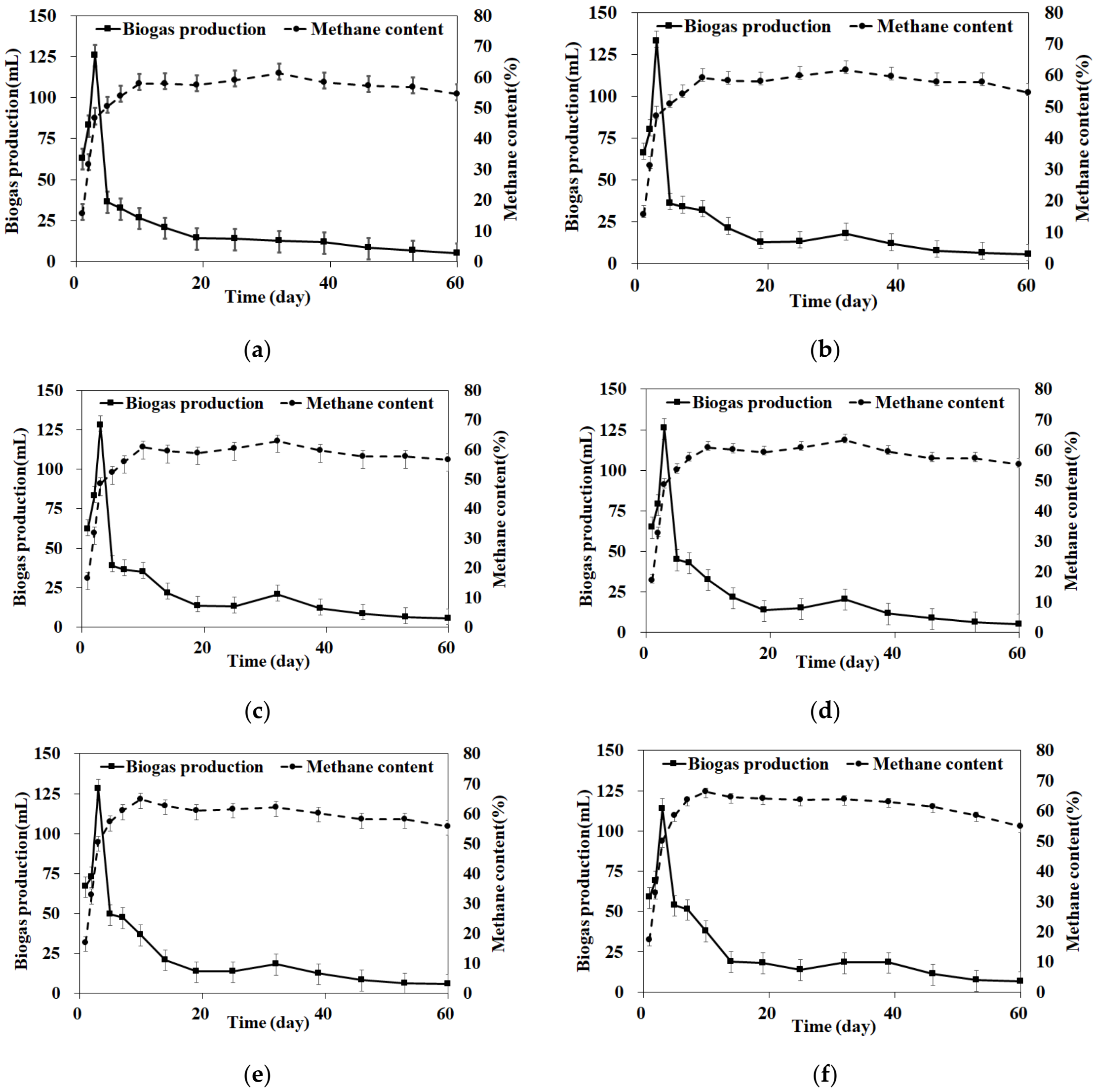

Figure 2. Methane content by condition (biochar content); (**a**) control 0%, (**b**) 0.1%, (**c**) 0.5%, (**d**) 1.0%, (**e**) 3.0%, (**f**) 5.0%.

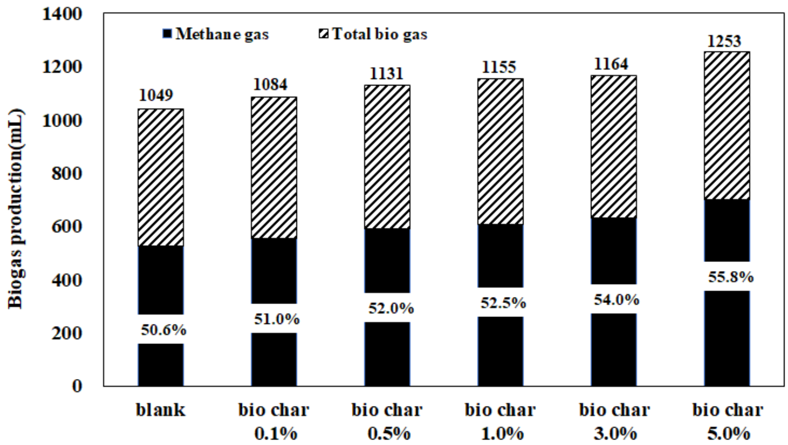

Figure 3. Comparison of total gas generation and methane content with biochar content.

The volume of digestion gas produced was converted into unit volume per initial volatile suspended solids (VSS): 116, 120, 125, 128, 129, and 139 mL $CH_4 \cdot g^{-1}$ $VSS_{in,}$ increasing from the control with increasing quantities of biochar, respectively. The unit amount increased with increasing biochar, with the largest increase at 0.5% biochar.

Similar to gas production, the methane content (Figure 2) was low at 16.5% for the first two days due to the stabilization of the reactor and the generation of N_2 by denitrification. However, from day 3, the methane content was maintained at 50% or higher. The average methane content of the control condition and the 0.1–5.0% biochar conditions (excluding the first two days of the stabilization phase) increased to 55.6%, 56.5%, 57.5%, 57.7%, 59.4%, and 61.1%, respectively (Figure 3).

The maximum daily gas production occurred on the third day with 0.1% biochar, while the methane content was highest at 5.0% on day 10. Zhang et al. [46] reported that the growth and activity of anaerobes could be increased by supplying trace elements. Therefore, it can be inferred that trace substances were eluted from the biochar, leading to the growth of methane-producing microorganisms and the continuous increase in the number of microorganisms.

3.2.2. Changes in Total Suspended Solids and Volatile Suspended Solids

Total suspended solids (TSS) and VSS before and after the BMP test were analyzed to examine sludge reduction in the digestion reaction. TSS and VSS after the BMP test were analyzed including biochar (Figure 4). Both TSS and VSS decreased in biochar in the various conditions up to 0.5% and increased rapidly when 3% biochar was added. The VSS was lower than the initial value of 9020 $mg \cdot L^{-1}$ when less than 3% biochar was added; however, it increased with more than 3% biochar. These results are opposite to the typical AD digestion reaction, in which the decomposition of organic matter increases with gas production, and thus the VSS decreases. Biochar is reported to serve as a medium when it is added to the digestion tank [47], and according to Montalvo [48], the population of microorganisms increases when zeolite, which plays the role of medium, is put into the digestion tank.

3.3. *Changes in Biochar before and after the Biochemical Methane Potential Test*

Figure 5 shows the results of the scanning electron microscopy (SEM) analysis performed to examine the changes in biochar before and after digestion (biochar was added to increase digestion efficiency.) As in the biochemical methane potential analysis, many pores were found in the biochar (Figure 5a,b), which appeared similar to those of the ceramic carrier suggested by Sun et al. [49]. Foreign substances were attached to the pores and surfaces after the digestion reaction (Figure 5c,d). The substances were similar to the images of methane-forming microorganisms reported by Yu et al. [50].

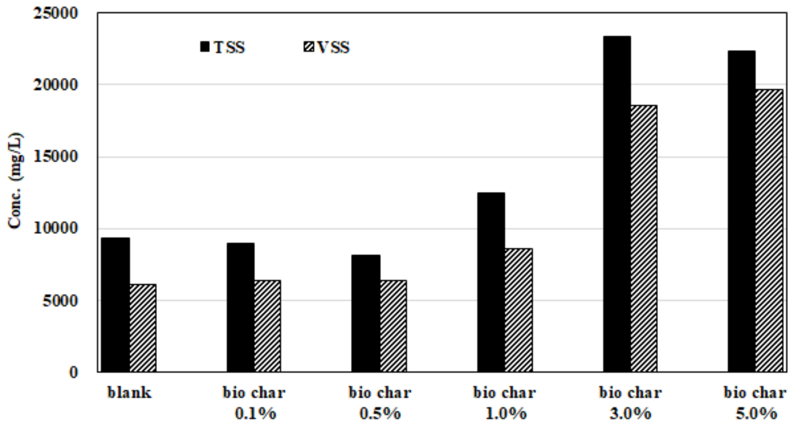

Figure 4. Total suspended solids (TSS) and volatile suspended solids (VSS) before and after the biochemical methane potential test.

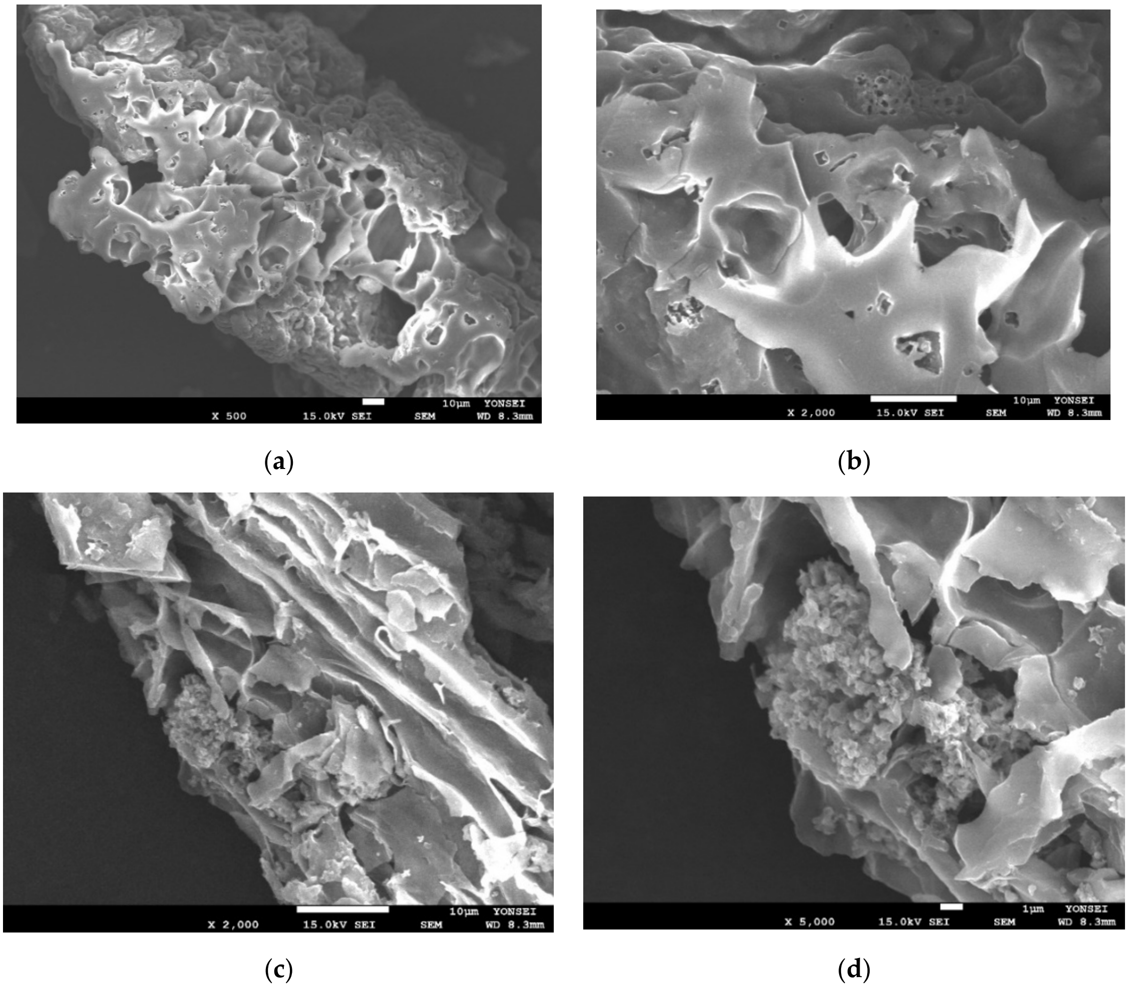

Figure 5. Scanning electron microscopy analysis before and after the biochemical methane potential test (**a**) before, ×500; (**b**) before, ×2000; (**c**) after, ×2000; and (**d**) after, ×5000.

The EDS analysis indicated that O and P content, constituting significant proportions of the microorganisms, increased after the BMP test, leading to a relative reduction in C content (Table 3). Other trace substances, including Na, Mg, Al, and K, were not found after the BMP test.

Table 3. Energy dispersive spectroscopy results before and after the biochemical methane potential test.

Element	C	O	P	Na	Mg	Al	S	Cl	K	Ca
Before	84.98	10.85	-	1.04	0.14	0.08	0.11	1.33	1.10	0.36
After	66.92	31.51	0.48	-	-	-	0.37	-	-	0.71

3.4. Results of Methane Production Potential

Applying the cumulative production curves of methane gas obtained from the BMP test to the modified Gompertz model for optimization showed that R^2 was 0.95 or higher (maximum 0.9673), indicating that the results of the BMP test on methane production with organic waste were correctly simulated (Figure 6). Accordingly, the methane potential (the volume of methane produced) increased as biochar was added (182.8, 191.2, 201.9, 209.1, 222.3, and 228.8 mL $CH_4 \cdot g^{-1}$ VS), and the highest methane production rates were 21.5, 21.8, 22.1, 22.8, 25.0, and 22.5 mL $CH_4 \cdot g^{-1}$ g VS per day. Based on the methane potential and the highest methane production rates, 3% biochar achieved the highest efficiency. The rates increased up to 3% biochar but decreased at 5%, which can be attributed to the decrease in microbial activity due to the increased addition of biochar [44].

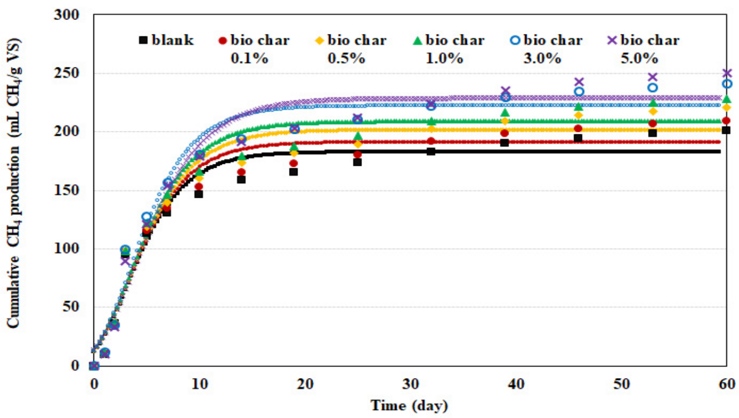

Figure 6. Comparison of the derived modified Gompertz equations using the results obtained in the current study.

Figure 6 describes the fitted results obtained using the modified Gompertz equation. The experimental value matches the model value at 32 days. The dots indicate the experimentally obtained values. The model shows that the maximum gas production volume was achieved near day 17. However, the dots show that gas was continuously generated for more than 60 days, indirectly indicating that methane is produced from the organic material of the biochar.

4. Conclusions

Comparing and examining changes in digestion efficiency by adding food-waste-based biochar to the digestion tank indicated that the efficiency increased in the biochar-added conditions compared with the control condition as follows:

1. Food-waste biochar added at a rate of 1% of the volume of the digestion tank increased the production of digestion gas by approximately 10% and methane by 4%;
2. Increasing the biochar increased the number of microorganisms in the biochar. The 3% biochar condition had a higher VSS after the reaction compared to the initial stage of the reaction;
3. The 3% biochar achieved the maximum methane production rate of 25.0 mL $CH_4 \cdot g^{-1}$ VS per day.

The results confirmed that food-waste-based biochar injected into digestion tanks enhanced digestion efficiency by serving as a medium contributing trace elements and increased the number of microorganisms. Therefore, using food-waste-based biochar to improve AD tank methane-production efficiency could be a practical and effective method for recycling food waste.

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