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Effect of Proximate Composition Ratios for Biogas Production

Min-Jee Kim, Soo-Ah Kim, Sang-Hun Kim*

Division epartment of Horticulture and Biosystems Engineering, College of Agriculture and Life Sciences,
Kangwon National University, Hyoja 2 Dong, 192-1, Chuncheon 24341, Republic of Korea

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Abstract

Purpose: The objective of this study was to evaluate the biogas productivity of agricultural by-products (ABPs) based on their proximate composition. Specifically, the effects of proximate composition were investigated, and a new mixing method was developed using various ABPs that are difficult to digest for biogas production. **Methods:** Experiments were conducted to compare the biogas productivity between a single ABP and a mixture of ABPs that had the same proximate composition as the single ABP. To match the proximate compositions of radish waste and corn distiller's dried grains with solubles (DDGS), mixed ABPs were made from various ABPs. Biogas potential tests (BMP tests) were performed at an organic loading rate (OLR) of 2.5 g VS/L and a feed to microorganism ratio (F/M) of 0.5 under the mesophilic condition. **Results:** The individual ABPs (radish and corn DDGS) and the mixed ABPs (cabbage waste with skim milk waste, bean-curd waste with skim milk waste, and some others) produced similar amounts of biogas. **Conclusions:** The new mixing method based on proximate composition can be applied to other ABPs and organic wastes from factories and municipal waste treatment plants to develop renewable energy and effective waste treatment methods.

Keywords: agricultural by-products, anaerobic digestion, biogas production, BMP test, proximate composition

Introduction

In the past, Korea dumped organic wastes into the ocean and into landfills (Lee et al., 2006); however, as a result of the London Protocol (2012), which banned ocean dumping, there has been a need to develop treatment and disposal technologies for converting organic wastes into stable substances (Kim, 2014). Highly concentrated organic wastes have been treated by physical, chemical, and biological methods (Kim et al., 1995). One of the biological treatment methods, anaerobic treatment, consumes less energy and has lower maintenance costs than aerobic treatment, and it produces methane gas that can be used as a fuel (Choi et al., 2003). Interest in developing alternative energy strategies in combination with waste treatment has increased. Consequently, the demand for research on measurement of methane production, methods for increasing methane production efficiency, and the anaerobic digestion characteristics of various biomass wastes has also increased (Kim et al., 2012).

Biogas production is influenced by the amount of added organic material, the pH of the digester, any toxic substances, and the anaerobic condition C/N ratio. Additionally, biogas production is affected by the proximate composition and characteristics of the initial organic material, which have significant effects on the decomposition efficiency of the anaerobic organic material and methane production (Chynoweth et al., 1993; Walker et al., 2009). Yang et al. (2015) examined the characteristics of protein and carbohydrate, which are important factors in the anaerobic digestion process. They reported that the degradation rate of carbohydrate (0.007/day) was faster than the rate of protein (0.0197–0.0018/day) after analyzing

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***Corresponding author:** Sang-Hun Kim
Tel: +82-33-250-6492; **Fax:** +82-33-255-6406
E-mail: shkim@kangwon.ac.kr

the degradation rate constants of a first-order kinetic model.

The chemical oxygen demand (COD), biological oxygen demand (BOD), and variance of volatile solids (VS) have been used to quantify initial organic materials. However, more accurate methods of quantifying the characteristics of the organic materials are needed to examine the optimum conditions for microbial growth and modeling the processing efficiency (Jimenez et al., 2013). Kafle and Kim (2013) evaluated the anaerobic process by classifying agricultural by-products (ABPs) based on their proximate composition (PC), and they applied the results to silage production. Proximate composition includes the six components of moisture, crude ash, crude protein, ether extract, crude fiber, and nitrogen-free extracts, and it describes the nutrient constituents of the living body and the contents of animal feed and silage. This study used proximate composition in the classification of the processing of organic wastes with biological treatments.

Thus, the objective of this study was to examine the method of converting the proximate composition of ABPs that are difficult to digest in anaerobic digestion into a composition that is easy to digest. This study created the same proximate composition as an ABP that is easy to digest by mixing ABPs with and examined the characteristics of the anaerobic digestion.

Materials and Methods

Experimental materials

Swine manure collected from Gwangil farm, Ansong, Republic of Korea, was processed by anaerobic treatment in a continuous digester at medium temperature (36.5°C), and the effluent was used as an inoculum. The ABPs were purchased at a market, and cheese whey was collected from the Green Dairy Division at Sunchon National University and refrigerated at 4°C. The pH of the inoculum was 8.71–8.54, and the volatile solid to total solid (VS/TS) ratio of the ABPs was 0.856–0.927 (Table 1). Each experiment was repeated three times, and the mean value was used for the study.

Batch digester start-up and experimental design

A batch digester was used to analyze the amount and components of the biogas production (Fig. 1). A 1.3 L vial was used in the study, but the actual volume used in the experiments was 0.8 L. The feed to microorganism ratio (F/M) was maintained at 0.5 for all experiments, and sludge and organic materials were input into the digester after determining their amounts. Distilled water was then added to match the actual volume. Nitrogen was injected to maintain the anaerobic conditions, and the digester was sealed with a silicone rubber stopper. The experiments were conducted in an incubator to keep the batch digester at a medium temperature of 36.5°C, and the digester was stirred for two minutes before measurement of biogas production per day for accurate measurement.

Table 2 shows the experimental design of this study. This study created the same proximate composition of the desirable ABP by mixing other ABPs and compared

Table 1. Characteristics of inoculum and agricultural by-products (ABPs)

	TS[a] (%)	VS[b] (%)	VS/TS	pH
Inoculum 1	1.95 (0.03)	0.86 (0.02)	0.439	8.71
Inoculum 2	1.71 (0.02)	0.76 (0.02)	0.442	8.54
Skim milk waste (SMW)	8.69 (0.07)	7.90 (0.07)	0.909	6.31
Corn DDGS (DDGS)	84.57 (0.19)	72.81 (0.86)	0.861	-
Cabbage waste (CW1)	10.33 (0.44)	9.10 (0.37)	0.881	6.18
Carrot waste (CW2)	10.29 (0.10)	8.97 (0.09)	0.872	6.19
Radish waste (RW)	5.76 (0.15)	5.19 (0.16)	0.901	6.11
Perilla seed waste (PSW)	97.24 (0.08)	87.62 (1.96)	0.901	6.65
Bean-curd waste (BCW)	16.91 (0.01)	15.80 (0.04)	0.934	6.29
Molasses waste (MW)	69.33 (0.25)	59.35 (0.24)	0.856	5.25
Cheese whey (CW3)	7.09 (0.09)	6.58 (1.59)	0.927	4.50

[a]TS: Total Solid; [b]VS: Volatile Solid; Values in parentheses are standard deviation

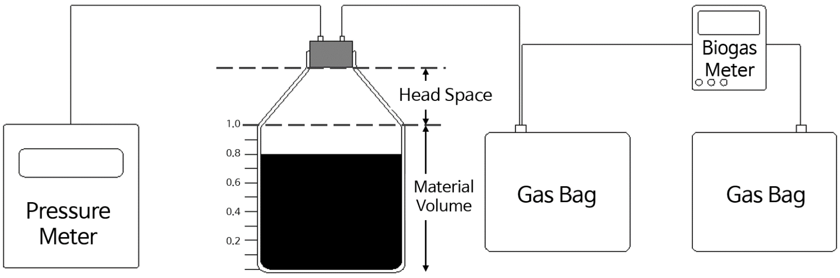

Figure 1. Batch test set up (Kim and Kim, 2015).

Table 2. Performance of anaerobic digestion by proximate composition (Kim and Kim, 2015)

Feedstock	F/M	Volume (L)	TC (%)	CP (%)	EE (%)	Mixing ratio (%, VS basis)
RW	0.5	0.8	57.04	21.17	1.18	100
MW:SMW	0.5	0.8	62.13	22.08	2.07	11.8:88.2
CW1:SMW	0.5	0.8	62.21	23.91	1.62	46.5:53.45
CW2:SMW:CW3	0.5	0.8	56.50	25.21	2.77	87.5:11.7:0.8
PSW:MW:SMW	0.5	0.8	63.57	23.05	2.89	23.6:59.1:17.3
DDGS	0.5	0.8	44.13	34.53	5.95	100
BCW:RW	0.5	0.8	45.98	30.01	7.41	9.9:90.1
BMW:SMW	0.5	0.8	48.21	38.83	5.33	38.8:48.2

the amount of biogas between the mixed ABPs and the individual ABP. The ABPs were determined based on the previous study of Kim and Kim (2015), and the contents of total carbohydrate (TC), crude protein (CP), and fat (ether extract, EE) of the mixtures were fixed to the desired content levels by adjusting the mixing ratio of the individual ABPs (Standard Table of Feed Composition in Korea, 2012). Molasses and skim milk were mixed with a ratio of 11.8:88.2, based on VS, to match the level of radish waste. Cabbage waste was also mixed with skim milk, and carrot waste was mixed with skim milk and cheese whey. Perilla seed waste was mixed with molasses and skim milk. Carbohydrate, protein, and fat showed an error range of 1–5%. Additionally, bean-curd waste and radish waste were mixed with a ratio of 9.9:90.1, and bean-curd waste and skim milk were mixed with a ratio of 38.8:48.2, based on VS, to match the levels of corn distiller's dried grains with solubles (DDGS). The carbohydrate, protein, and fat showed an error range of 1–5% (Table 2).

Biogas measurement and analytical methods

This study measured methane emissions during the anaerobic incubation period, and the temperature inside the digester and headspace pressure were calibrated using equation (1) to obtain the cumulative methane production curve. A WAL-BMP-Test system (Type 3150, Wal, Germany) was used to measure the gas production in the digester (Kafle and Kim, 2012; Kafle and Kim, 2013). A biogas analyzer (Biogas5000, Geotech, England) was used to measure methane (CH_4), carbon dioxide (CO_2), oxygen (O_2), and hydrogen sulfide (H_2S), and a gas chromatograph (GC-2014, Shimadzu, Japan) was used for periodical calibration. Standard methods (APHA, 1998) were used to measure the TS and VS, and Official Methods of Analysis (AOAC) methods (1990) were used for the analysis of crude fiber (CF), ether extract (EE), and crude protein (CP). Statistical analysis was conducted using SPSS software (IBM SPSS statistics 21, NY, USA). A p-value of less than 0.05 was considered significant.

$$V_B = \frac{(P_f - P_i) \times V_H \times C}{R \times T} \tag{1}$$

In equation (1), V_B = biogas volume (L); P_i = initial pressure in the reactor head space (mbar); P_f = final pressure in the reactor head space after 24 h (mbar); V_H = volume of the head space (L); C = molar volume (22.41 L/mol); and R = the universal gas constant (83.14 L mbar/K/mol).

Results and Discussion

Comparison of radish waste and mixed ABPs

Figure 2 shows the cumulative biogas and methane yields of the mixtures of molasses waste (MW), skim milk waste (SMW), cabbage waste (CW1), carrot waste (CW2), cheese whey (CW3), and perilla seed waste (PSW), which were mixed to match the contents of carbohydrate, protein, and fat in radish waste (RW). The cumulative biogas yield of the radish waste was 457 mL/gVS. The mixtures of molasses waste and skim milk waste (MW+SMW), cabbage waste and skim milk waste (CW+SMW), carrot waste, skim milk waste, and cheese whey (CW2+SMW+CW3), and perilla seed waste, molasses waste, and skim milk waste (PCW+MW+SMW) produced biogas yields of 441, 433, 431, and 438 mL/gVS, respectively. The methane yields were in the range of 60.7–62.0%. The results of an analysis of the biogas yield differences between the single ABP and the mixed ABPs through independent-sample t-tests showed that the p-value did not represent a significant difference by 0.303, 0.224, 0.078, and 0.101 ($p > 0.05$). The null hypothesis that biogas production is not different between the single ABP and the mixed ABPs was formulated. Similarly, Adeyosoye et al. (2012) examined the biogas production from two individual ABPs, sweet potato and wild cocoyam, which have similar proximate compositions, and there was no significant difference ($p > 0.05$) in the volumes of methane produced.

The T90 of the radish waste was 28 days, and the T90 of the ABPs was 27–28 days (Table 3). Table 4 shows the initial and final results of the chemical analysis of the radish waste and the mixed ABPs measured in the digester. The pH range was 7.18–7.75, which is proper for methane production. Raposo et al. (2009) reported that the digester was stable at volatile fatty acid (VFA) to alkalinity ratios of 0.30–0.40 or less and unstable at ratios of more than 0.70. The VFA to alkalinity ratios of this study were in the range of 0.273–0.320, indicating digester stability. The TS and VS of the mixed ABPs were almost the same as those of RW. The NH_3-N values of this study were 2,307–3,487 mg/L, which is within stable conditions (Lettinga et al., 1979). The TCOD removal rate was as high as 51.2% with the mixed ABPs.

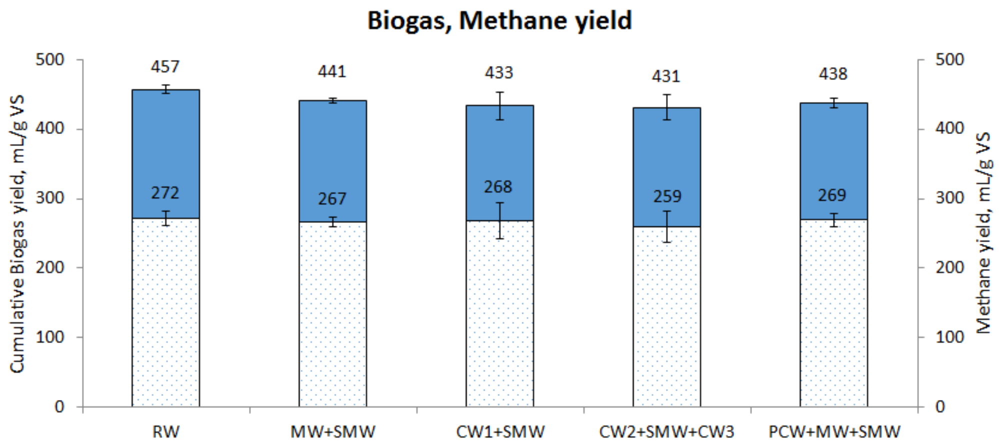

Figure 2. Cumulative biogas and methane yields of the RW and mixed ABPs.

Table 3. Biogas yields, methane contents, and T90 of the RW and mixed ABPs

Parameter	Unit	RW	MW+SMW	CW1+SMW	CW2+SMW+CW3	PCW+MW+SMW
F/M		0.5	0.5	0.5	0.5	0.5
Cumulative biogas yield	mL/gVS	457 (6.21)	441 (2.99)	433 (19.88)	431 (17.81)	438 (6.23)
P-value		-	0.303[a]	0.224[a]	0.078[a]	0.101[a]
Methane content	%	59.5	60.7	61.8	62.0	61.5
Methane yield	mL/gVS	272 (10.19)	267 (6.75)	268 (25.60)	259 (22.49)	269 (9.88)
T90	day	28	28	27	28	27

[a)] $P < 0.05$; Values in parentheses are standard deviation

Table 4. Initial and final characteristics of the digester contents (RW and mixed ABPs)

Parameter	Unit		RW	MW+ SMW	CW1+ SMW	CW2+SMW+CW3	PCW+MW+SMW
pH		Initial	8.25 (0.04)	8.29 (0.04)	8.25 (0.03)	8.32 (0.02)	8.27 (0.04)
		Final	7.75 (0.04)	7.74 (0.03)	7.17 (0.03)	7.18 (0.02)	7.19 (0.03)
VFA	mg/L	Initial	2,324 (299)	2,461 (165)	2,278 (292)	2,424 (202)	2,679 (72)
		Final	2,668 (75)	2,745 (32)	2,919 (90)	2,872 (188)	2,741 (200)
Alk	mg/L	Initial	9,018 (714)	8,371 (314)	8,242 (308)	9,833 (466)	8,112 (258)
		Final	10,032 (1089)	9,060 (260)	9,097 (249)	8,997 (432)	9,038 (347)
VFA/Alk		Initial	0.271 (0.04)	0.294 (0.03)	0.296 (0.01)	0.251 (0.03)	0.331 (0.01)
		Final	0.273 (0.03)	0.303 (0.01)	0.320 (0.01)	0.320 (0.04)	0.303 (0.03)
TS	%	Initial	1.39 (0.05)	1.39 (0.05)	1.28 (0.06)	1.30 (0.10)	1.39 (0.04)
		Final	1.19 (0.09)	1.19 (0.01)	1.15 (0.01)	1.20 (0.04)	1.03 (0.14)
VS	%	Initial	0.73 (0.03)	0.71 (0.02)	0.63 (0.04)	0.66 (0.08)	0.71 (0.03)
		Final	0.50 (0.05)	0.50 (0.01)	0.49 (0.01)	0.51 (0.03)	0.49 (0.01)
TCOD	mg/L	Initial	11,804 (1995)	24,604 (4157)	15,431 (5941)	10,311 (3618)	13,404 (2047)
		Final	8,120 (2494)	19,057 (7576)	8,720 (2248)	8,366 (1524)	6,542 (2178)
NH_3-N	mg/L	Initial	2,900 (340)	2,933 (244)	2,987 (302)	2,120 (12)	2,113 (29)
		Final	2,307 (272)	2,347 (566)	3,487 (1449)	2,593 (519)	2,867 (122)
TCOD removal	%		31.2	22.5	43.5	18.9	51.2

[a)]P Values in parentheses are standard deviation

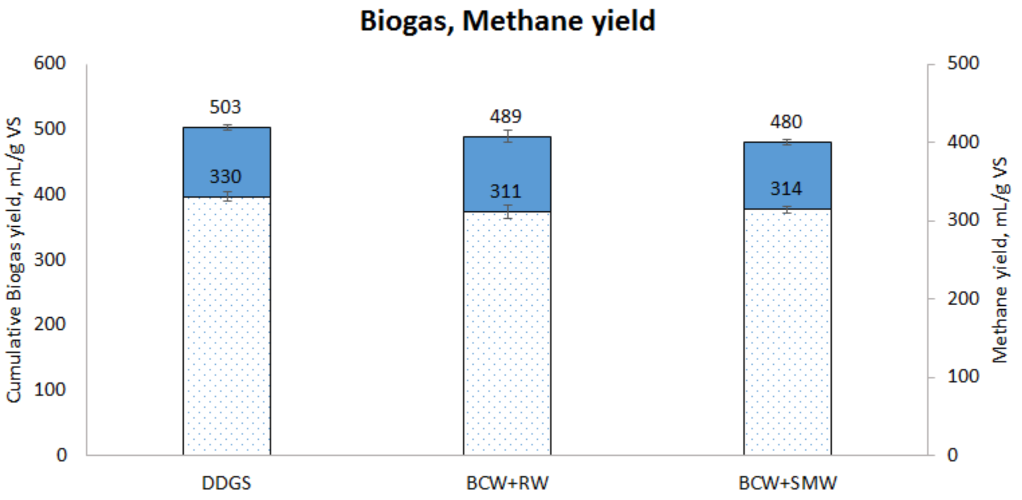

Figure 3. Cumulative biogas and methane yields of the DDGS and mixed ABPs.

Comparison of corn DDGS and mixed ABPs

Figure 3 shows cumulative biogas and methane yields of the mixtures of bean-curd waste and radish waste (BCW+RW) and bean-curd waste and skim milk (BCW+SMW), which were mixed to match the contents of carbohydrate, protein, and fat in corn DDGS. The cumulative biogas yields of corn DDGS and the mixtures of BCW+RW and BCW+SMW were in the range of 503–480 mL/gVS, and the methane yields were in the range of 63.5–65.7%. The results of the analysis of the biogas yield differences between the single ABP and the mixed ABPs through independent-sample t-tests showed that the p-value did not represent a significant difference by 0.218 and 0.072 ($p > 0.05$). Thus, the null hypothesis that biogas production is not different between the single ABP and the mixed ABPs was formulated. The T90 of the corn DDGS was 32 days, which was longer than that of the mixed ABPs (28 days), as shown in Table 5. Generally, the hydraulic retention time for mesophilic and thermophilic digestion is considered as 25 to 35 days (Yoon, 2003), and the test

Table 5. Biogas yields, methane contents, and T90 of the DDGS and mixed ABPs

Parameter	Unit	DDGS	BCW+RW	BCW+SMW
OLR	gVS/L/d	2.5	2.5	2.5
F/M		0.5	0.5	0.5
Cumulative biogas yield	mL/gVS	503 (3.83)	489 (8.63)	480 (4.45)
P-value		-	0.218[a]	0.072[a]
Methane content	%	65.7	63.5	65.5
Methane yield	mL/gVS	330 (5.96)	311 (9.02)	314 (4.59)
T90	days	32	28	28

[a] $P < 0.05$; Values in parentheses are standard deviation

Table 6. Initial and final characteristics of the digester contents (DDGS and mixed ABPs)

Parameter	Unit		DDGS	BCW+RW	BCW+SMW
pH		Initial	8.27 (0.03)	8.27 (0.01)	8.37 (0.05)
		Final	7.76 (0.04)	7.76 (0.03)	7.81 (0.04)
VFA	mg/L	Initial	2470 (256)	2772 (478)	2241 (157)
		Final	2690 (237)	2548 (87)	2968 (35)
Alk	mg/L	Initial	8305 (161)	8531 (177)	8530 (201)
		Final	9001 (297)	8807 (310)	8850 (280)
VFA/Alk		Initial	0.299 (0.04)	0.288 (0.02)	0.264 (0.02)
		Final	0.283 (0.01)	0.293 (0.02)	0.337 (0.01)
TS	%	Initial	1.47 (0.07)	1.45 (0.07)	1.42 (0.01)
		Final	1.21 (0.06)	1.39 (0.15)	1.20 (0.04)
VS	%	Initial	0.72 (0.04)	0.76(0.05)	0.74 (0.003)
		Final	0.54 (0.01)	0.53 (0.03)	0.52 (0.02)
TCOD	mg/L	Initial	14578 (3407)	16320 (3737)	22151 (6756)
		Final	10369 (2052)	8561 (2980)	6506 (1727)
NH_3-N	mg/L	Initial	3247 (29)	2427 (127)	2240 (87)
		Final	2347 (475)	2387 (512)	2447 (432)
TCOD removal	%		28.9	47.5	70.6

[a] Values in parentheses are standard deviation

results were in the range of efficient biogas production. Table 6 shows the initial and final results of the chemical analysis of corn DDGS and the mixed ABPs measured in the digester. The pH range was 7.76–7.81, which was higher than the proper pH range for methane production. The VFA to alkalinity ratios were 0.283, 0.293, and 0.337, respectively, which indicate digester stability. The TS and VS of the mixed ABPs did not show a significant difference compared with the single ABP, DDGS. The NH_3-N values of this study were 2,347–2,447 mg/L, within stable conditions. The TCOD removal rate increased to 70.6% with the mixture of SMW.

Conclusions

It is necessary to digest various agricultural by-products that have been considered non-digestible organic wastes because of their difficulty of digestion. This study examined the method of converting the proximate composition of ABPs that are difficult to digest by anaerobic digestion into an a proximate composition that is more easily digested. This study created the same proximate composition as the individual ABPs that are easily digestible by mixing other ABPs that are not and examined the characteristics of their anaerobic digestion. The results of the biogas and methane yields from the mixtures of the ABPs that had the same content ratios as the proximate compositions (carbohydrate, protein, and fat) of radish waste and corn DDGS showed differences between the mixed and single ABPs that were within the range of 3.5–5.6%. The biogas yield differences between the single ABPs and the mixed ABPs showed no statistically significant differences. Therefore, biogas production can be improved by mixing ABPs that have a low biogas production rate to achieve the same proximate composition as an ABP that has a high biogas production rate.

Conflict of Interest

The authors have no conflicting financial or other interests.

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