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Original paper

Predicting Methane Production on Anaerobic Digestion to Crop Residues and Biomass Loading Rates

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혐기 소화 시 식물체 잔사 및 투입량에 따른 메탄 생산량 예측

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ABSTRACT: Objective of this experiment was to predict the potential methane production with crop residues at different loading rates. Anaerobic digestion of barley and rapeseed straw substrates for biogas production was performed in Duran bottles at various biomass loading rates with crop residues. Through kinetic model of surface methodology, the methane production was fitted to a Gompertz equation. For the biogas production at mesophilic digestion with crop residues, it was observed that maximum yield was 37.2 and 28.0 mL/g at 6.8 and 7.5 days after digestion with 1% biomass loading rates of barley and rapeseed straws, respectively. For the methane content of mesophilic digestion, there were highest at 61.7% after 5.5 days and 75.0% after 3.4 days of digestion with barley and rapeseed straw on both 5% biomass loading rates, respectively. The maximum methane production potentials were 159.59 mL/g for 1% barley straw and 156.62 mL/g for 3% rapeseed straw at mesophilic digestion. Overall, it would be strongly recommended that biomass loading rate was an optimum rate at mesophilic digestion for using 1% barley and 3% rapeseed straws for feed stocks.

Keywords: Anaerobic digestion, Cumulative methane yield, Gompertz equation, Barley straw, rapeseed straw, Methane production

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초 록: 본 연구의 목적은 농업에서 발생하는 식물체 잔사 종류별 투입비율에 따른 메탄 잠재 발생량을 예측하는 것이다. 바이오가스를 생산하기 위하여 보릿짚 및 유채대 등의 식물체 잔사를 다양한 투입율로 사용하여 세름병에서 실험을 수행하였다. 표면 방법론의 운동방법을 통하여 메탄 생산은 Gomperz 수식에 적합한 것으

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로 나타났다. 중온소화 시 식물체 잔사별 바이오가스 생산에 있어, 최대생산량은 보릿짚 및 유채대 투입율 1%로 혐기소화 후 각각 6.8일에 37.2 mL/g과 7.5일에 28.0 mL/g로 나타났다. 중온소화 시 메탄 함량은 보릿짚 및 유채대 투입율 5%로 혐기소화 후 각각 5.5일에 61.7%와 3.4일에 75.0%로 가장 높게 관측되었다. 중온 소화 시 최대 메탄 잠재발생량은 1% 보릿짚 투입율에서 159.59 mL/g 와 3% 유채대 투입율에서 156.62 mL/g로 산정되었다. 전반적으로 중온소화 시 바이오매스 투입율은 유채대 3% 및 보릿짚 1%를 투입하는 것이 적정 비율인 것으로 나타났다.

주제어: 혐기소화, 누적 메탄 생산량, Gomperz 수식, 보릿짚, 유채대, 메탄 생산

1. Introduction

Due to the limited resources and ever-increasing greenhouse gas emission, fossil fuels should be substituted for renewable bio-energy (United Nation of Framework Convention a Climate Change; UNFCCC). According to the United Nations by 2050 up to 77% of the world's energy demand could be supplied by renewable[1]. However, as biomass is gaining more and more economic interest further expansion of biogas production increasingly depends on exploitation of new sources of biomass.

Biomass is carbon rich materials including all plants, animals, nutrients, excrements and bio-waste from household and industry[2].Unused or discarded biomass residues from agriculture have a potential energy resource, but those materials can be a source of GHG emission causing a significant environmental problem. Potential energy production from crop and animal residues is globally estimated about 34 EJ out of total 70 EJ[3]. Biomass is a renewable energy resources derived from all the organic materials produced by human and natural activities. It is a complex mixture of organic materials such as carbohydrates, fats and proteins. The carbohydrates are mainly consisted of cellulose, which provides strength property to the plant structure, and hemi-cellulose, which contributes to strengthening the cell wall by interaction with cellulose and lignin. Lignin is an aromatic compound which fills spaces among cell wall fibers. The plant residues are regarded as a good biomass resources because they contain 40~50% cellulose ($[C_6(H_2O)_5]_n$), 20~35% hemi-cellulose ($[C_5(H_2O)_4]_n$), and 15~30% lignin ($[C_{10}H_{12}O_3]_n$). Therefore, biomasses as plant residues of rapeseed, rice, barley and wheat could be good raw materials for alternative fuel resources. In Korea, grand total of generated waste from livestock, agro-industrial waste and crop residues was 58,010 Gg/yr in Korea. Calculated total methane production of representative categories for livestock, crop residues and agro-industrial wastes was 435.5 Gg/yr in Korea[4]. The interest of biomass in resource-poor country like Korea is therefore apparently increasing.

Anaerobic digestion (AD) is a biological process that converted the solid or liquid biomass into a gas in the absence of oxygen. Many studies on anaerobic digestion in Korea have focused on the pig manure and food wastes as substrates[5,6]. Anaerobic digestion has many environmental benefits including the production of a renewable energy carrier, the possibility of nutrient recycling and reduction of waste volumes[7,8,9]. Different types of organic wastes have been anaerobic digested in a successful way, such as sewage sludge, industrial waste, slaughterhouse waste, fruit and vegetable waste, manure and agricultural biomass. The wastes have been treated separately and in co-digestion processes[2),3),10)].

Anaerobic digestion for methane production using crop residues in agricultural sector is becoming necessary for having the limited natural resources like Korea. Methane produced by the digester can be used as energy source for electricity and heat generation for agricultural practices, which can reduce the treatment cost and methane emission into atmosphere. For effects of digestion temperatures and loading amounts on methane production from anaerobic digestion with crop residues as rice and wheat straws, the results strongly indicate that a 1% biomass loading rate for both crops and temperatures could be used as the optimum loading amount and feeding stocks[11)].

The objective of the current study was to predict the potential methane production with crop residues at different loading rates.

2. Materials and Methods

2.1. Seeding sludge

Seeding sludge was taken from an anaerobic digester in a local waste water treatment plant. Once collected, the seeding sludge was stored in a refrigerator at 4℃ for one week before analyzing its volatile solids (VS) contents. Then it was pre-heated to 35℃ for 24 hours and inoculated with substrates. The VS concentration of seed microorganism was 0.05%.

2.2. Substrate

Barley and rapeseed straws were used as substrates in this study. The straws from experimental field of National Institute of Agricultural Science were collected and grinded by an electrical blender, and passed through 2mm sieve. The substrates were loaded into each Duran bottle (250 mL). The loading rates of the biomass were adjusted with 200 mL of seed of microorganism at 1, 3 and 5% based on dry weight (v/w), respectively. Physicochemical parameters as pH, TSS, VSS, T-N and T-P were determined according to Standard Methods[12)]. The physicochemical characteristics of substrate are presented in [Table 1].

2.3. Digestion procedure

The experiment was conducted with 200 mL of working volumes by using 250 mL of Duran bottles by 3 replications of randomized factorial design. Main plots were 1, 3 and 5% loading rates of crop residues based on dry weight. Sub-plots were different crop residues as barley and rapeseed straws. Each bottle was added an appropriate amount of each loading rates calculated, and massed up 200 mL of seeding

Table 1. Physicochemical Characteristics of Seed of Microorganism and Substrates used in this Study

Parameters	Seed of microorganism	Barley straw	Rapeseed straw
pH	8.00	-	-
EC[1)] (mS/cm)	11.53	-	-
SS[2)] (%)	0.59	1, 3, 5	1, 3, 5
VS[3)] (%)	0.05	-	-
T-C[4)] (%)	-	42.14	41.67
T-N[5)] (%)	0.75	0.29	0.49
T-P[6)] (mg/L)	176.58	-	-

[1)] EC; Electrical conductivity, [2)] SS; Suspended solids, [3)] VS; Volatile solids,
[4)] T-C; Total carbon, [5)] T-N; Total nitrogen, [6)] T-P; Total phosphate

sludge. Subsequently, the headspace of each bottle was flushed with N_2 gas for 2 min, degassed after 3 hour with a glass syringe, and sealed tight with a clamp. The bottles were then placed in a shaker at 40 rpm at 35℃ of incubation temperatures.

2.4. Biogas analysis

The amount of biogas production was measured by using 20~200 mL of a glass syringe[13]. At the same time, methane concentration of the produced gases was periodically determined. Methane content in the biogas was measured by a gas chromatography (GC: Varian CP-3800) with a thermal conductivity detector and a 1.0 m × 2 mm stainless steal packed column with N_2 gas as a carrier. The temperatures of detector and column were kept at 189 and 40℃, respectively.

2.5. Kinetic Model

In many biological fields, the basic knowledge of phenomena is insufficient to build a mechanistic model. In this case, responding to surface methodology, an empirical model or a statistical analysis can be formulated to elucidate basic mechanisms underlying a complex system and thus providing better guidance in process design and control[14]. In this study, the effect of loading rates and crop residues to methane production in the anaerobic digester was analyzed using a Gompertz model[15] as shown below.

$$M_p = P_m \exp\left[-\exp\left\{\frac{R_m}{P_m}(x_0 - x)e + 1\right\}\right] \qquad (1)$$

Where M_p was cumulative methane production (mL), P_m was ultimate methane production (mL), R_m was methane production rate (mL/day), x_0 was lag-phase time (days), and e was exponential 1.

All the parameters in the above equation were evaluated by performing regression with a Newtonian algorithm to minimize the sum of the square errors (SSE) between the experiment and estimation using Sigma plot version 12.0. The goodness of the parameter fit was diagnosed by SSE, correlation coefficient (r^2), standard errors (SE), 95% of confidence limits, T-test, and F-test.

3. Results and Discussions

3.1. Biogas production

The estimation of the potential biogas production and its methane contents are one of most important aspects in the design of anaerobic digester. Biogas production rates in mesophilic stage during the digestion of crop residues are shown in [Fig. 1].

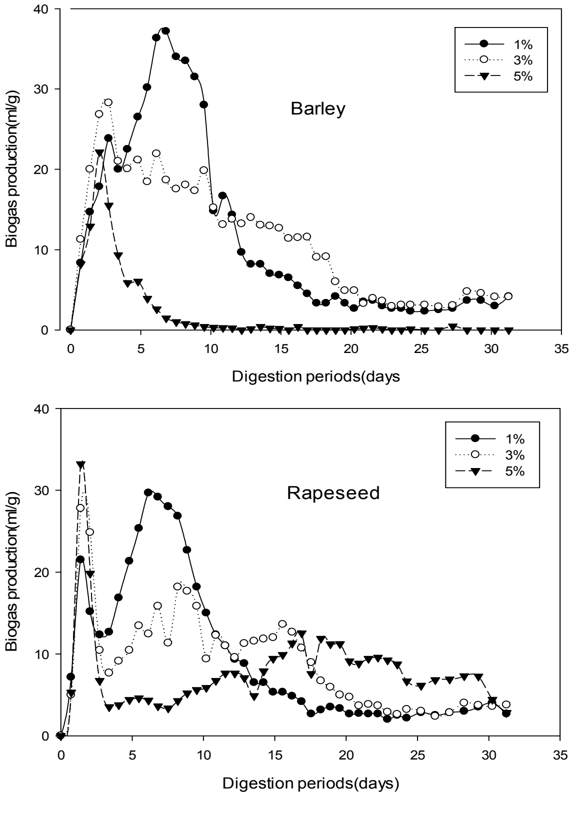

Fig. 1. Effects of biomass loading rates on biogas production over digestion periods.

For the biogas production at mesophilic digestion with crop residues, it was observed that maximum yield was 37.2 and 28.0 mL/g at 6.8 and 7.5 days after digestion with 1% biomass loading rates of barley and rapeseed straws, respectively. Untreated wheat16) and rice straw17) substrates had resulted into biogas production yields of 18.8 and 14.0 mL/g VS, respectively, with 4.4% VS of substrate concentration at 37℃. This biogas production yield was lower at over 2 folds than those of our research's result even if our unit was based on dry weight. Chandra *et al.*(2012)16) indicated that the maximum biogas production yield occurred up to only initial 20 day of retention time for barley straw substrate. However, this retention time was shorten at about three folders as compared with our result. It might be due to over loading rate for anaerobic digestion. It was appeared that its barley straw substrate was higher at 1.3 folders than that of rapeseed straw substrate because of different compositions of raw materials (especially for total nitrogen content) in the residues ([Table 1]).

For the methane content at mesophilic stage, there were highest at 52.1, 53.7 and 61.7% after 23.6, 22.9 and 5.5 days of digestion with barley straw, but were highest at 50.1, 55.1 and 75.0% after 23.6, 22.2 and 3.4 days of digestion periods with rapeseed straw at 1, 3 and 5% biomass loading, respectively ([Fig. 2]). The highest methane contents were observed for short periods from 4 to 8 days after anaerobic digestion with 5% biomass loading rate of barley straw, but in 1 and 3% biomass loading rates it was observed at 23 days after digestion. However, the trends of methane contents with rapeseed straw were not consistent with digestion periods. These values of methane contents with wheat straw substrate were similar to those observed between 50.1 and 75.0%18). It was appeared that methane contents in the biogas were similar patterns 1 and 3% biomass loading rates with barley straw, but decreased with lower biomass loading rates with rapeseed straw.

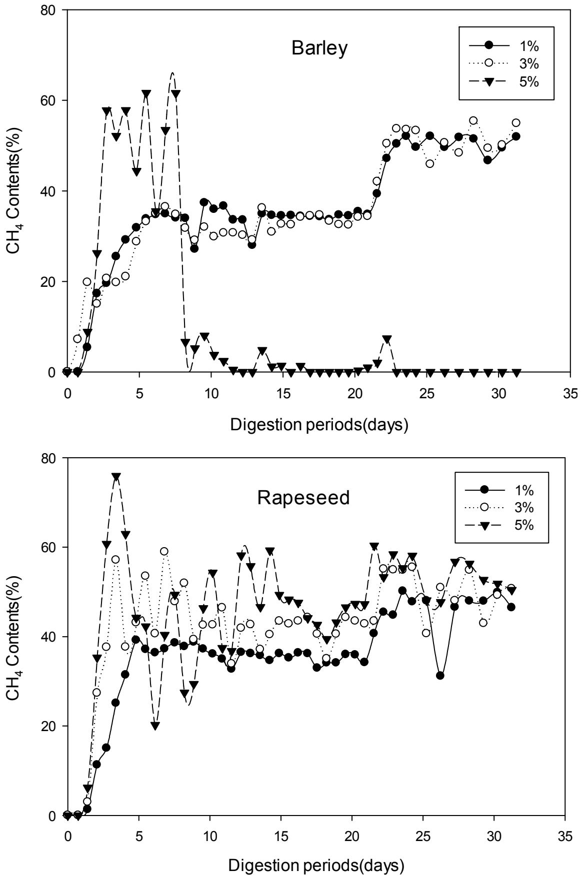

Fig. 2. Effects of biomass loading rates on CH_4 contents in the produced biogas over digestion periods.

Li *et al.*(2010)19) indicated that the maximum methane content of 63.4 and 59.4% were obtained for mesophilic and thermophilic anaerobic digestion. These methane contents were low with 11.6% for mesophilic digestion when compared with our research results. These might be attributed to different loading rates.

3.2. Estimation of Methane Production Potential using the Logistic Regression Model

The regression model provided in Eq.(1) was applied to fit the methane production profiles and the goodness of each fit was determined using the model p value.

The cumulative methane production curves from the 2 crop residues and 3 loading rates were well described with Eq.(1). All the model p values were less than 0.0001 in [Table 2], suggesting that the regression model is statistically significant. Although the hydrogen production curve was fitted to a modified Gompertz equation[15], which was used as a suitable model for describing the hydrogen production in a batch system[20),21)].

It was observed that Gompertz model was also proper to predict the methane production with crop residues. [Fig. 3] illustrates that the methane production potential was varied from 29.24 to 215.52 mL/g at mesophilic digestion with different loading rates, but these values were lower than the reported maximum values, 268, 229 and 213 mL/g VS fed, from co-digestion with cow manure and crop residues such as grass, sugar beet top and straw, respectively[22]. Also these values can be compared with maintain yields of 160~260 mL/g VS for batch degradation of wheat straw presented in a review by Gunaseelan[23], depending on experimental conditions and particle size. It was observed that the maximum methane production potentials were 159.59 mL/g for 1% barley straw and 156.62 mL/g for 3% rapeseed straw at mesophilic digestion ([Table 2]). The ultimate methane production from the reactor with only barley straw substrate was lower than that of rapeseed straw substrate, but loading rates in both crop residues did not have consistent pattern.

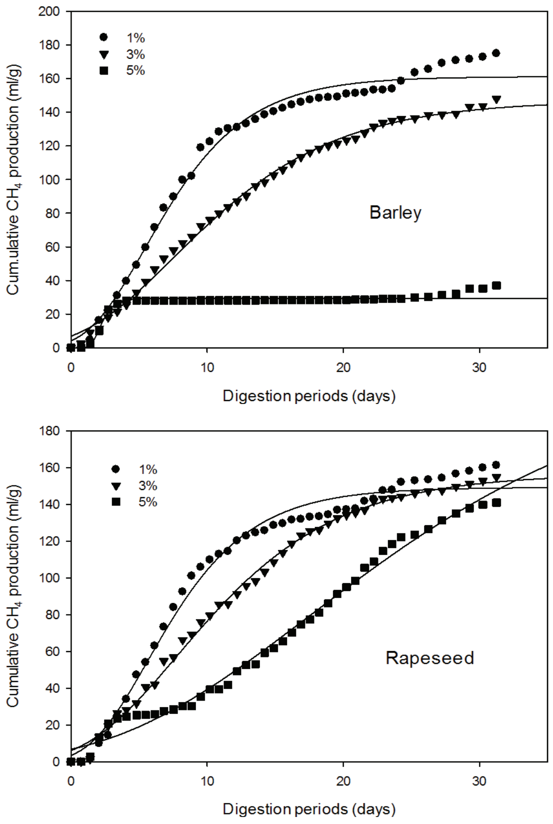

Fig. 3. Fitting results of the Gompertz model to methane production profile in mesophilic digestion according to different crop residues and loading rates.

3.3. Effects of different loading rates and crop residues on digestive methane production

[Table 2] demonstrates that each variable of the model was calculated with different treatment for methane production potential. The activity of methane production bacteria would be decreased if too much crop residues residue was provided [Table 2] and [Fig. 3]. The yield of biogas production from barley was greater than its rapeseed ([Table 2]). It is because methanogenic activity can be affected by carbon contents from crop residues ([Table 1]). It was appeared that ultimate methane production potentials in the mesophilic digestion was ranged from 29.24 to 159.59 mL/g for barley straw substrate and ranged from 121.52 to 156.62 mL/g for rapeseed straw substrate ([Table 2]). It

Table 2. Model Parameters identified from Regression of the Methane Production Profiles in Mesophilic Digestion

Feeding stocks	Loading rates (%)	P_m[1]	R_m[2]	x_0[3]	r^2
Barley straw	1	159.59	14.90	1.45	0.98^{**}
	3	146.91	7.96	0.81	0.99^{**}
	5	29.24	20.39	1.54	0.94^{**}
Rapeseed straw	1	149.03	12.98	1.41	0.98^{**}
	3	156.62	8.71	1.17	0.99^{**}
	5	121.52	5.61	3.38	0.99^{**}

[1] P_m : Ultimate methane production (mL)

[2] R_m : Methane production rate (mL/day)

[3] x_0 : lag-phase time (days)

(** denote significance at 1.0% levels.)

was shown that this ultimate methane production of 1% biomass loading rate of barley was lower at three fold than its swine waste alone, 492.36 mL/g VS fed (VS 2% basis), the reported maximum value[6]. However, Shin *et al.*(2015)[11] reported that the highest ultimate methane production potential was 250.0 mL/g for the rice straw substrate and 248.3 mL/g for the wheat straw substrate during a thermophilic AD.

These values of maximum methane yield with barley were approximately over two folders lower than 385.8 mL/g for maximum biogas yields based on fresh weight, respectively, at mesophilic stages when considering their methane contents[17].

Overall, it would be strongly recommended that feeding stocks use 1 and 5% biomass loading rates for barley and rapeseed straws, respectively, when operating the anaerobic reactor on site if not have treatment of its anaerobic waste water.

4. Conclusions

The objectives of the current study were to predict the potential methane production with different loading rates and crop residues.

Through kinetic model of surface methodology, the methane production was fitted to a Gompertz equation. It was appeared that maximum methane production potentials in the mesophilic digestion was ranged from 29.24 to 159.59 mL/g for barley straw substrate and ranged from 121.52 to 156.62 mL/g for rapeseed straw substrate.

Overall, it would be strongly recommended that feeding stocks use 1 and 3% biomass loading rates for barley and rapeseed straws, respectively, when operating the anaerobic reactor on site at both digestion stages if not have treatment of its anaerobic waste water.

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