Biogas Production by Anaerobic Co-Digestion Process between Community Distillery Slop with Glycerol Waste

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Abstract

This research aimed to increase the efficiency of biogas production from the community distillery slop (CDS) and the glycerol waste (GW) through the anaerobic co-digestion process. The feasibility study of using GW together with the CDS as co-substrate was tested by the bio-methane potential (BMP) in which different concentrations of GW ranging from 1-5% (v/v) were employed. The findings revealed that an anaerobic co-digestion process of the GW at 5% (v/v) concentration and the CDS were potentially improved both in terms of quality and quantity of biogas production. The experiment could produce maximum methane and methane production up to 2,245 $mLCH_4$ and 706 $mLCH_4$/g VS respectively, which increased around 300%, higher than the only CDS single-digestion. The methane yield was well predicted by the Modified Gompertz Model compared with the data obtained from the experiments. This could be seen from the statistical regression coefficient values which higher than 95% (R^2 > 0.95). The obtained data which predicted by the Modified Gompertz Model would be used to design the continuous system in the next step.

Keywords: Biogas production, Community Distillery Slop, Co-digestion, Glycerol waste

Introduction

Community liquor production is a small industry which rapidly and continuously expanded since 2003 to present. The agricultural raw materials such as distillery slop, sticky rice, coconut palm sugar, and palmyra palm sugar were used to produce ethyl alcohol in Thailand. During the distillation process, wastewater or distillery slop around 30 cubic meters a month or 1 cubic meter daily was created. Its dirtiness values in form of COD was high and ranged from 50-104 grams per liter (Chanpalakorn, 2008). The distillery slop composed of organic matter, yeast, ammonia, phosphate, and some sugar, which could not be drained directly to the water resource. In contrary, the distillery slop needs some treatment or utilization (EPPO, 2000). The biological wastewater treatment is a bacteria technology used for digesting the organic matter. This technology is called anaerobic digestion. During the digestion process, the organic matter would produce methane 60-70%, carbon dioxide 28-38%, and biogas. Biogas was used as heat energy in distillation process for reducing costs in the production process.

The distillery slop could produce the biogas about 8-10 L CH_4/L wastewater (Chanpalakorn, 2008). Causing the biogas production from distillery wastewater had low production rate due to high protein. In anaerobic process, protein was degraded to ammonia effect to methanogen growth. Less methane production rate from distillery wastewater compared to other wastewater such as cassava wastewater could product 10-15 L CH_4/L wastewater (Ma, Wambeke, Carballa, & Verstraete, 2008), palm oil mill effluent (POME) could product 20-25 L CH_4/L wastewater (Wonga et al., 2014) etc. Because of the distillery slop had low C: N ratio (less than 15) and had high protein, which tends was decomposed into ammonia nitrogen quickly in anaerobic process. The concentration of ammonia nitrogen about 52 g/l inhibited the methanogen growth resulting in methane production reduced (Tang, Fujimura, Shigematsu, Morimura, & Kida, 2007; Wasterholm, Hansson, & Schnurer, 2012).

One of the interesting solutions was to use the co-digestion strategies in which the two or more organic matters were digested at the same time in order to improve an anaerobic digestion process. The benefit of co-digestion was to balance the amount of nutrient in the system which increased the carbon dioxide per nitrogen ratio (C/N ratio). Besides, it diluted the toxin which has effected on the Methanogen; the type of microorganisms for methane production in the waste water. Therefore, the methane yield was also increased (Kangle, Kore, Kore, & Kulkarni, 2012; Koupaie, Leiva, Eskicioglu, & Dutil, 2014). The agents which added into the process was called "co-substrate". The agents such as manure, glycerol, distillery slop, and the agricultural biomass et cetera. If the co-digestion was positively synergized, it would balance the carbon per nitrogen ratio (C/N ratio) and increased the methane yield due to the fact that the carbon per nitrogen ratio (C/N) plays a crucial role for the stability of the process. Besides, it also determined the microorganisms' health within the biogas production process. If the C/N ratio was too high, the nitrogen would be used and quickly gone. On the other hand, if there was not enough nitrogen, the birth rate of microorganisms' cells would decline, so that the biggest production would also decrease. If the C/N ratio was too low, nitrogen excesses would occur and it would be digested by the microorganisms. As a result, Ammonia nitrogen was generated. The occurrence of Ammonia nitrogen might be toxic to the microorganisms and it suppressed the system (Kangle et al., 2012; Hosseini, Barrantes, Eskicioglu, & Dutil, 2014). According to Santibáñez, Varnero, and Bustamante (2011), the co-digestion could increase the methane production around 50-200% depends on the experimental condition and the co-substrate.

Glycerol waste was a by-product of the biodiesel production system which was about 10 % obtained from the raw materials (Yazdani & Gonzalez, 2007). In 2011, there were around 3,000,000 tons of glycerol waste globally and it tentatively increases up to 4,600,000 tons by the year 2020 which depends on the expansion of biodiesel production (Viana, Freitasb, Leitaoc, Pintoc, & Santaellad, 2012). As regards the less demands and the large amounts of glycerol waste availability so that it had low economic values (Siles López, Martín Santos, Chica Pérez, & Martín, 2009). Besides, the glycerol waste contained high COD, had low price, and could be kept at a room temperature for a long time without decaying, and it can easily be digested under the anaerobic condition (Jingxing, Mariane, Marta, & Willy, 2008; Ma et al., 2008; Hutnan, Kolesarova, Bodok, Spalkova, & Lazor, 2009) so that it was one of the interesting choices to be used in the co-digestion process. Using glycerol waste as a co-substrate in an anaerobic co-digestion, increased the carbon per nitrogen ratio and diluted the toxins in the system as regards it consisted of high carbon. According to Fountoulakis and Manios (2009) and Athanasoulia, Melidis, and Aivasidis (2014), using the glycerol waste at 2-4% (v/v) concentrations as co-substrate in the anaerobic co-digestion process, it could increase the biogas production efficiency around 3.8-4.7 folds.

The Biochemical methane potential (BMP) analysis was the indicator of methane production potential. It was made in a form of maximum methane volume that could be produced per gram from the fatty acid, which it was easily evaporated. The BMP analysis would normally conduct in a reactor batch under the anaerobic experimental condition (Esposito et al., 2012). The BMP analysis could be illustrated in forms of LCH_4/kg-waste, LCH_4/L-waste, mass volatile solids added $(LCH_4/kg\text{-}VS)_{added}$ or CODadded $(LCH_4/kg\text{-}COD)_{added}$ (Angelidaki & Sanders, 2004).

Hence, the researchers were interested in developing the biogas production process from the distillery slop which co-digested with the glycerol waste. The physical and chemical compositions were investigated. The obtained information was used to design the experiment. The study of methane production potential was conducted in a batch system, which investigating the raw materials ratio per co-substrate. The findings obtained information would lead to the study of methane production potentiality in order to effectively yield the maximum energy of biogas production from the distillery slop.

Material and methods

1. Materials

Two major materials were used in this study as follows:

1.1 The samples of community distillery slop (CDS) were supported from the Parichat Distillery Enterprise, which located in the Kuan Kalong district, Satun province, whereas the samples of glycerol waste (GW) were supported from the biodiesel factory, Prince of Songkhla University, Hat Yai district, Songkhla.

1.2 The mixed microorganisms starters for methane production was kept at 35 °C. They were supported from the United Palm Oil Industry Public Company Limited (UPOIC), which located in Huay Yoong sub-district, Nua Khlong district, Krabi.

2. The chemical compositions of the community distillery slop and glycerol waste

As mentioned earlier that the samples for this study consisted of community distillery slop (CDS) and glycerol waste (GW). The CDS was kept at 4 °C while the GW was kept at a room temperature. After that, the elements analysis of each sample was carried out. The chemical elements such as pH, COD, Volatile fatty acid (VFA), Alkalinity, Total kjeldahl nitrogen (TKN), Total phosphorus (TP), Total solid (TS), Protein, Carbohydrate, and Lipids (APHA, 2012) were investigated.

3. Preparing starters (Inoculums)

The mixed microorganisms for methane production at 35 °C was added to the waste water which extracted from the crude palm oil factory in order to become a food source for the starter culture. The waste water from the crude palm oil factory per starter culture ratio was 1:1 (v/v) then adjusting the pH values which ranges between 7-7.5. After that, added 25 grams per liter concentration of wood ashes and $NaHCO_3$ in order to get the alkalinity of 5 grams per kilogram calcium carbonate. The next step was to stir and mixed them well and cured them at the temperature of 35 °C for two weeks. While on a curing process, biogas measurement should be conducted using the Gas Counter. Then, analyzed the biogas elements using Gas Chromatography (O-Thong, Boe, & Angelidaki, 2012). Once the starter culture performed stable rate of biogas production and yielded microbial sediment concentration no lesser than 50 grams per liter, it was then enabled to be tested for methane production potentiality from the community distillery slop and the co-digestion substrate.

4. The study of community distillery slop per glycerol waste ratio using the co-digestion strategy for methane production

The study of CDS and GW per methane production potential ratio was experimented in the serum bottle which its size was 500 milliliters (ml). However, only 200 ml volume was used by mixing CDS and 1.5% of GW (v/v). The pH value was adjusted with $NaHCO_3$ ranging between 7-7.5 then added the starter culture around 80% (the concentration of VSS was 15 grams per liter) of the experimental volume. The waste water per starter culture ratio was 20:80%, then mixed them well and added nitrogen and carbon dioxide in which its ratio was 80:20% for about 5 minutes in order to control the anaerobic condition in the serum bottle. After that, capped the bottle with rubber stopper or the aluminum lid with the hand crimper. The bottle was then cured at the 35 Co for 45-70 days. During the digestion process, the methane yield was volumetric measured using the water replacement (Angelidaki et al., 2009). Besides, the biogas elements were also analysis using the Gas Chromatography (O-Thong et al., 2012) in order to investigate the optimal ratio of CDS per GW which increased the efficiency to produce biogas. Moreover, the experiments were carried out three times.

5. The Investigation of Kinetic Coefficients Values

This study used the Modified Gompertz Model to explain the biogas production from the CDS in the Batch reactor under the anaerobic condition as shown in the equation (1) when G (t) was the accumulated Methane ($mLCH_4$/g VS-added); G_0 was maximum methane yield ($mLCH_4$/g VS-added); e was exp (1) = 2.7183; and λ was the lag times (day) (Kafle, Kim, & Sung, 2013).

$$G(t) = G_0.\exp\left\{-\exp\left[\frac{R_{\max}.e}{G_0}(\lambda - t) + 1\right]\right\} \qquad (1)$$

Results

1. Chemical properties of the community distillery slop and the substrate used as a co-digestion

The chemical properties studied of the distillery slop and the glycerol waste, which was used as a substrate for the co-digestion in this experiment in order to increase the biogas production potential, the chemical element analysis could be illustrated in Table 1 below.

Table 1 The chemical properties of community distillery slop and glycerol waste

Properties	CDS	GW
pH	4.6	8.8
COD (g/L)	130	1,760
VFA (g/L)	3.85	6.65
TKN (g/L)	11	1.67
TS (g/L)	21	969
VS (g/L)	15	910
Protein (g/L)	9.8	1.28
Carbohydrate(g/L)	75.85	845
Lipids(g/L)	3.55	63.76
C/N ratio	12	949

2. The biogas production potential from the community distillery slop which co-digested with the glycerol waste

According to the accumulated methane production and the methane composition (%) which obtained from the digestion process between the CDS and the GW, it was found that the methane accumulation was increased based on the concentration of the GW used. Each experiment used a different concentration of GW as regards the adding of GW was to increase the COD and the C/N ratio, which also increased the volume of organic substrate and diluted the toxicity in the system. As a result, the methanogen could work better so that the accumulated methane production was increased. Another finding was that the durations for methane production used since the beginning state to the steady state were different resulted from the unequal volumes of organic substrate starter used in the system, in form of COD were unequal. This is because of the different concentration of GW which added into the system. As a result, the lesser concentration of GW which added into the system became steady faster as shown in Figure 1 and Figure 2. It could be said that the GW was an effective co-substrate which could be noticed from all experiments when adding the GW, the methane composition (%) was higher than 65% when it reached the steady state. It indicated that the GW has the potentiality to increase the efficiency of biogas production from the CDS both in terms of quality and quantity. The adding of GW at 5% concentration was an optimal condition which resulted in the increasing of C/N ratio from 8 into 28 (see Table 2) and led to maximum methane production yield for 706 ml CH_4/g VS (as shown in Figure 3 and Table 3). The biogas production from the CDS using a co-digestion strategy together with the using of GW was to balance the volume of food nutrition in the system as regards the GW was the external carbon source which has potentiality. As a result, it increased the C/N ratio, diluted the toxin which effected on the methanogen; the type of microorganisms which produce methane in the wastewater so that the methane production was increased (Kangle et al., 2012; Hosseini et al., 2014), and the optimal C/N ratio was during 25-32 (Angelidaki & Ellegaard, 2003).

Moreover, the adding of GW at 2-4% (v/v) concentration into the CDS could increase the C/N ratio, which resulted in increasing the methane production yield compared with the single-digestion, and the obtained values were ranged from 17-23 only as shown in Table 2. Therefore, the results from the experiments indicated that the adding of 5% (v/v) concentration of GW into the CDS was the most optimal ratio in order to increase the efficiency of biogas production. Table 3 illustrated the methane accumulation, methane production, and the COD efficiency. The ratio indicated the highest methane accumulation, methane production, and the COD efficiency comparing with other ratios and the values were 2,245 milliliters, 706 ml CH_4/g VS, and 97% respectively (see Table 3.), while the methane production from the solely CDS (100% CDS) was only 235 ml CH_4/g VS.

Panpong, Srisuwan, O-Thong, and Kongjan (2014) proposed that the usage of GW as co-digestion with waste water from the seafood factory at 1:99 (v/v) ratio could produce methane 577 ml CH_4/g VS which was 108% increased comparing with the usage of solely waste water from the seafood factory. Moreover, the co-digestion between manure and the GW with concentration ranged from 3-6% (v/v) could produce methane 570-680 ml CH_4/g VS (Amon et al., 2006). It indicated that the adding of 5%(v/v) GW resulted in increasing the biogas production potentiality around 3 times or 300% compared with the biogas production from the only CDS (100% CDS). Besides, the adding of 5% (v/v) GW was also increased the pH from 4.60 to 7.10 (see Table 2), and the optimal pH value of biogas production through the anaerobic process was during 7.0-7.2 (Esposito et al., 2012). Another benefit of using GW as a co-substrate was that it could save the budget from using chemical to adjust the pH value(s). However, the weak point of GW was that, it was the carbohydrate, organic substrate in a group of sugar which has small molecules so that the methanogen could easily be digested. This could be noticed from the COD elimination efficiency through the single digestion of the GW at 1-5% (v/v) concentration, which ranged from 90-96% as shown in Table 3.

Table 2 The chemical properties of community distillery slop (CDS) after adding the glycerol waste (GW) at 1-5 % (v/v) concentration

Experiments	pH	COD (g/L)	VS (g/L)	TKN (g/L)	C/N ratio
100% DWCRLP	4.60	130.0	15.00	18	8
DWCRLP + 1%GW	5.90	140.0	68.10	9.887	14
DWCRLP +2%GW	6.40	150.0	72.20	8.993	17
DWCRLP +3%GW	6.60	161.0	76.42	7.004	20
DWCRLP +4%GW	6.80	170.0	82.64	6.827	23
DWCRLP +5%GW	7.10	186.0	90.86	6.047	28
1%GW	8.00	17.0	10.50	0.019	890
2%GW	8.10	33.0	15.6	0.033	1,000
3%GW	8.20	50.1	24.5	0.050	1,002
4%GW	8.30	68.2	33.5	0.067	1,017
5%GW	8.40	83.5	42.5	0.074	1,128

When comparing the methane production of single-digestion and co-digestion methods as shown in Figure 3, it was found that the results' differences of methane production were positive which ranged from 29-108 ml CH4/g VS. It indicated that the usage of GW as co-substrate synergize each other, thus, the methane production potential was increased. The adding of 5% (v/v) concentration of GW could maximize the biggest production effectiveness. Panpong (2013) proposed that, the differences of methane production were positive which was 88 ml CH_4/g VS in the co-digestion process of the canned seafood wastewater and the GW at 1% (v/v) concentration.

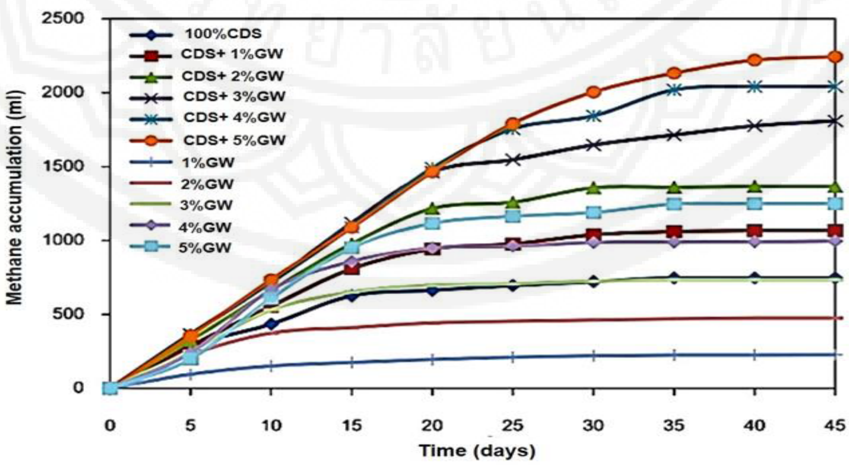

Figure 1 The methane accumulation from the co-digestion process of the community distillery slop (CDS) and the glycerol Waste (GW)

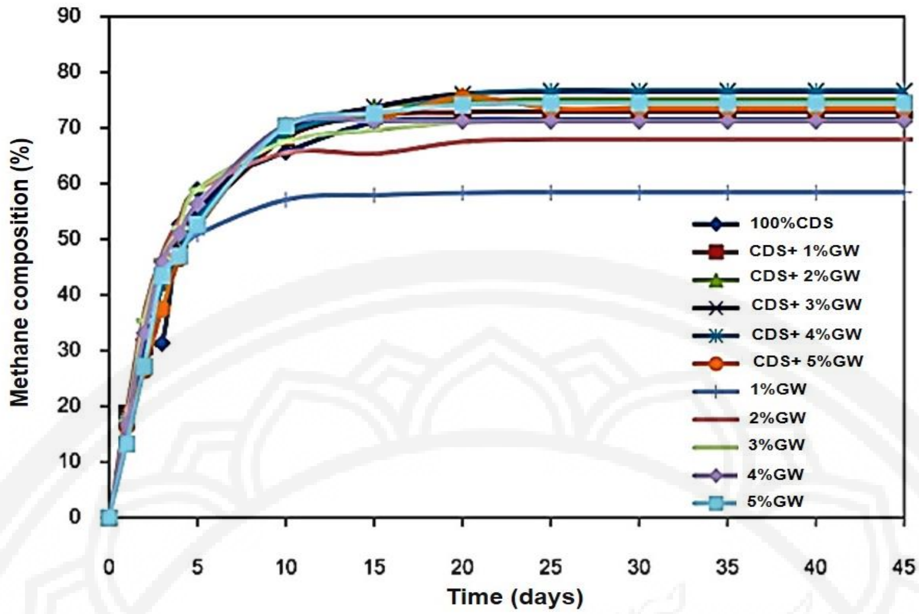

Figure 2 Methane composition from the co-digestion process of the community distillery slop (CDS) and the glycerol waste (GW)

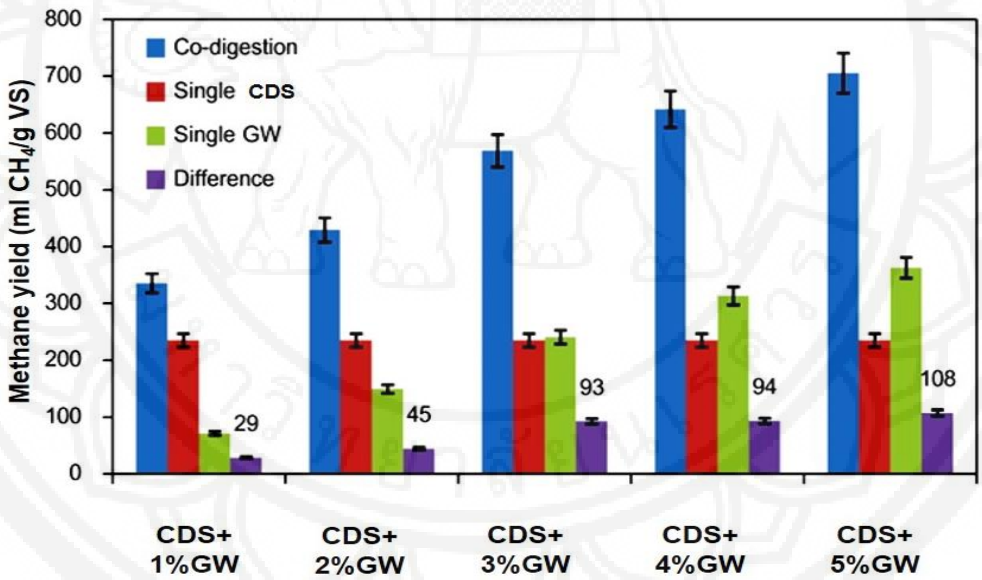

Figure 3 The comparison of methane yield from single-digestion and the co-digestion

Remarks: Difference referred to the results of co-digestion, which was positively synergize and it could be calculated as follows:

Difference = (Co-digestion) - Single CDS- Single GW

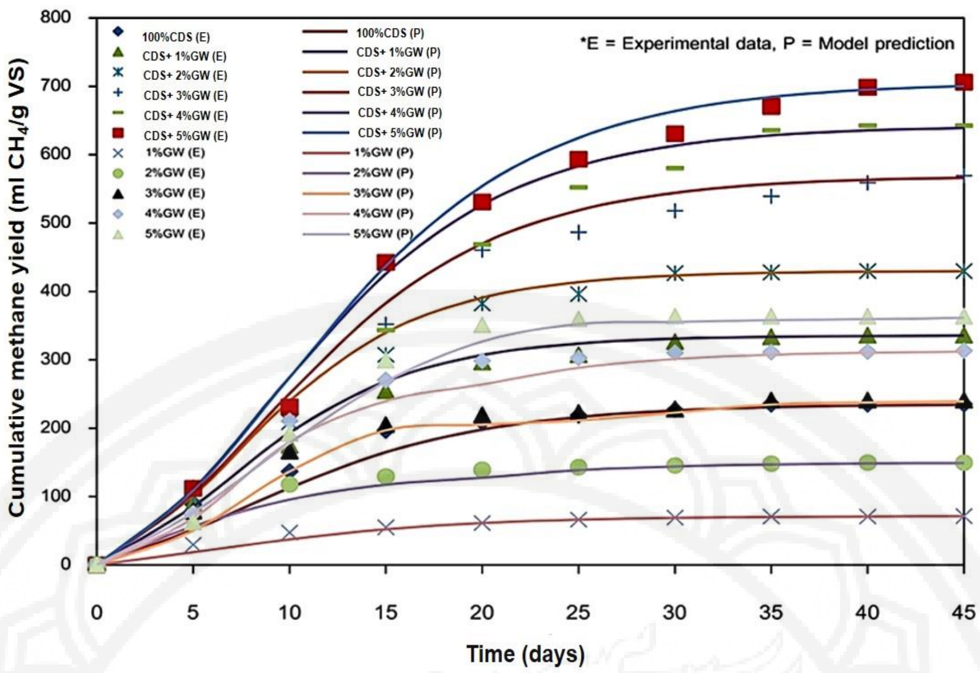

Figure 4 The Comparison of cumulative methane yield from the experimental data and the model prediction using the Modified Gompertz Model

Table 3 The biogas production and the kinetic coefficients from the experiment using the Modified Gompertz Model

Experiments	Final pH	Total biogas (ml)	CH_4 (ml)	CH_4 yield (ml CH4/g VS)	COD Efficiency (%)	Modified Gompertz Model parameter			
						G_0 (ml CH_4/g VS)	R_{max} (ml CH_4/g VS-day)	λ (day)	R^2
100%CDS	7.09	1046	748	235	70	234.13	15.68	1.00	0.963
CDS+ 1%GW	7.33	1465	1068	336	78	335.37	22.38	1.20	0.995
CDS+ 2%GW	7.24	1822	1367	430	80	429.36	28.65	1.50	0.992
CDS+ 3%GW	7.12	2365	1810	569	85	566.31	37.95	1.75	0.995
CDS+ 4%GW	7.11	2664	2043	643	95	639.02	42.83	2.00	0.981
CDS+ 5%GW	6.99	3054	2245	706	97	700.33	44.13	2.25	0.994
1%GW	7.28	390	227	72	90	71.22	4.77	0.10	0.974
2%GW	7.05	701	476	150	92	149.07	9.98	0.50	0.974
3%GW	7.15	1032	735	241	96	239.35	16.08	0.75	0.985
4%GW	6.96	1401	997	314	96	312.07	20.90	1.00	0.985
5%GW	7.08	1680	1250	363	95	361.37	24.21	1.50	0.992

3. Kinetic coefficients for methane production

The analysis of Kinetic coefficients for methane production using the equation of the Modified Gompertz Model, the linear equation explained the relationship between the volumes of cumulative methane per durations. It was found that the statistical regression coefficient values (R^2) were higher than 95%, which indicated the maximum Methane production rate (R_{max}), the adjusting time of microorganism in the system, and the methane yield (G_0) obtained from the experiment which was predicted by the Modified Gompertz Model were tentatively increased due to the durations and the glycerol concentration which added in the experiments as shown in Table 3. The results were in line with the study of Methane production potentiality (BMP) in which the R_{max} values increased from 15.68 to 44.13 ml CH_4/g VS-day, the methane production rate was also increased 3 times or 300% when adding the 5% concentration of GW in the anaerobic co-digestion process.

As a result, the G_0 increased from 234.13 to 700.33 ml CH_4/g VS, the methane production increased 3 times, and the values were also increased from 1.00 to 2.25 days respectively. It could be seen that, the Modified Gompertz Model was used to predict the methane yield in the co-digestion process of the CDS and the GW as shown in Figure 4.

Conclusion

The increasing of biogas production efficiency from the community distillery slop (CDS) through the co-digestion process of 1-5 % (v/v) concentration of the glycerol waste (GW). The results indicated that the usage of GW at 5 % (v/v) concentration was the most optimal concentration for producing highest methane yield and methane production volumes as 2,245 milliliters and 706 ml CH_4/g VS respectively. The biogas production potentiality was increased about 3 times or 300% when compared with the single digestion (100% CDS) as regards the GW was increased the external carbon source toward the CDS. Besides, it also balanced the food nutrition volume in the system so that the C/N ratio was increased from 8 to 28 which diluted the toxin, one which effected onto the methanogen and resulted in increased the methane yield. The Modified Gompertz Model was used to predict the methane yield during the co-digestion process between the CDS and the GW. The statistical regression coefficient values was higher than 95% (R^2) in which it indicated the maximum methane production ratio (R max), the duration for adjusting times (λ) of the microorganism in the system, and the methane yield (G_0) which taken from the experiments. The Modified Gompertz Model was tentatively increased relied on the duration and the concentration volumes of the glycerol waste which added.

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