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Anaerobic digestion of pig manure and glycerol from biodiesel production

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Abstract
Increasing biodiesel production causes a surplus of glycerol. This work aims to investigate the crude glycerol pretreatment method and then apply the glycerol as a co-substrate with pig manure for anaerobic digestion. The optimum crude glycerol pretreatment method was acidification with 6% of H_2SO_4 that highest glycerol recovery was obtained with lowest cost. Co-digestions of glycerol and pig manure enhanced biogas and methane productions compared with mono-digestions. Biogas and methane productions in semi-continuous digestions were highly effected by OLR. The optimum OLR was 3.06 kg SCOD/m^3 that biogas production was maintained at 3 L/d with methane composition of 72% and SCOD removal higher than 80%.

Keywords: Biogas; Crude glycerol; Pig manure; Anaerobic digestion; Biodiesel.

1. Introduction

Anaerobic digestion has become a proven technology for the treatment of organic wastes such as municipal solid waste, industrial organic waste, agricultural residues, and animal manure. The digestion is the decomposition of organic materials by microorganisms in the absence of oxygen to produces biogas which is rich in methane, followed by carbon dioxide, ammonia and traces of other gases, volatile fatty acids, and water [1]. Composition of biogas varies depending upon the raw materials and fermentation conditions [2]. Biogas yield depends on type of substrate. The biogas yield of pig manure is comparable to other feedstock [3]. Pig production is increasing because of increased consumer demands for pork resulting to large volumes of manure to be managed in a sustainable manner by optimizing usage of the nutrients and energy in the manure while at the same time minimizing the negative impact on the external environment, food safety and human health [4]. The anaerobic digestion is a complex sequence composed of four major microbial steps, hydrolysis, acidogenesis, acetogenesis and methanogenesis [5]. Biogas can be used as a vehicle fuel or for co-generation of electricity and heat, and thus, can lead to reductions in greenhouse gas emissions [6].

Biodiesel produced by the transesterification of vegetable oils or animal fats with an alcohol to produce esters has been widely used worldwide. During the biodiesel production process, about 10% (w/w) of glycerol is generated as a primary by-product [7]. The rising of the biodiesel industry causes a surplus of glycerol resulting to a decrease in crude glycerol costs [8]. The crude glycerol is a mixture of glycerol itself, with alcohols, water, salts, heavy metals, free fatty acids, unreacted mono-, di- and triglycerides, and methyl esters. It has few direct uses and possesses a very low value [9]. Crude glycerol purification is high cost and not economic feasibility of the small and medium size plants [10]. Using of co-substrates in anaerobic digestion can enhance the process, because co-substrates can supply nutrients which may be deficient, and at the same time have an overall positive synergistic effect in the digestion medium, leading to stable digestion and enhanced biogas yields [11]. Several successful studies, in batch and/or continuous experiments, have been published with reference to the benefits of the addition of glycerol to enhance the anaerobic digestion of various substrates including animal manure. Co-digestion of animal manure and glycerol shows advantages as (1) the water content in manure acts as solvent for glycerol; (2) the high alkalinity of manure gives a buffering capacity for the temporary accumulation of volatile fatty acids; (3) the wide range of nutrients in manure are essential for bacterial growth; and (4) glycerol supplies rapidly biodegradable matter [12]. Astals et al. [7] studied the co-digestion of the pig manure and glycerol in batch tests. It was found that the mixture of 80% pig manure and 20% glycerol (w/w) produced the highest methane production with 0.215 L/g COD, while the one with 20% pig manure and 80% glycerol was clearly inhibited by the volatile fatty acid due to the low nitrogen concentration of the mixture. Nuchdang and Phalakornkule [13] reported that the anaerobic digestion of acid-treated glycerol with supplement in a synthetic medium was satisfactory at organic loading rates of 1.3-2.6 g COD/L.d with maximum methane yield of 0.32 L/g COD. While anaerobic digestion of acid-treated glycerol with pig manure (80:20 by COD ratio, providing a suitable C:N ratio of 20 g C/g N) was successful at organic loading rates of 1.3-5.0 g COD/L.d with maximum methane yield of 0.24 L/g COD.

In the first part of this study the crude glycerol from biodiesel production was purified by three methods. The treated glycerol from optimum method was then applied as a co-substrate with pig manure for digestion at mesophilic temperature using granular sludge from upflow anaerobic sludge blanket (UASB) as microorganisms in batch and semi-continuous experiments. Effects of chemical oxygen demand: total kjeldahl nitrogen (COD:TKN) ratio, hydraulic retention time (HRT) and corresponding organic loading rate (OLR) on biogas yield were investigated.

2. Materials and methods

2.1 Crude glycerol pretreatment

Crude glycerol was obtained from the Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops, Faculty of Engineering, Prince of Songkla University, Hat Yai, Thailand from production of biodiesel by transesterification of waste cooking oils and palm oil using potassium hydroxide catalyst. The crude glycerol was a brown viscous liquid at room temperature. Three crude glycerol purification methods, (a) acidification with 6% H_2SO_4, (b) acidification with 30% H_2SO_4, and (c) acidification with HCl and coagulation with 6% cationic polyamine (PA) blending with 94% poly-aluminium chloride (PACl) [14], were performed as follows:

(a) Acidification with 6% H_2SO_4, 6% of H_2SO_4 was added to 500 ml of crude glycerol and pH of the mixture was adjusted from 9.8 to 2. The mixture was left over night to separate into three layers. The top layer was methyl ester and free fatty acid, the middle layer was glycerol, water and methanol. Potassium sulfate and sodium sulfate were found in the bottom layer. The glycerol layer was obtained by using separatory funnel.

(b) Acidification with 30% H_2SO_4, The procedure was the same as method (a), but using 30% H_2SO_4 instead of 6% H_2SO_4

(c) Acidification with HCl and coagulation with 6% PA blending with 94% PACl, 500 ml of crude glycerol was pH adjusted from 9.8 to 5 with 2% HCl and left for one night. The mixture was separated into two layers. The top one was methyl ester and free fatty acid and the bottom one contained glycerol. The bottom layer was obtained to adjust pH to 8 with 30% NaOH and then 6% PA blending with 94% PACl with 25%v/v was added. The mixture was left for separation and the glycerol layer at the bottom was separated.

2.2 Substrate preparation

Fresh pig manure was collected from Faculty of Natural Resource, Prince of Songkla University, Hat Yai, Thailand. The pig manure was from the fattening pigs as it possesses high nutrient content. The pig manure was blended and kept at 4 °C before used. Glycerol was from the optimum pretreatment method. Granular sludge was obtained from the UASB unit at Chotiwat Manufacturing Co., Ltd. Hat Yai, Thailand.

2.3 Anaerobic batch digestion

Anaerobic batch digestion was performed in mono-digestion and co-digestion with a substrate composition prepared as shown in Table 1. In co-digestion the amount of pig manure was kept constant while varied amount of glycerol was added in order to investigate optimum COD:TKN ratio. The inoculums of 37,500 mg volatile suspended solids/L (VSS/L) granular sludge and deionized (DI) water were filled up to a volume of 1 L in each digester. The mixture was mixed with stirrer to obtain uniform properties, purged with nitrogen gas for five minutes to create an anaerobic environment and then kept at mesophilic temperatures (33±3 °C) with initial pH of 7.2 for 1 week. Each digester was shake-mixed manually once a day [15]. The biogas produced was sampled from digester headspace for quality analysis and collected in gas collection bottles for volume determination using liquid displacement. All experiments were performed in duplicate and average results are reported.

Table 1. Anaerobic batch digestion

Pig manure [g]	Glycerol [g]	COD [mg/L]	TKN [mg/L]	COD:TKN ratio
20	45	26,962	392	70:1
20	40	24,335	375	65:1
20	35	22,105	354	60:1
20	30	18,482	341	55:1
20	25	14,216	285	50:1

2.4 Anaerobic semi-continuous digestion

Digestion was operated in 3-L continuous stirred tank reactors (CSTR) with operational volume of 2.5L. The experiments were performed in semi-continuous mode with daily feeding. In the start-up, the inoculums of 37,500 mg VSS/L granular sludge was added followed by the mixture of pig manure and glycerol and DI water with COD:TKN ratio of 40:1 and HRT of 50 days corresponding to OLR of 0.16 kg SCOD/m^3.d into three identical reactors. Other three identical reactors were operated with COD:TKN ratio of 50:1. The digestion was maintain at pH 6.8-7.2 and mesophilic temperatures (33±3 °C) until reached steady state conditions. The HRT was reduced stepwise from 10 to 5 and 2.5 days corresponding to OLRs as shown in Tables 2 and 3. The biogas produced was sampled from reactor headspace for quality analysis and collected in gas collection bottles for volume determination using liquid displacement. The digesters were operated for 96 days.

2.5 Analytical methods

Crude and treated glycerol were analyzed for glycerol content by standard method (ASTM D7637) [16], water content by Karl Fischer titration method and ash and matter organic non-glycerol (MONG) by standard method developed by the International Union of Pure and Applied Chemistry [17]. Performance of anaerobic digestion was evaluated by biogas yield. The biogas production was collected by liquid displacement method and biogas composition was analyzed by a gas chromatography (HP6890N) equipped with a silcosteel packed column (Restek Corporation, USA) and a thermal conductivity detector (TCD). Determination of COD, soluble COD (SCOD), TKN, pH, alkalinity, volatile fatty acid (VFA), and VSS were carried out according to the Standard Methods for the examination of Water and Wastewater [18].

Table 2. Anaerobic semi-continuous digestion with COD:TKN ratio of 40:1

Reactor	SCOD [mg/L]	HRT [d]	Flow rate [L/d]	OLR [kg SCOD/m^3.d]
1	7,646	10	0.25	0.76
		5	0.50	1.53
		2.5	1.00	3.06
2	3,852	10	0.25	0.39
		5	0.50	0.77
		2.5	1.00	1.54
3	1,917	10	0.25	0.19
		5	0.50	0.38
		2.5	1.00	0.77

Table 3. Anaerobic semi-continuous digestion with COD:TKN ratio of 50:1

Reactor	SCOD [mg/L]	HRT [d]	Flow rate [L/d]	OLR [kg SCOD/m^3.d]
1	10,679	10	0.25	1.07
		5	0.50	2.14
		2.5	1.00	4.27
2	5,339	10	0.25	0.53
		5	0.50	1.07
		2.5	1.00	2.14
3	2,645	10	0.25	0.26
		5	0.50	0.53
		2.5	1.00	1.06

3. Results and discussions

3.1 The optimum crude glycerol pretreatment method

The crude glycerol consisted of 36-50% glycerol, 4-12% water, 3-6% ash and 35-47% MONG with pH 9.6-10.2. Highest glycerol recovery (30%) was obtained by acidification with HCl and coagulation with 6% PA blending with 94% PACl followed by acidification with 6% H_2SO_4 (26%) and acidification with 30% H_2SO_4 (12%). However, cost of acidification with HCl and coagulation with 6% PA blending with 94% PACl was extremely higher than acidification with 6% of H_2SO_4. Therefore, acidification with 6% of H_2SO_4 was selected as the optimum crude glycerol pretreatment method.

3.2 Anaerobic batch digestion

It was distinctively noticed that the biogas and methane productions were all enhanced in co-digestions of pig manure and glycerol compared with mono-digestions. The highest biogas production (446 mL/d) was obtained by fermentation with 50:1 COD:TKN ratio at day 2 (Figure 1) and the highest accumulative biogas production (1,062 mL) was also obtained by this COD:TKN ratio (Figure 2). The biogas compositions were analyzed and it was found that methane increased markedly during the initial 2 days while CO_2 reduced. The CH_4 composition was about 64% at day 3 for all COD:TKN ratios. Therefore, 50:1 COD:TKN ratio was chosen for anaerobic semi-continuous digestion. In addition, 40:1 COD:TKN ratio was also investigated.

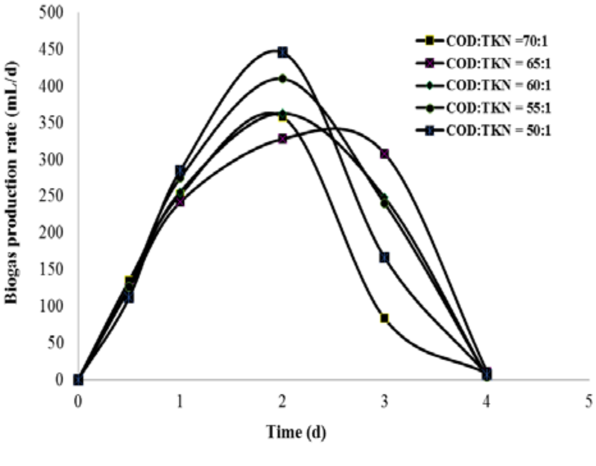

Figure 1. Biogas production rate from anaerobic batch digestion

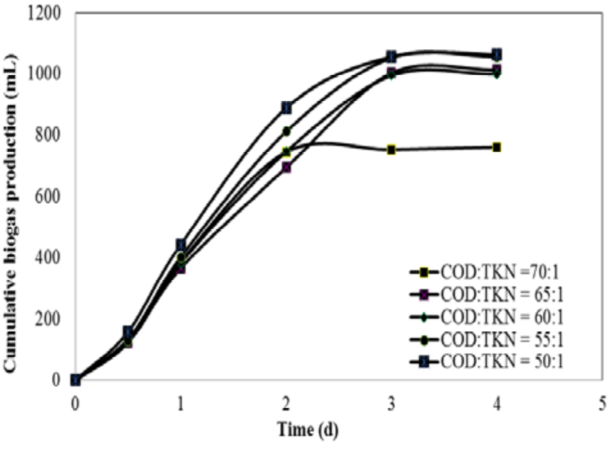

Figure 2. Cumulative biogas production from anaerobic batch digestion

3.3 The optimum conditions for anaerobic semi-continuous digestion

The start-up periods with HRT of 50 days for both 40:1 and 50:1 COD:TKN ratios were carried out for 16 days. After that HRT was decreased stepwise from 10 to 5 and 2.5 days, respectively. The pH of each digester decreased when HRT was changed from 50 to 10 days due to increasing of volatile fatty acids. Volatile fatty acids are the main intermediates products formed during the anaerobic breakdown of organic matter to methane and carbon dioxide. Sufficient buffering capacity (alkalinity) is required to solve pH decreasing problem. Sodium bicarbonate was then added to adjust the pH to maintain within the optimum values, 6.8-7.2 [19]. Daily biogas production increased with reducing of HRT for both COD:TKN ratios (Figures 3 and 4). At lower organic loadings biogas production rates were more stable. With the highest OLR (3.06 kg SCOD/m^3.d) of 40:1 COD:TKN ratio the biogas production immediately increased and fluctuated at the beginning, then remained approximately at 3 L/d. With the highest OLR (4.27 kg SCOD/m^3.d) of 50:1 COD:TKN ratio the biogas production rates were initially high (4-4.3 L/d) and then reduced sharply to maintain approximately at 0.9 L/d because of high amount of volatile fatty acids (700-1290 mg/L CH_3COOH) and high VFA/Alkalinity ratios (1.2-4.4). The optimum VFA concentrations were reported to be 50-500 mg/L CH_3COOH [20] and VFA/Alkalinity ratio > 0.8 inhibited methane production [21]. Methane composition in biogas was about 66-72% excepted at OLR 4.27 kg SCOD/m^3.d that methane composition was about 46%. The theoretical methane composition is 72% for glycerol substrate [13].

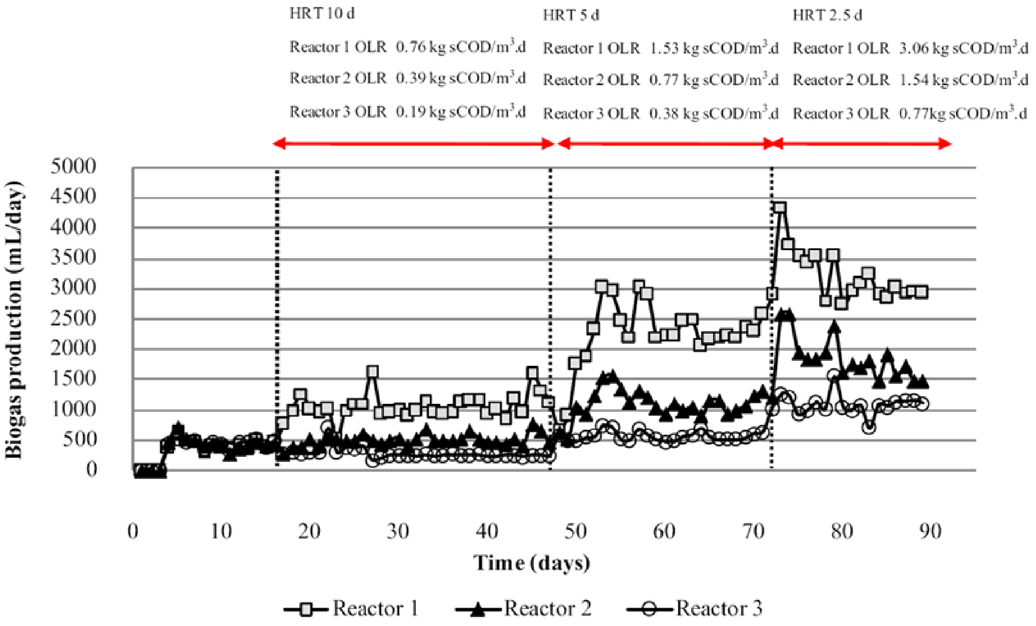

Figure 3. Biogas production from anaerobic semi-continuous digestion with COD:TKN ratio of 40:1

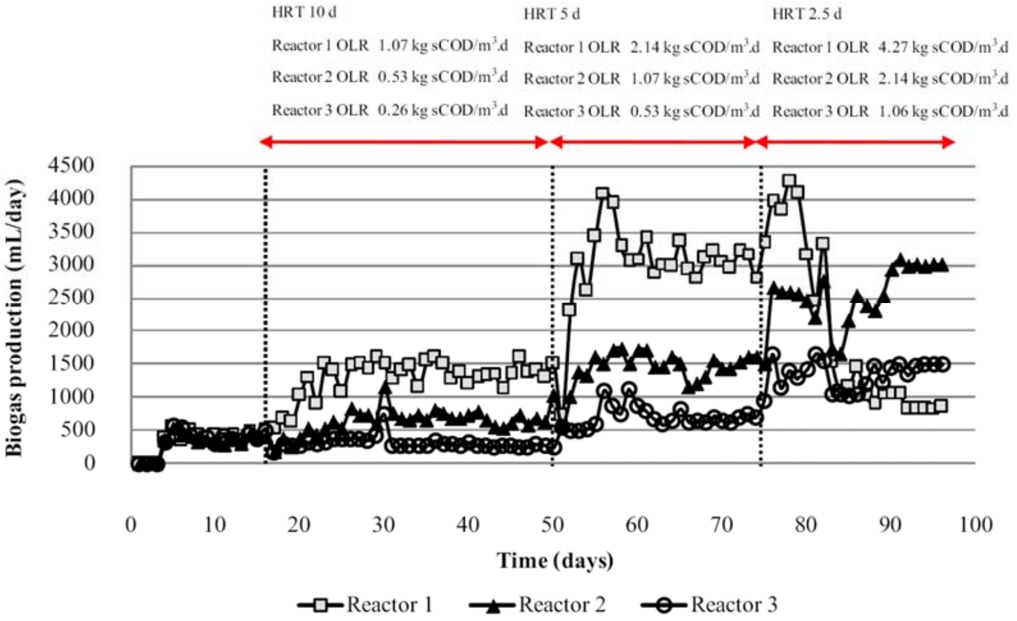

Figure 4. Biogas production from anaerobic semi-continuous digestion with COD:TKN ratio of 50:1

SCOD removal efficiencies were maintained higher than 80% during OLR of 0.16-3.06 kg SCOD/m^3.d. With OLR of 4.27 kg SCOD/m^3.d average SCOD removal efficiencies were 75.76 ± 6.73%. Microbial concentration in the digesters was monitored in term of mixed liquor volatile suspended solids (MLVSS). At the end of digestion MLVSS in all reactors increased from 37,500 to 40,900-41,564 mg/L. It can be seen that biogas and methane yields increased with increasing of OLR for both COD:TKN ratios (Tables 4 and 5) excepted at OLR of 4.27 kg SCOD/m^3.d that biogas and methane yield were lowest since pH could not be maintained within the optimum values. Therefore, 3.06 kg SCOD/m^3.d was the optimum OLR. The biogas production with COD:TKN ratios of 40:1 and 50:1 were not significantly different as OLR was more predominant.

Table 4. Biogas yield and methane yield from anaerobic semi-continuous digestion with COD:TKN ratio of 40:1

Reactor	HRT [d]	OLR [kg SCOD/m^3.d]	Biogas yield [L/g SCOD$_{removed}$]	Methane yield [L/g SCOD$_{removed}$]	pH
1	10	0.76	0.75 ± 0.143	0.51 ± 0.093	6.97 ± 0.22
	5	1.53	0.70 ± 0.061	0.47 ± 0.036	6.82 ± 0.10
	2.5	3.06	0.57 ± 0.029	0.36 ± 0.023	6.82 ± 0.42
2	10	0.39	0.69 ± 0.199	0.48 ± 0.136	6.96 ± 0.15
	5	0.77	0.70 ± 0.170	0.49 ± 0.116	6.80 ± 0.08
	2.5	1.54	0.72 ± 0.031	0.49 ± 0.025	6.80 ± 0.57
3	10	0.19	0.60 ± 0.016	0.41 ± 0.017	6.96 ± 0.15
	5	0.38	0.75 ± 0.203	0.53 ± 0.139	6.84 ± 0.21
	2.5	0.77	0.63 ± 0.150	0.46 ± 0.093	6.80 ± 0.66

Table 5. Biogas yield and methane yield from anaerobic semi-continuous digestion with COD:TKN ratio of 50:1

Reactor	HRT [d]	OLR [kg SCOD/m^3.d]	Biogas yield [L/g SCOD$_{removed}$]	Methane yield [L/g SCOD$_{removed}$]	pH
1	10	1.07	0.56 ± 0.004	0.37 ± 0.006	6.83 ± 0.16
	5	2.14	0.61 ± 0.034	0.40 ± 0.027	6.89 ± 0.13
	2.5	4.27	0.11 ± 0.004	0.05 ± 0.009	5.39 ± 0.06
2	10	0.53	0.48 ± 0.020	0.33 ± 0.014	6.86 ± 0.17
	5	1.07	0.64 ± 0.047	0.44 ± 0.028	6.87 ± 0.16
	2.5	2.14	0.70 ± 0.017	0.46 ± 0.016	6.80 ± 0.11
3	10	0.26	0.43 ± 0.005	0.30 ± 0.009	6.84 ± 0.29
	5	0.53	0.59 ± 0.050	0.42 ± 0.032	6.81 ± 0.22
	2.5	1.07	0.64 ± 0.028	0.47 ± 0.032	6.80 ± 0.10

4. Conclusions

The crude glycerol from biodiesel production consisted of 36-50% glycerol, 4-12% water, 3-6% ash and 35-47% MONG. The optimum crude glycerol pretreatment method was acidification with 6% of H_2SO_4. The glycerol obtained after treatment could be applied as the co-substrate with pig manure in biogas production successfully. Biogas and methane productions in semi-continuous digestions were primarily effected by OLR. The optimum OLR was 3.06 kg SCOD/m^3 that biogas production was maintained at 3 L/d with methane composition of 72% and SCOD removal higher than 80%.

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