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CO-DIGESTION STUDIES OF SALEABLE GLYCERIN WITH PALM OIL MILL EFFLUENT AND POULTRY MANURE

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Abstract

The oversupply of glycerin as by-product from biodiesel industry has raised price crisis. However, the high nitrogen content of saleable glycerin (Gly) makes it a suitable co-substrate for anaerobic process. This study aims to evaluate the feasibility of anaerobic co-digestion (ACD) of Gly with two separate primary substrates namely palm oil mill effluent (POME) and poultry manure (PM). The study disclosed that the ACD of POME:Gly is best at ratio 1.6:0.4 with highest biogas production (Fgas) of 6.49 L/day and chemical oxygen demand (COD) removal of 96% while PM:Gly is ideal at ratio 0.6:1.4 with Fgas of 6.89 L/day and volatile solids (VS) removal of 94%.

Keywords: Anaerobic co-digestion, Saleable Glycerin, Poultry manure, Palm oil mill effluent, Anaerobic batch reactor.

1. Introduction

Biodiesel industry has gained high attention due to worldwide demand of biodiesel which serves as an alternative fuel that can be generated from renewable feedstock including animal fats and waste cooking oils. The principal by–product of biodiesel production is glycerin which is about 10% wt of vegetable oil [1]. To be used for a variety of applications, this glycerin has to be refined via highly energy intensive refining process. The demand for glycerin is 950,000 tonnes while the worldwide glycerin production is 2 times more than demand [1], hence oversupply of glycerin has occurred. The oversupply situation in the glycerin market could worsen thus driving down the prices of the lower grade of glycerin (Gly) from USD 0.25 per tonne to valueless eventually [1]. As more glycerin is

Abbreviations

ACD	Anaerobic Co-Digestion
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
Fgas	Biogas Production Rate (L/day)
Gly	Sealable Glycerin
O&G	Oil and Grease
OLR	Organic Loading Rate
PM	Poultry Manure
POME	Palm Oil Mill Effluent
TN	Total Nitrogen
TSS	Total Suspended Solids
VFA	Volatile Fatty Acids
VS	Volatile Solids

continuously generated, it is crucial to utilise Gly to meet the cost of biodiesel production in the growing global market. The non-toxic, high organic carbon and easily biodegradable nature of Gly along with a suitable nitrogen source makes it a suitable co-substrate candidate for the anaerobic process [2]. Anaerobic treatment has been suggested the most fitting approach for Gly in reducing the high chemical oxygen demand (COD) besides producing useful biogas [3].

On the other hand, poultry manure (PM) is a by-product in poultry industry with high nutrient inputs that is normally utilised as a soil fertiliser. Due to the mass production of manure, farmers face difficulties as they do not have sufficient land to utilise the manure as fertiliser. Hence, the large amount of manure production leads to critical environmental and economic challenges. The current waste management methods employ anaerobic and aerobic treatments, composting, dehydration and incineration [4]. However, these methods required high investment, labour intensive and low biogas production (Fgas). Since poultry manure has high ammonia content at 4 g/L as ammonia-N, it is advisable to serve as a primary substrate to be co-digested with waste that has high carbon content such as Gly to achieve optimum C/N ratio of 16/1 [5]. This is because high ammonia causes growth inhibition and only up to 1.1 g/L free ammonia is tolerable in digester provided a gradual adaptation of microbial [6].

Another potential primary substrate is palm oil mill effluent (POME) produced from palm oil industry as polluted wastewater and could cause serious environmental impact if discharges untreated. This is due to its high biochemical oxygen demand (BOD) at 25,000 mg/L, COD at 53,630 mg/L, oil and grease (O&G) at 8,370 mg/L, and total solids at 43,635 mg/L [7]. Industry current practice treatments are ponding system and open tank digester [7]; however, these methods have several drawbacks. This includes lengthy hydraulic retention time (HRT), large areas of lands or digesters are needed and methane produced is difficult to be collected and utilised, hence contributing to greenhouse effect to the environment. Although many improved high rate bioreactors have been introduced to treat POME, there is still lacking of large scale implementation due to low performances and costly operation [8].

Therefore, anaerobic co-digestion (ACD) has been suggested to be the alternative approach to overcome the aforementioned problems. In the ACD, it is proposed that Gly which is the organic rich material acts as a co-substrate and it can be added into the primary substrates which are PM and POME separately in order to boost up Fgas besides increasing the COD removal efficiency. So far, several wastes (hog manure, pig manure, chicken manure and potato processing waste) have been investigated as a suitable substrate for Gly and those wastes when mixed in appropriate proportion have proved to be a potential biogas resource [8-11]. It has been reported by [10] who testified an enhancement of Fgas of 0.74 L biogas/ml and 6 times higher biomass yield when Gly is added to potato processing wastewater during ACD. Also, [12] demonstrated that the addition of 20:80 ratio of Gly:pig manure produced the higher methane production with 0.215 L/gCOD while 80:20 ratio was constrained by the volatile fatty acid (VFA) due to the low nitrogen concentration of the mixture. This positive effect is possibly due to improved micro-nutrient availability and optimised rheological qualities for multiple sources.

There are abundant studies on ACD of Gly with various wastes; nonetheless, the ACD incorporated animal manure and POME with Gly as potential co-substrate are still in its infancy and have limited studies. Hence, the objective of this study is to evaluate the feasibility of ACD of Gly with two separate primary substrates which are PM and POME based on the maximum Fgas. Besides, the optimum digestion ratio for each primary substrate was investigated as well.

2. Methods

2.1. Sample collection and preparation

Gly was obtained from Sime Darby biodiesel plant, Carey Island in Malaysia. POME and seed sludge were collected from Ulu Kanchong Mill, Selangor state of Malaysia while PM was taken from a chicken farm in Semenyih, Malaysia. POME was preserved at $4^{o}C$ whereas PM was converted into paste form from solid by adding distilled water and blending. The paste was stored in refrigerator for further use. The characterisation of substrate and co-substrates were analysed according to [13] in the Engineering Research Laboratory of the University of Nottingham, Malaysia Campus and their characteristics are shown in Table 1.

Table 1. Characteristics of Gly, POME and PM.

		Gly	POME	PM
Parameters	**Units**	**Average**	**Average**	**Average**
pH	-	10.3	4.5	7.3
BOD	mg/L	97,030	30,100	-
COD	mg/L	1,200,000	70,000	-
VS	mg/L	700,000	1,260	95,000
TSS	mg/L	-	28,900	5,020
TN	mg/L	850	980	7,200
TP	mg/L	15,034	608	100
VFA	mg/L	-	470	-
O&G	mg/L	-	10,540	-

2.2. Acclimatisation, start-up and operation

The ACD was investigated in six identical batch reactors with an effective working volume of 5 L, operated mesophilically in semi-continuous mode. The set-up of the batch reactors is shown in Fig. 1. All ports were sealed and the reactors were closed during the experiment in order to maintain anaerobic conditions and to prevent biogas from escaping. The experiments were conducted in two sets and in each set, different primary substrate (POME and PM) were added with the co-substrate, Gly. There are two phases in each set.

In the first phase, acclimatisation of seed sludge with the primary substrate was conducted. POME was fed at the lowest organic loading rate (OLR) of 0.5 gCOD/L.day initially and progressively increased until 2 gCOD/L.day. However, the OLR for PM was based on the volatile solids (VS). Although the suggested OLR for PM is ranging from 1.5-6 gVS/L.day, higher OLR are associated with drawbacks such as low treatment performance and reactor failures. Since VS concentration is lower than COD concentration, the initial loading rate was started with 1 gVS/L.day and progressed towards 2 gVS/L.day.

The second phase involved the slow addition of Gly to the substrate at 2 gCOD/L.day with different digestion ratios (Table 2). Three reactors were allotted for each primary substrate, referred to as POME1, which was used as a control without the addition of Gly, POME 2 (POME + Gly) and POME3 is the duplicate for POME2. Similarly, the reactors for the second primary substrate, PM were labeled as PM1, PM2 and PM3. Both set were operated simultaneously. All the batch reactors were fed once a day and shaken by hand twice a day to enhance the mixing in the batch reactors. Biogas produced was then collected and measured using water displacement method.

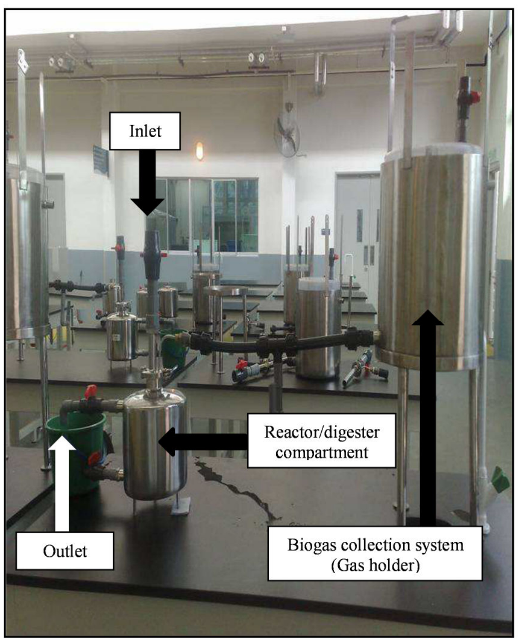


Fig. 1. The setup of the batch reactors.

3. Results and Discussion

3.1. Phase one: The start-up process

In the acclimation stage (Phase one), the OLR in the reactors of POME 1 to 3 was gradually increased from 0.5 gCOD/L.day to 2 gCOD/L.day at an increment of 0.5 gCOD/L.day. Whereas for PM1, PM2 and PM3, the OLR was gradually increased from 1 gVS/L.day to 2 gVS/L.day. This is to minimise the transient impact on the batch reactors that might be induced by a sudden increase in loading as well as to avoid any overload risk. The performances of the three reactors in each set (POME1 to POME3 and PM1 to PM3) were very comparable, and therefore, the results shown are the average values of all the three reactors.

In the first few days, the reactors POME1, 2 and 3 were acidified very fast and the pH was less than 5 in almost all the reactors. Therefore, sodium bicarbonate solution was added to the anaerobic sludge until pH 7 is achieved. Then it was decided to neutralise the POME prior to feeding. In addition, pH was checked three times a day and if the pH is low, immediately buffer will be added.

In contrast to the ACD of POME, neutralisation for PM was not required. Obviously, surplus nitrogen content in the PM buffered the PM from being acidified. Since the first day, Fgas in all the reactors was noticeable and from then on, there was a progressive and a steady state increase in the Fgas in all the reactors

Table 2. Co-digestion ratios of POME/PM: Gly.

POME/PM[a] (OLR gCOD/L.day)	Gly (OLR gCOD/L.day)
1.8	0.2
1.6	0.4
1.4	0.6
1.2	0.8
1.0	1.0
0.8	1.2
0.6	1.4
0.4	1.6
0.2	1.8
0.0	2.0

[a]The OLR of PM is based on VS/L.day

As shown in Fig. 2, the Fgas and specific methane production rate for both POME and PM was increased with the increase of OLR. This is mainly due to the increase of readily available organic matter in both substrates at higher OLR and thus more biogas was produced. PM displays higher specific methane production rate than that in POME. These indicate that PM is more favourable by methanogens. This may be due to the nutrient content accessible for the growth of microorganisms. This is supported by the high phosphorus and nitrogen content observed at 100 and 7,200 mg/L respectively. It is also reflecting the high treatability of PM by biological means. On the other hand, Fgas and specific methane production rate in POME appeared lower and this may be caused by the lower nitrogen concentration at 1,900 mg/L compared to PM. Although the phosphorus concentration is higher than PM at 200 mg/L, it indicates the higher percentage of phospholipids present in the overall O&G content of POME which has caused the lower affinity by methanogens [14].

The acclimation stage is completed in 17 days as the Fgas, effluent COD and effluent TSS were relatively constant. Besides, high COD of 89% was achieved in the POME reactors and high VS removal efficiencies of 78% was achieved in the PM reactors at the end of phase one, indicating the success of the start-up of the reactors.

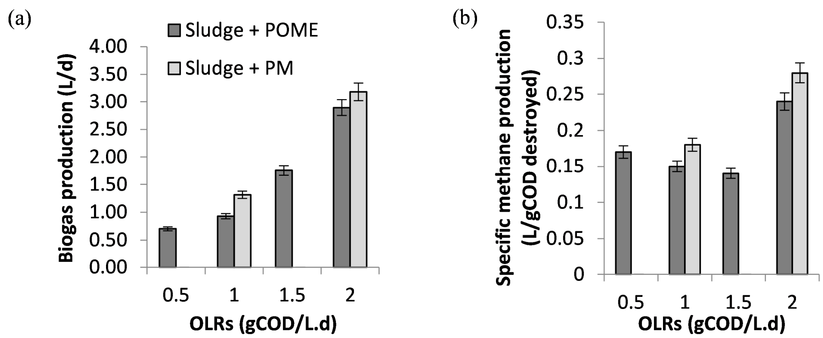


Fig. 2. (a) Biogas production rate and (b) Specific methane production at different OLRs in the acclimation stage.

3.2. Phase two: ACD performances with different digestion ratios

In order to determine the optimum digestion ratio in both POME and PM, a series of experiments by using different ratios of POME and PM to Gly were conducted at a fixed OLR of 2 gCOD/L.day in accordance to Table 2. At each digestion ratio, the batch reactors were operated until a steady state reached as indicated by a constant methane production rate (±5%) as well as effluent COD level (±5%). Accordingly, 10 experiments with different digestion ratio were completed in 5 months.

The average Fgas, COD and VS removal efficiencies for each ratio are presented in Figs. 3-4. The results of the batch reactors which were served as a control (POME1 and PM1) are indicated as 'control'. The average values taken from the results of the POME2 and POME3 as well as PM2 and PM3 were labelled as 'test' in Figs. 3-4.

Throughout the whole experimental period in phase two, the control reactors for both POME and PM recorded stable production of biogas, which were in the range of 4.5 to 4.9 L/day and 4.7 to 5.5 L/day respectively. As clearly shown in Fig. 3, the Fgas in all the co-digesters (POME 2, POME 3, PM2, and PM3) was observed to be higher than their respective control reactor. This indicates that the bacteria were able to co-digest the Gly efficiently due to the synergism established in the ACD and thus more biogas is produced.

Initially, the Fgas in the POME:Gly ACD increased with the increase of Gly ratio. It reached the maximum point of 6.49 L/day at POME:Gly ratio of 1.6:0.4 (corresponding to 1.6% Gly). This brings about 39% improvements in the biogas production. This can be explained by the ideal COD:N:P which is 250:5.83:0.9 obtained in this digestion ratio . This is very close to the suggested value for anaerobic treatment which is 250:5:1 [15]. This signifies that the microorganisms in the reactor were able to perform effectively due to the sufficient nutrients and appropriate nutrient balance. However, after its maximum point, the biogas production showed a tendency to fall with the further increase of Gly ratio. This is mainly attributed to the imbalance of its nutrient content. Excessive addition of Gly (more than 1.6% Gly) has reduced the COD:N:P ratio to 250:1.02:0.51 (at 37.5% Gly). The poorer biogas production also coincided with the decline in pH and alkalinity from 7.3 to 6.5 and from 4.31 to 3.35 g/L respectively. This may be due to facts that some portion of the alkalinity was used to neutralise the volatile fatty acid (VFA) concentration for maintaining the pH within an acceptable level. However, it is worth noting that the alkalinity level was distinctly above 2 g/L in every ratios, which is the lower limit for effective anaerobic digestion process [6]. This signifies that the addition of Gly into POME have contributed to the alkalinity, attributed by its alkaline nature (pH 10.3). This is desirable as POME is acidic in nature and least cost can be incurred on the dosing of chemicals to maintain the pH at 6.8 to 7.2, which is suitable for methanogenesis.

Similarly for PM, the increase in Gly ratio from 1.8:0.2 to 0.6:1.4 (corresponding to 0.8% to 15.6% Gly) has boosted up Fgas from 5.10 to 6.89 L/day, Fig. 3(b). This is attributed to the appropriate C:N ratio (16:1) in the mixture of 84.4% PM and 15.6% Gly. However, the Fgas appeared to have a decreasing trend with the further increase of Gly from 24.1% to 100%. This may be due to the fact that acidogenic bacteria produced more VFA than the amount that could be utilised by acetogenic and methanogenic bacteria. As evidence, the decline of alkalinity from 4.05 to 2.80 g/L was observed at the similar ratios has resulted in deposition of VFA causing inhibition of methanogens. Therefore, alkalinity clearly has an effect on the Fgas. Alternatively, this can be improved by the addition of sodium bicarbonate solution.

(a)

(b)

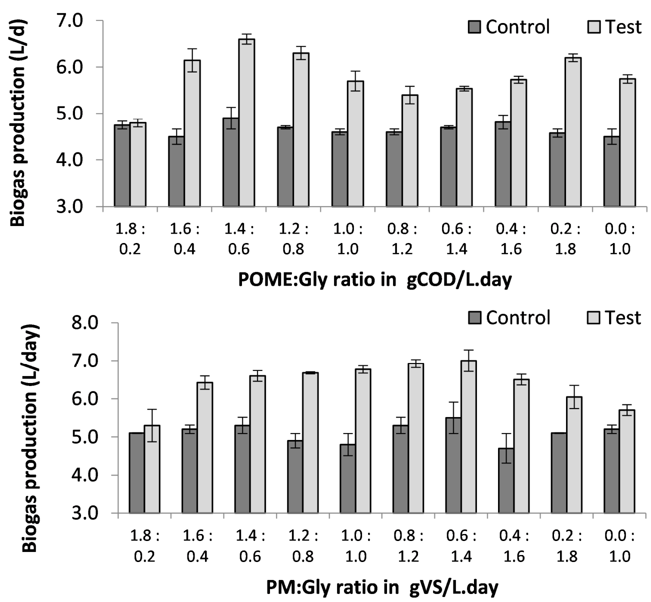
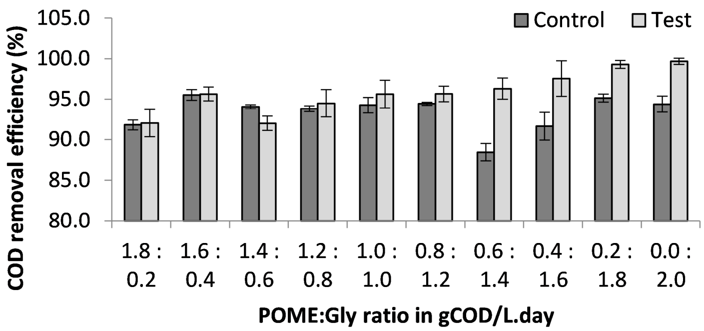


Fig. 3. Biogas production rate (L/day) of (a) POME and (b) PM at different digestion ratios.

(a)



(b)

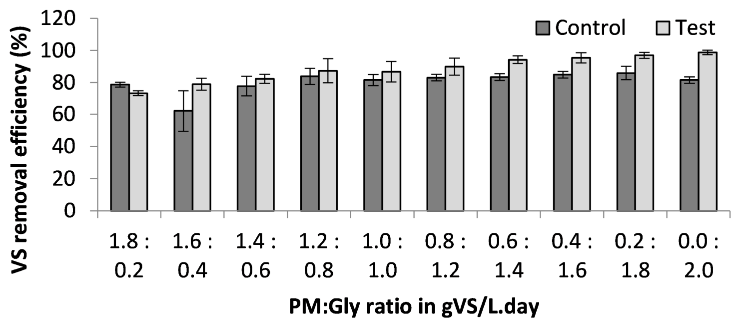


Fig. 4. COD and VS removal efficiencies (%) of (a) POME and (b) PM at different digestion ratios.

Although Fgas of POME and PM cannot be compared directly due to its different OLR of substrates mix, the methane yield is comparable where PM achieved 0.48 LCH_4/gVS removed at ratio 0.6:1.4 which is higher than POME (0.45 LCH_4/gCOD removed) at ratio 1.6:0.4.

On the other hand, the COD and VS removal efficiencies in both controls were observed to be acceptable at above 85% whereas the test reactors for both POME and PM clearly showed better efficiencies at above 97% for all ratios (Fig. 4). This is coherent to the results of Fgas. This indicates the presence of high biodegradability COD in both mixtures which can be easily utilised by the microorganisms.

4. Conclusions

The key findings in this study concluded the following below:

- POME and PM are suitable primary substrates to co-digest with Gly from POME/PM:Gly digestion ratio of 1.8:0.2 to 0.0:2.0 at the fixed OLR of 2 gCOD/L.day.
- The addition of Gly can improve the biogas production up to 40% due to the appropriate nutrient balance in the ACD.

- Optimum COD:N:P ratio of 250:5.83:0.9 in the mixture of POME and Gly and optimum C:N of 16:1 in the mixture of PM and Gly were achieved due to the high carbon content and alkaline nature of Gly.
- It is recommended to perform ACD of POME:Gly at ratio 1.6:0.4 (1.6% Gly) for highest Fgas (6.49 L/day), methane yield (0.45 LCH_4/gCOD) and COD removal (96%). Whereas, ACD of PM:Gly is optimum at ratio 0.6:1.4 (15.6% Gly) for highest Fgas (6.89 L/day), methane yield (0.48 LCH_4/gVS) and VS removal (94%).
- ACD of Gly with POME/PM are both feasible; however, PM is a more suitable substrate to produce higher Fgas and methane yield.

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