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Improvement of Biohydrogen Fermentation by Co-digestion of Crude Glycerol with Palm Oil Decanter Cake

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This study focuses on enhancement the efficiency of biohydrogen production from co-digestion of crude glycerol (GLC) with palm oil decanter cake. Decanter cake with the characteristic of high biodegradable organic contents and nutrient rich compositions is an attractive feedstock for biogas production. The biochemical methane potential tests, the applied method to determine hydrogen production, were conducted to evaluate the effect of crude glycerol in decanter cake fermentation at the varying glycerol concentration of 0.25-2% wv^{-1} under thermophilic condition (55°C). The results revealed that the maximum hydrogen potential production (P) (562 mL) and hydrogen yield (871mL/gTSremoval) were observed at the 2% wv^{-1} crude glycerol. Decanter cake was used as 2 functions 1) feedstock and 2) microbial source in hydrogen fermentation. Crude glycerol displayed strong effect on the pH maintenance for the overall process including hydrolysis and fermentation process. The final pH > 5 was obtained for all cases. Waste utilization based on TS and COD removal trended to decrease at the increase of crude glycerol loading (0.75 and 2% wv^{-1}). This study displayed the feasibility of waste to energy from palm oil industry and biodiesel production besides the biogas plant from POME. Semi-continuous fermentation in 20 L bioreactor expressed the optimal HRT of 2 days could be maintain to dilute the acidity condition. The maximum yield of hydrogen production of 43.33 $L/kgTS_{added}$, hydrogen production rate of 0.89 L/L.d and energy recovery of 0.11 $kWh/kgTS_{added}$ were obtained from the HRT of 2 days with 1.5% GLC co-digestion. However, better performance in both hydrogen production and waste utilization from decanter cake and crude glycerol fermentation could be more effectively improved by using two-stage fermentation.

1. Introduction

The current scarcity of fossil fuels, growing emissions of combustion-generated pollutants and their increasing costs have made alternative fuel sources more attractive. Biodiesel (fatty acid methyl esters) produced by the process of trans-esterification of methanol with animal fats or vegetable oil are can replace petroleum-based diesel fuel. In general, crude glycerol of approximately 10% is generated in biodiesel production (Athanasoulia et al., 2014). Glycerol Purification, used in factories such as food, cosmetics and pharmaceuticals, seemed to be oversupplied. However, the amount of crude glycerol is excess of current requirements. Thus, crude glycerol disposal and utilization has become a serious issue and problem environmental liability for the biodiesel industry. Glycerol is generated not only when biodiesel fuels are produced chemically, but also when production of bioethanol. The fact that the projected production volume of crude glycerol will exceed the present commercial demand for purified glycerol and the cost to refine this crude glycerol will expensive than stabilized and disposal. Therefore, the alternative waste utilization of crude glycerol has been attractive for many researchers. Anaerobic digestion is an attractive waste treatment practice in which both energy recovery and pollution control can be achieved. Many agricultural and industrial wastes are suitable for anaerobic digestion because they contain high levels of easily biodegradable materials (Chen et al., 2008). However, the

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impurities of crude glycerol such as salts, methanol and long chain fatty acids make biodegradation by microorganism more difficult. Thus, it could be used as co-digestion with the other carbohydrate-rich waste to improve the efficiency of the overall fermentation process. In general, palm oil mills generate 3.5% of oil palm decanter cake (OPDC) for each tonne of fresh fruit brunches (FFB) and 42 kilograms per tonne fresh fruit brunches (Kanchanasuta and Pisutpaisal, 2016). Decanter cake is one type of waste produce from palm oil industry. High biodegradable organic contents and nutrient rich compositions make palm oil decanter cake as an attractive feedstock for biogas production.

This study aimed to improve the efficiency of waste utilization on biohydrogen fermentation by using co-digestion of crude glycerol with palm oil decanter under thermophilic (55°C) condition.

2. Materials and methods

2.1 Crude glycerol

Crude glycerol was used as the substrate for anaerobic hydrogen production. This crude glycerol was obtained from Trang Palm Oil Co., Ltd. Trang, Thailand. The crude glycerol contained 657.27 ± 14.45 g glycerol per liter.

2.2 Decanter cake

Decanter was used as the inoculum for hydrogen production and the substrate for methane production. The decanter was obtained from palm oil milling plant, Suksomboon palm oil industry in Chonburi, Thailand. Characteristics of decanter consisted of 197.67 g total solids (TS) and 169.74 g volatile solids (VS) per kilograms including biomass fraction of 50 %ww^{-1} of cellulose, 31 %ww^{-1} hemicellulose and 10% %ww^{-1} of lignin. The sample was stored at 4°C before use.

2.3 Batch fermentation

The batch test was carried out in 100 mL serum bottle (80 mL working volume) sealed with rubber with three replicates. The pH of each test was adjusted to 7 with 3 N NaOH or 3 N HCl. The serum bottle was feed with nitrogen gas for 1 min (flow rate of 1,780 mL min^{-1}) to create an anaerobic condition. Crude glycerol and decanter cake were used as substrate and inoculum. The batch was cultivated under thermophilic condition (55°C). Each serum bottle contained 8.1 g of the decanter (corresponding with 2% TS) and glycerol (0.25, 0.5, 0.75 and 2% wv^{-1}GLC, respectively).

2.4 Semi-continuous hydrogen production in 20 L bioreactor

The reactor with working volume of 16 L was operated at 4 and 2 days HRT. It was started with co-digestion of 2% wv^{-1} total solid (TS) of decanter cake (DC) and 1 g of glycerol (GLC) without the external anaerobic sludge. Subsequently, 4 and 8 L of new mixture substrate was daily fed into the reactor while digestate was removed to keep the operating volume at 16 L and HRT of 4 and 2 days. The concentration of glycerol was slightly increased by 0.25, 0.5 and 0.75% wv^{-1} GLC, respectively while decanter cake was fixed at 2% TS throughout the fermentation process. Increase glycerol loading of 0.75% for 5 days, 1% for 59 days and 1.5 % for 21 days were added into the reactor afterwards. The reactor was operated at the control HRT of 4 days for 33 days and the control HRT of 2 days for 54 days The substrate was adjusted to pH 7 with 3 N NaOH or 3 N HCl. The reactor was operated under thermophilic condition (55˚C).

2.5 Analytical methods

Analysis of soluble chemical oxygen demand (SCOD), total chemical oxygen demand (TCOD) and total solid (TS) were conducted according to the standard methods for the examination of water and wastewater (APHA/AWWA/WEF, 2005). Gas composition (H_2 and CO_2) in the headspace of batch reactor and continuous stirred-tank reactor (CSTR) were measured on a gas chromatograph (Shimadzu GC-2014, Japan) equipped with thermal conductivity detectors (TCD) fitted with stainless steel column packed with Unibeads C (80/100 mesh). Helium was used as a carrier gas. The temperatures of the injection port, column and detector were 120, 70 and 150°C, respectively.

2.6 Kinetics analysis

The modified Gompertz equation (Eq.1) was used to fit cumulative hydrogen/methane production data obtained from each batch experiment (Kanchanasuta and Pisutpaisal, 2016). This model has long been used for describing hydrogen, methane, or biogas production in batch fermentation experiments.

$$H(t) = P \cdot \exp\left\{-\exp\left[\frac{R_m \cdot e}{P}(\lambda - t) + 1\right]\right\} \quad (1)$$

Where $H(t)$ is cumulative biogas production (mL) during the incubation time, t (h), P (H_{max}) is the biogas production potential (mL), R_m is the maximum production rate (mL h^{-1}), λ is the lag phase duration (h), and e is the exp (1) = 2.718

3. Results and Discussion

3.1 Batch fermentation

The efficiency of biohydrogen fermentation based on the hydrogen production potential (H_{max}) and energy recovery was observed under the condition of combined 2%wv^{-1} TS DC with varying glycerol loading of 0.25-2 % wv^{-1} GLC. Types of the inoculum seeds played the vital role on the biogas compositions. In this study, the external sludge was not added into the reactor. In the absence of anaerobic sludge seed, the indigenous microbes from decanter cake were used as the function of inocula for anaerobic digestion. Results showed that only H_2 was found in the range of 20-36, 27-43, 26-46 and 32-46% vv^{-1} for 0.25, 0.5, 0.75 and 2% GLC co-digestion and CH_4 was not detected throughout the fermentation (data not shown). Fermentation periods with the 0.25% GLC co-digestion was the shortest compared with the other conditions that hydrogen production was stopped at the 4th day cultivation. The highest cumulative H_2 production about 384 mL at the 23th day cultivation was obtained with the 2% GLC co-digestion. The cumulative H_2 fermentation profile data was S-shape trend and well fitted to the modified Gompertz equation (R^2> 0.99) for all experiments. The kinetics data from the equation, hence, was statistically significant. Organic loading of glycerol also strongly affected the overall fermentation process. Hydrogen production with the 2% GLC co-digestion achieved the maximum hydrogen production potential (H_{max}) and hydrogen content detected in the reactor of 562 mL and 46%, respectively. Environmental conditions and types of existing active organism groups play the important role of the efficiency of bioproduct production in the overall fermentation. Generally, microorganisms related to the anaerobic fermentation process consist of diverse bacterial groups such as hydrolytic bacteria, acidogens, acetogens, and methanogens. The hydrolytic bacteria degrade complex substrates or polymeric substrates to simple structures, which are further converted to various products such as volatile fatty acids (acetic, propanoic, lactic, butyric etc.) and alcohol (O-Thong et al., 2016). The results of the biogas production with the presence of the indigenous microbes from the decanter cake indicated that these microbes contained no methanogen, but hydrolytic, acidogenic, and acetogenic bacteria. The suitable pH maintaining in the reactor plays the major factor resulting in the efficiency of hydrogen fermentation. In this study, all conditions with crude glycerol co-digestion could maintain the pH throughout the fermentation in the proper range of higher than 5 (Table 1). The final pH detected in the reactor tended to increase with the increase glycerol loading. However, the condition with high glycerol loading resulted in the longer lag time that microbe used for adapting in the fermentation system. The maximum TS and soluble COD removal of 35 and 51% were observed at the 0.5 and 0.75 % GLC co-digestion (Figure 1, 2). However, the highest efficiency of H_2 fermentation based on the maximum H_2 potential production of 562 mL and H_2 yield of 871 mL H_2/g $TS_{removal}$ was obtained at the 2 % GLC co-digestion.

Table 1: The summary of kinetic parameters in the fermentation batch test

Condition (%GLC)	The final pH	Yield		λ (day)	H_{max} (mL)	Energy recovery (kJ)
		mL H_2 / g $TS_{removal}$	mL H_2 / g $COD_{removal}$			
0.25	5.07	313.41	473.66	0.36	136.18	1.446
0.5	5.19	464.21	2,307.63	0.37	356.65	3.787
0.75	5.14	483.30	1,302.55	0.37	365.27	3.879
2	5.3	871.13	816.57	2.80	561.88	5.967

High efficient waste utilization in the H_2 fermentation with co-digestion of decanter cake and crude glycerol potentially benefits the management of the crude glycerol and palm oil decanter cake from palm oil industry. Maximum energy recovery equivalent to 6 kJ was observed at the 2 % GLC co-digestion. However, to improve the efficiency of biogas production and waste utilization from crude glycerol and decanter cake, adding the external anaerobic sludge and integrating with two-stage fermentation have been further investigated.

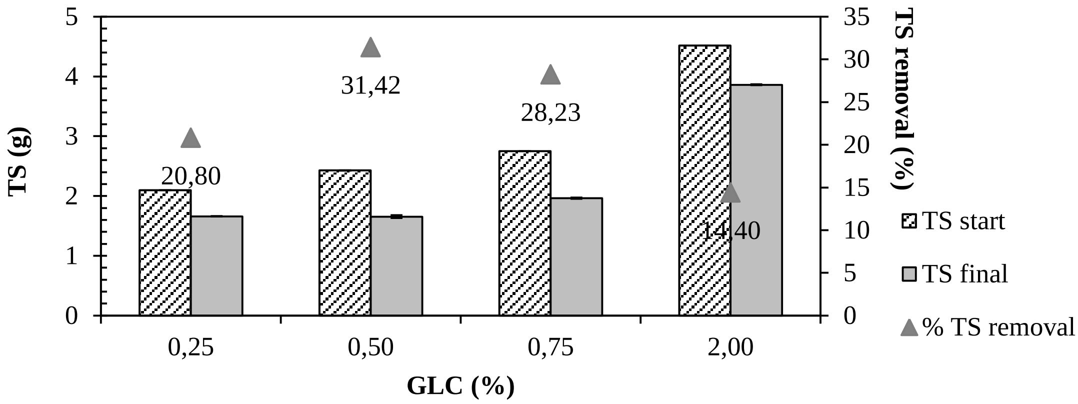

Figure 1: The efficiency of TS removal at the varying glycerol loading of 0.25-2% GLC.

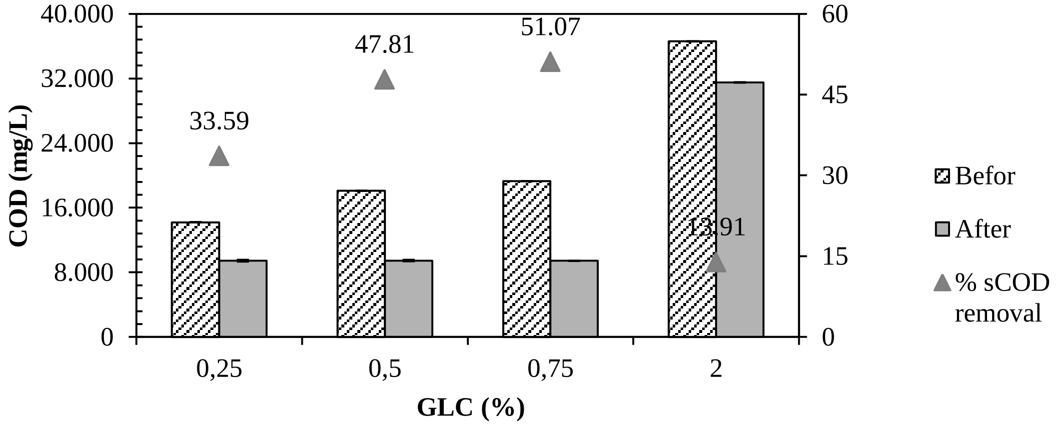

Figure 2: The efficiency of soluble COD removal at the varying glycerol loading of 0.25-2% GLC.

3.2 Semi-continuous fermentation in 20 L bioreactor

Co-digestion of 2% TS wv^{-1} of palm oil decanter cake with the varying glycerol concentration and hydraulic retention time (HRT) for hydrogen production under the control thermophilic condition of 55°C and 100 rpm in the continuous stirred tank reactor (CSTR) was investigated. The time course profile of hydrogen production in each condition was illustrated in figure 3. Results indicated that HRT and organic loading of glycerol also strongly affected the overall fermentation process. Hydrogen production with the 1% GLC under the HRT of 2 days yielded the hydrogen production better than that under the HRT of 4 days. The maximum hydrogen production and hydrogen content detected in the reactor of 16,301 mL and 49% were obtained at the 1.5 % GLC under the HRT of 2 days. The methane content was not observed throughout the fermentation, indicating that there was no methanogenic activity in the reactor. Butyrate was the main metabolites accumulated in the reactor. It was significantly decreased after starting the HRT of 2 days (the 33th fermentation) (data not shown). Results supported the previous study reported that the optimal HRT for hydrogen production from organic fraction of municipal solid wastes is about 1-2 day (Liu et al., 2006). HRT is a key factor of the acidity condition, a limitation factor, in the semi-continuous reactor. Due to the dilution condition from the daily new feeding, short HRT condition achieved better performance based on volume and content of hydrogen production. Stability of pH (higher than 5) under the HRT of 2 days could be observed and it further resulted in continuous hydrogen fermentation.

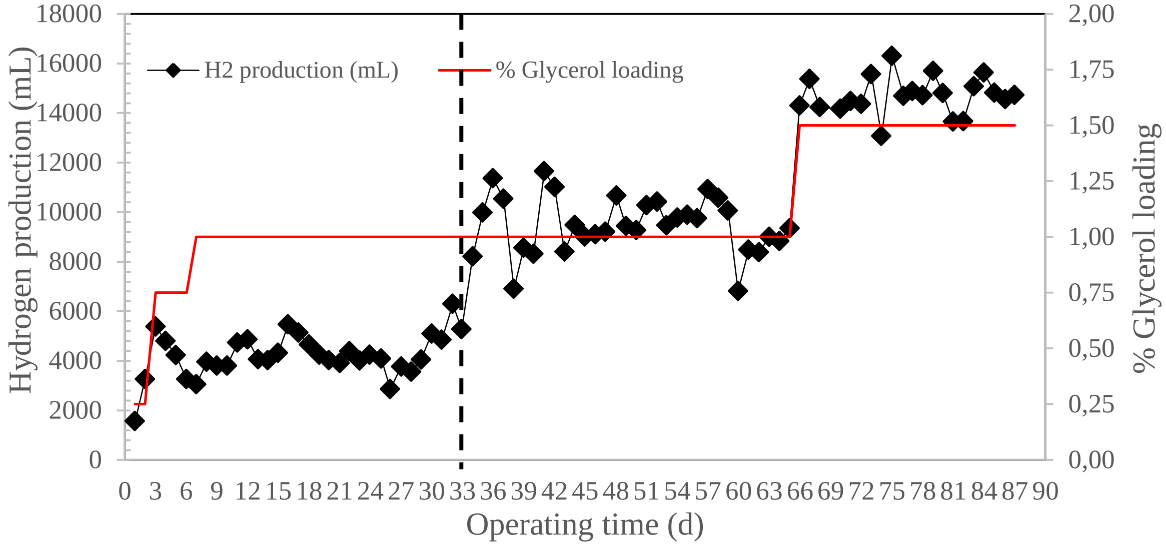

Figure 3: Hydrogen production and glycerol loading during fermentation in 20 L semi-continuous bioreactor.

The maximum efficiency of waste reduction based on TS (67%) removal was obtained at the 1.5% GLC under the HRT of 2 days (Figure 4). Similarly, trend of TCOD removal under the HRT of 2 days was higher than that under the HRT of 4 days (Figure 5). Moreover, the maximum yield of hydrogen production of 43.33 L/kgTS$_{added}$, hydrogen production rate of 0.89 L/L.d and energy recovery of 0.11 kWh/ kgTS$_{added}$ were obtained from the HRT of 2 days with 1.5% GLC co-digestion. Therefore, to enhance the efficiency of semi-continuous biohydrogen production, optimal HRT of 2 days could be suggested. Combining two-stage fermentation could be an alternative operation mode to improve the overall process. However, result from our previous study (Kanchanasuta and Sillaparassamee, 2017) showed that high organic fraction based on the value of COD remained in the effluent of the second stage. Complex structure of remained solid fraction might be an obstacle for the existing microorganism. Therefore, pretreatment of hydrogenic effluent before using as feeding in the second stage has been further investigated.

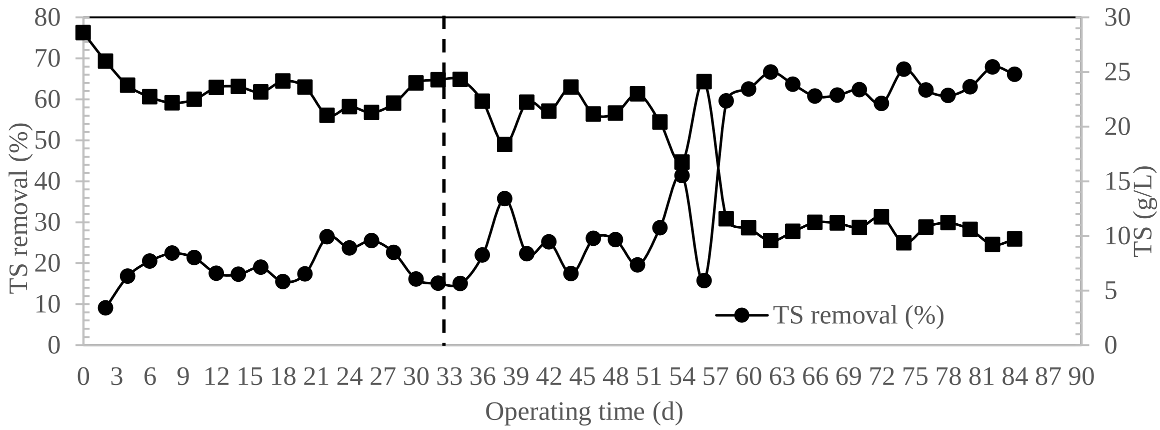

Figure 4: The efficiency of TS removal during fermentation in 20 L semi-continuous bioreactor.

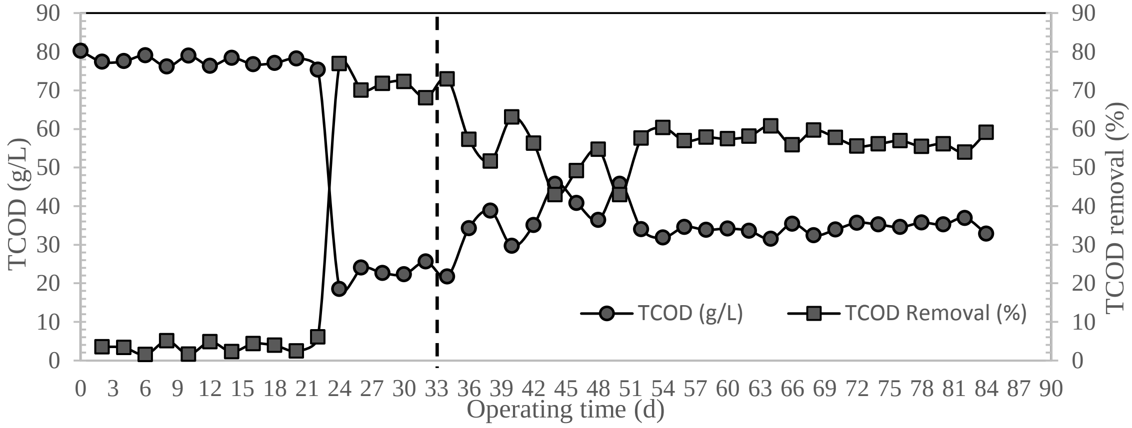

Figure 5: The efficiency of total COD removal during fermentation in 20 L semi-continuous bioreactor.

4. Conclusion

Co-digestion of crude glycerol with palm oil decanter cake on biohydrogen fermentation could enhance the efficiency of waste utilization. Organic loading of glycerol also strongly affected the overall fermentation process. Maximum H_2 yield and energy recovery were observed from the 2% GLC co-digestion. Moreover, High glycerol loading tends to maintain the pH in the reactor. Decanter cake could be used in both feedstock and microbial source in hydrogen fermentation. This study has been demonstrated that co-digestion of crude glycerol with decanter cake in thermophilic (55°C) is an environmentally-attractive method. Semi-continuous fermentation in 20 L bioreactor expressed the optimal HRT of 2 days could be maintain to dilute the acidity condition which directly affected hydrolysis and acidogenesis of the hydrogen producing bacteria groups. However, to enhance the efficiency of biohydrogen production and waste utilization, two-stage fermentation and pretreatment of hydrogenic effluent have been further investigated.

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