EFFECT OF CO-DIGESTION AND HYDRAULIC RETENTION TIME ON ANAEROBIC DIGESTION OF DECANTER CAKE AND BLOCK RUBBER WASTEWATER FOR BIOGAS PRODUCTION

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Abstract

This paper aims to study biogas production using anaerobic digestion for wastewater from a block rubber factory alone, and anaerobic co-digestion for decanter cake from a palm oil mill factory together with the wastewater from the block rubber factory and the effect of the hydraulic retention time (HRT). The anaerobic co-digestion was studied using a continuously stirred tank reactor (CSTR). The experiments were conducted at a laboratory scale. The mixing time of all CSTRs was 24 h using the inner mixing devices. From a previous study using the biochemical methane potential test, the suitable ratio of the anaerobic co-digestion between the decanter cake from the palm oil mill factory and the wastewater from the block rubber factory was 5 g of the decanter cake and 200 mL of the wastewater. The experiments consisted of 4 CSTRs, namely R1, R2, R3, and R4. The R1 contained the wastewater of the block rubber factory alone at 30 d of HRT. The R2, R3, and R4 contained the same ratio of the 5 g of decanter cake and 200 mL of wastewater with 30, 20, and 10 d of HRTs, respectively. The results show that the anaerobic co-digestion provides higher biogas production than that of the anaerobic digestion using wastewater alone. The decanter cake from the palm oil mill factory can improve the biogas production potential of the wastewater from the block rubber factory using anaerobic co-digestion. The HRT of the anaerobic co-digestion shows the effect on anaerobic digestion. The 10 d of HRT can increase the organic substrates in chemical oxygen demand (COD) form. The efficiency of the COD, total solids (TS), and total volatile solids (TVS) removal was the highest value in the R4 (10 d of HRT using anaerobic co-digestion). The maximum biogas

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production occurred when HRT of 10 d was used on anaerobic co-digestion. The R4 provided 580-1088 mL/d of biogas production rate, 1088±27 mL/d of maximum biogas production rate, 47.5-56.8% of methane production and 56.8±2.4% of maximum methane production. The COD, TS, and TVS removal efficiencies were 99.6-99.8%, 87.5-91.1%, and 89.3-95.4%, respectively in R4. The maximum COD, TS, and TVS removal efficiencies were 99.8±4.6%, 91.1±3.9%, and 95.4±2.9%, respectively. From the results, it can be concluded that the best HRT for the anaerobic co-digestion is the 10 d in R4.

Keywords: Decanter cake, block rubber factory wastewater, anaerobic co-digestion, hydraulic retention time, biogas production

Introduction

Anaerobic digestion is a widely used technology for converting organic wastes into biogas under an absence of oxygen. Typically, the biogas consists of 55-80% of methane, 20-45% of carbon dioxide, and less than 3% of hydrogen sulfide with other impurities (Nallathambi, 1997; Kaosol and Sohgrathok, 2014). Its application includes heating, cooking, and electricity. Therefore, the biogas can be used as a renewable energy source (Speece, 1996). Renewable energy is one of the most important factors for global prosperity. It can also reduce the greenhouse gas emissions from fossil fuels.

The HRT is the amount of time the manure spends in the digester. It has been reported as the ratio of the digester volume to the amount of organic substrate added per day. The HRT is one of the most important design parameters affecting the economics of an anaerobic digester. A smaller anaerobic digester (a lower capital cost) results in a shorter HRT. Conventional anaerobic digestion is a slow process such as a plug flow and cover lagoon. The HRT is 30-50 d for the conventional anaerobic digestion process. The long HRT leads to a large volume of the anaerobic digestion reactor. Therefore, the investment cost could be high for the anaerobic digestion process. The HRT is 10-25 d for the completely mixed digester. However, there are many options to improve the biogas production (Shabee et al., 2010). One interesting option is anaerobic co-digestion. Anaerobic co-digestion of different raw materials may improve the digestibility due to a better carbon source and nutrient balance (Mshandete et al., 2004). The

low organic load of block rubber factory wastewater may not be sufficient to produce a cost- effective biogas plant. The anaerobic co-digestion of block rubber factory wastewater combined with other organic-rich residues seems to be an attractive method which has been used to overcome its low digestibility.

One interesting agro-industry waste for anaerobic co-digestion is the decanter cake from palm oil mill factories (Er et al., 2011). A palm oil mill factory produces significant quantities of solid wastes such as empty fruit bunches, shells, fibers, ash from boilers, and decanter cake. These solid wastes from palm oil mill factories could affect the environmental and lifestyle qualities of communities. Normally, the decanter cake is utilized as a soil conditioner in the palm oil plantation areas. Some researchers have studied methods to utilize the decanter cake for anaerobic digestion. The decanter cake is used as co-digestion material for anaerobic co-digestion with frozen seafood wastewater which results in an improved biogas production rate for anaerobic co-digestion. The optimum HRT is 20 d. The biogas production is 2.88 L/d, with 64.5% of methane composition. The maximum biogas production rate is 1.87 L/d (Kaosol and Sohgrathok, 2014). Therefore, decanter cake offers an interesting way for biogas production. In comparison to most thermal processes, the capital cost of anaerobic digestion is relatively low. The anaerobic digestion technology for various homogenous waste streams is widely known in the south of Thailand; however, no full anaerobic co-digestion plants are in operation for any palm oil mill wastes. Efficiency and process stability are shown to be the parameters for the anaerobic digestion performance (Lv *et al.*, 2010).

In this research, the methane production potential is evaluated on anaerobic digestions at different HRTs of continuously stirred tank reactors (CSTRs) between the rubber block factory wastewater alone and the rubber block factory wastewater together with the decanter cake under mesophilic conditions. Moreover, the methane composition in biogas is analyzed to determine the effect of the HRT on anaerobic co-digestion. The anaerobic co-digestion of decanter cake and frozen seafood wastewater could substantially reduce the emission of methane, carbon dioxide, and the foul smell from anaerobic waste ponds of the palm oil mill factories. Because anaerobic co-digestion is a totally enclosed system, it can reduce the environmental impacts. Therefore, anaerobic co-digestion has the energy recovery potential (methane production) and it could be possible to sell the surplus.

Materials and Methods

Raw Materials for Anaerobic Co-digestion

The wastewater from a block rubber factory was obtained from a block rubber factory in Songkla province, Thailand. The block rubber factory wastewater contains 6.8±0.3 of pH, 4575±225 mg/L as CH₃COOH of volatile fatty acids (VFA), 1525±71 mg/L as CaCO₃ of alkalinity, 4380±208 mg/L of total chemical oxygen demand (TCOD), 3554±155 mg/L of soluble chemical oxygen demand (SCOD), 6120±120 mg/L of TS, 3340±145 mg/L of TVS, 692±23 mg/L of total Kejeldahl nitrogen (TKN), and 222±9.6 mg/L of ammonia-N. The wastewater contains high amounts of TCOD and SCOD which are the main harmful causes for the environment. Thus, wastewater treatment is required before discharging the effluent to any receiving water source. However, the COD is not enough for biogas production, especially the anaerobic digestion process. By adding the decanter cake, the COD will be increased for biogas production as an anaerobic co-digestion.

The decanter cake was obtained from a palm oil mill factory in Krabi province, Thailand. The decanter cake is characterized by a high percentage of moisture content (>75%) and has a high biodegradability (Yahya et al., 2010). It contains 5.1±0.1 of pH, 22716 ± 1075 mg/g (dry basis) of TCOD, 16705±769 mg/ g (dry basis) of SCOD, 252±11.8 mg/g of TS, 191±8.8 mg/g of TVS, 26. 4±1. 2 mg/g (dry basis) of TKN, and 0.2 ± 0.01 mg/g (dry basis) of ammonia. The decanter cake contains high amounts of TCOD, SCOD, TS, and TVS. Therefore, an addition of decanter cake can increase the organic substrates for biogas production (Chavalparit et al., 2006). The seeding was cow dung, which contains 7.5±0.3 of pH, 1074±45 mg/L as CH₃COOH of VFA, 1925±82 mg/L as CaCO₃ of alkalinity, 33624±1551 mg/L of TCOD, 1828±76 mg/L of SCOD, 36665±1496 mg/L of TS, 25930±986 mg/L of TVS, 1047±35 mg/L of TKN, and 28.9±0.7 mg/L of ammonia. The collected decanter cake and the block rubber factory wastewater were stored at 4°C before mixing.

Experimental Setup

The reactor was set up as a CSTR. The inner mixing action occurred continuously in all reactors during the experiments. The CSTR was in a 6 L reactor with 5 L of working volume. The reactor was filled with 5 L of co-digestion materials, and the headspace of the reactor was flushed with nitrogen for 3 min in order to remove the oxygen and to create an anaerobic environment (Waki et al., 2008). The mixing time was 24 h. The CSTR consisted of 4 reactors, namely R1, R2, R3, and R4. R1 contained only the wastewater from the rubber block factory as a control (Table 1). The raw materials loading in R1 obtained 194±7.6, 271±11.3, and 148±6.5 mg/d of COD, TS, and TVS, respectively, at 30 d HRT. The ratio used in the other 3 reactors (R2-R4) was observed as the suitable ratio for the selected co-digestion materials, using the biochemical methane potential test resulting from our previous study (Kaosol and Sohgrathok, 2014). The HRT was varied in these 3 reactors, including 30, 20, and 10 d of HRTs in R2, R3, and R4, respectively. At 30 d of HRT, 76383 \pm 2964 mg/L of COD, 4255 \pm 181 mg/L of TS, and 3028 \pm 85 mg/L of TVS were obtained from R2. At 20 d of HRT, 114346 \pm 4869 mg/L of COD, 6370 \pm 296 mg/L of TS, and 4533 \pm 173 mg/L of TVS were obtained from

R3. At 10 d of HRT, 228693±9628 mg/L of COD, 12740±456 mg/L of TS, and 9066±394 mg/L of TVS were obtained from R4.

The effluent was collected at the bottom valve of the CSTRs. In all experiments, several parameter data were analyzed, including

Table 1. The experimental setup

Reactors	HRT (d)	Raw materials	
R1	30	Wastewater alone	
R2	30	Wastewater + Decanter cake	
R3	20	Wastewater + Decanter cake	
R4	10	Wastewater + Decanter cake	



Note: 1) Mixed wastes inlet, 2) CSTR, 3) Outlet, 4) Sampling port, 5) Inner mixing devices, 6) Gas line, 7) Three-way valve, 8) Gas bag, and 9) Gas counter

Figure 1. The anaerobic co-digestion system



Figure 2. Variation in temperature during anaerobic co-digestion from the different HRTs

pH, temperature, COD, TS, TVS, alkalinity, VFA, ammonia-nitrogen, and biogas content. All analytical procedures were performed in accordance with the American Public Health Association (2005). All experiments were repeated 3 times to obtain the average values with an accuracy of $\pm 5\%$. The biogas production was recorded daily as the volume of biogas produced using a gas counter. The biogas was collected in a gas tube every 4 d for the biogas composition analyzation. The biogas was analyzed for methane composition using a gas chromatography analyzer (model GC7890A, Agilent Technology, Santa Clara, CA, USA) with a thermal conductivity detector. The percentage of methane was recorded as the representative of the methane content. All samples were conducted in triplicate.

Results

Anaerobic Co-digestion Operations

The anaerobic co-digestion experiments were performed for a period of 150 d. The variations of the COD, temperature, pH, ammonia-nitrogen, alkalinity, VFA, TS, and TVS with anaerobic co-digestion under different HRTs were studied in this research (Figures 2-10). The temperature of the anaerobic co-digestion operation ranged between 26-38°C (Figure 2). It showed the mesophilic phase of the anaerobic co-digestion (Gray, 1989). Thus, the temperature was suitable for the anaerobic co-digestion process. It can be observed that the temperature of R2-R4 containing anaerobic co-digestion was higher than that of the control reactor (R1). Thailand is located in a tropical area and, thus, the temperature is between 25-40°C all year round. These temperatures are suitable for bacteria growth under the anaerobic condition.

The pH is one of the factors in the anaerobic digestion operation. During the first 40 d of the anaerobic co-digestion, the pH values were slightly decreased. After the initial period, the pH values tended to move towards the neutral again, because the acidogenic bacteria responsible for hydrolysis and digestion can be adapted to a low pH value while the methanogenic bacteria will lose activity at the low pH value. During the hydrolysis stage, the organic matters are converted to soluble compounds and further degraded to acetate, hydrogen, butyrate, propionate, and carbon dioxide. The suitable pH is between 6.8 and 7.2 for methanogenic bacteria (Rajeshwari et al., 2000). The methane formers are pH sensitive. When the pH is lower than 6.6 or higher than 7.6, the VFA digestion efficiency will be decreased. The pH values outside of the suitable range will affect the metabolic rates and slow or completely stop methane production, resulting in decreased biogas production. In all experiments, the pH during the steady state ranged between 6.6 and 7.0 (Figure 3). The pH value of all experiments was neutral. Therefore, the methanogenic bacteria provided a good performance.



Figure 3. Variation in pH during anaerobic co-digestion from the different HRTs

The result shows that the alkalinity of all CSTRs had the same trend. In the first period (day 1 to 40), the alkalinity increased; after the system reached the steady state, the alkalinity decreased in all reactors (Figure 4). The alkalinity, a parameter in the anaerobic digestion operation which is the measure of its capacity to neutralize acids, is due primarily to the salts of weak acids (Qasim and Chiang, 1994). The optimum alkalinity for anaerobic digestion is between 1000 and 5000 mg/L as CaCO₃ (Agdag and Sponza, 2005).

The VFA is an important parameter because it indicates the stability degree of the anaerobic digestion process. If the VFA is accumulated excessively, the subsequent methane digestion will be reduced (Cho *et al.*, 1995). The influent of the VFA in all reactors had a very high variation. The effluent of the VFA tended to decrease during the first 40 d (Figure 5). The highest effluent of the VFA resulted in a decrease of the methane composition. This event is a result of the shift from the methanogenic process to hydrolysis or the acidogenic process in the anaerobic co-digestion reactors (Kaparaju et al., 2009). The VFA levels continued to decrease later on in all reactors because the first 40 d is the lag phase; the methanogenic bacteria are adjusting to the environment and the microorganisms have a low rate of substrate degradation. After 40 d, the rate of substrate degradation rose to optimize with the rate of substrate degradation of the fermentative bacteria. Its values could not induce the anaerobic digestion inhibition. For anaerobic digestion, the recommended VFA ranges between 50 and 500 mg/L CH₃COOH (Halber, 1981). After 45 d, the VFA in all reactors was in the range of the recommended values for anaerobic digestion.



Figure 4. Variation in alkalinity during anaerobic co-digestion from the different HRTs



Figure 5. Variation in VFA during anaerobic co-digestion from the different HRTs

An ammonia-N level which is higher than 1500 mg/L can cause toxicity for anaerobic digestion (Sterling *et al.*, 2001). The ammonia-N was lower than 250 mg/L in all reactors (Figure 6). Thus, the system inhibition could not occur during the anaerobic co-digestion in all reactors.

The average of the COD influent was $4380\pm195 \text{ mg/L}$ in R1. The COD of the anaerobic co-digestion between the wastewater and the decanter cake rose to 10 times that provided by the anaerobic digestion of the wastewater alone. Therefore, the anaerobic co-digestion could significantly increase the organic substrates. After the anaerobic co-digestion, the COD effluent was less than 800 mg/L (Figure 7). In all steady states, the COD removal was higher than 98% for anaerobic co-digestion. The COD removal efficiencies of R2, R3, and R4 showed no significant differences (Figure 8). Thus, the

co-digestion materials selected in this work compromised each other very well as shown by the good performances of R2, R3, and R4 in comparison with the performance of R1. Since R2, R3, and R4 were different in the HRT only, R4 is considered the best operational condition because it used only 10- d HRT while it provided a similar performance to those of R3 (20- HRT) and R2 (30-d HRT). The results show that the experimental hydraulic retention time is more than the time of the substrate degradation. The HRT may be reduced to less than 10 d if the anaerobic digestion process is a complete mix because the rate of digestion of the anaerobic bacteria will rise in comparison to that of its conventional counterpart. As a result, the anaerobic bioreactor size can be reduced and the investment cost can be reduced.

The anaerobic co-digestion between the wastewater from the block rubber factory and



Figure 6. Variation in ammonia during anaerobic co-digestion from the different HRTs



Figure 7. Variation in COD during anaerobic co-digestion from the different HRTs

the decanter cake from the palm oil mill factory can significantly increase the TS, TVS, and the digestibility in the anaerobic co- digestion due to the solid form of the decanter cake (Budiyono *et al.*, 2010). Figures 9 and 10 show the removal of the TS and TVS during anaerobic co-digestion from the

different HRTs. At the steady state, the TVS removal was 80-90% in R2-R4. The TS removal was 65-90% in R2-R4. The anaerobic co- digestion showed high performance for organic removal in the form of solids. The best performance of TS and TVS removal was observed in R4 which used the 10 d of HRT.



Figure 8. Variation in COD removal during anaerobic co-digestion from the different HRTs



Figure 9. Variation in TS removal during anaerobic co-digestion from the different HRTs



Figure 10. Variation in TVS removal during anaerobic co-digestion from the different HRTs

The TS and TVS removal efficiencies were 87.0-1.1% and 89.3-95.4%, respectively. The maximum removal efficiency of TS and TVS was $91.1\pm3.9\%$ and $95.4\pm2.9\%$, respectively.

Biogas Production for Anaerobic Co-digestion

The experiments were performed for a period of 150 d. The data on the average biogas production and percentage of methane composition are shown in Figures 11 and12. The biogas was produced immediately in all CSTRs. After 40 d, the maximum biogas production was reached. The steady state of biogas production was noticed during days 100-150 in all anaerobic co-digestion reactors, because the biogas production did not show any significant increment. This phenomenon is caused by the stationary phase of the bacteria growth (Torres-Castillo *et al.*, 1995). At the steady state, the biogas production was 5-60, 192-398, 271-556, and 580-1088 mL/d, for R1, R2, R3, and R4, respectively (Table 2). The maximum biogas production was 60 ± 2.4 , 398 ± 15.5 , 556 ± 25.3 and 1088 ± 27 mL/d,



Figure 11. Variation in biogas during anaerobic co-digestion from the different HRTs



Figure 12. Variation in methane composition during anaerobic co-digestion from the different HRTs

Table 2. The results of biogas and CH₄ composition in biogas

Reactors	Biogas production (mL/d)	Maximum biogas production (mL/d)	CH4 (%)	Maximum CH ₄ (%)
R1	5-60	60±2.4	13.4-14.7	14.7±0.5
R2	192-398	398±15.5	40.2-43.1	43.1±1.9
R3	271-556	556±25.3	46.0-51.6	51.6±2.3
R4	580-1088	1088±27	47.5-56.8	56.8±2.4

respectively. The methane production is often based on the VS portion of the organic substrates. The results of biogas production and methane composition in the anaerobic co-digestion reactors showed that the addition of decanter cake from the palm oil mill factory had a positive effect on biodegradation due to the high biogas production and the high methane composition. According to the results, increasing the HRT will reduce the biogas production significantly. The R4 (10-d HRT) provided the maximum biogas production because the organic loading per day of R4 was larger than that of R2 and that of R3. The conventional anaerobic digestion is a slow process because it requires more time to digest the organic matter. The slow process results in a large volume of the anaerobic digester and a high cost for construction. In this result, a short HRT for anaerobic co-digestion could lead to a small volume of anaerobic digester and a low construction cost.

Table 2 shows the methane composition from anaerobic co-digestion using the CSTRs. The methane composition ranged from 13.4% to 14.7%, 40.2% to 43.1%, 46.0% to 51.6%, and 47.5% to 56.8% for R1, R2, R3, and R4, respectively. The typical methane composition ranged from 55% to 75% (Troung and Abatzoglou, 2005) From the results, R4 (10-d HRT) provided the maximum methane composition (56.8 \pm 2.4%). However, too long an HRT can cause a decrease in the biogas potential production because the food is not enough for the bacteria. In the anaerobic co-digestion system, the bacteria cannot grow in a starvation situation.

R1, the wastewater from the block rubber factory alone for anaerobic digestion, showed the significantly lowest biogas production and methane composition in the biogas (Figure 11). The methane (CH4) composition in the biogas from the anaerobic co-digestion in R3 and R4 (20-d and 10-d HRT reactors) was in the range of the typical methane composition from anaerobic digestion (Figure 12). The typical methane composition was 55-75% (Karellas *et al.*, 2010). Adding the decanter cake as a co-digestion material for the block rubber factory wastewater can improve the

biogas potential production. Chuchat and Skolpap (2015) observed that the anaerobic co-digestion from poultry slaughter house and food processing wastes without microwave thermal pretreatment provided suitable characteristics for raw material in biogas production. Thus, the co-digestion material is suitable for biogas production. However, too long an HRT of anaerobic co-digestion can cause the potential biogas production to decrease because the bacteria metabolism decreases significantly due to the starvation situation in the system.

Finally, the conclusion can be drawn that the anaerobic co- digestion and variation of HRTs significantly affect the digestibility in the methane production. Nevertheless, the anaerobic co- digestion between wastewater from the block rubber factory and the decanter cake from the palm oil mill factory should be taken into consideration for scaling- up purposes in operating at an industrial scale with continuous systems.

Discussion

The biogas production of wastewater alone shows the lowest biogas production and methane composition. Anaerobic digestion of more than 1 substrate in the same digester could establish positive synergisms. The added organic substrates could support more microbial growth. During mesophilic co-anaerobic digestion of block rubber factory wastewater and decanter cake in the CSTR, the biogas and methane productions increased. The anaerobic co-digestion provided higher biogas production and higher methane composition than that of the block rubber factory wastewater digestion alone. The organic waste stabilization is directly related to the amount of biogas and methane production. The anaerobic co-digestion of various organic wastes increases the biogas production and offers a number of advantages for organic waste management. The main factors for the excellent performance observed from anaerobic co-digestion in this study were the high content of the COD, TS, and TVS of the loading in the reactors containing the wastewater and the

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decanter cake. Such conditions are the sources of food for methanogenic bacteria. The different HRTs have been considered as the potential factors for biogas and methane production. The results for anaerobic co-digestion show the significant impact of the HRT on anaerobic digestion (Kaosol and Sohgrathok, 2014). The HRT ranged from 10-25 d using the completely mixed digester as the CSTR. The best HRT is 10 d for anaerobic co-digestion between the wastewater from the block rubber factory and the decanter cake from the palm oil industry. The 10 d HRT can increase the organic substances in the form of the COD content. The amount of COD removal in the 10-d HRT reactor (R4) was the highest or close to the highest value among the 3 anaerobic co-digestion reactors (R2-R4). The maximum removal of TS and TVS also occurred in R4. The HRT that is too long can cause the biogas potential production to decrease due to the starvation situation of the decreasing bacteria metabolism in the system.

Conclusions

The organic waste stabilization is directly related to the amount of biogas and methane production. The biogas production of wastewater alone shows the lowest biogas production and methane composition. The anaerobic co-digestion provides higher biogas production and higher methane composition than that of the block rubber factory wastewater digestion alone. The anaerobic co-digestion of various organic wastes increases the biogas production and offers a number of advantages for organic waste management. The main factors of the excellent performance observed from anaerobic co-digestion in this study are the high content of the COD, TS, and TVS of the loading in the reactors containing the wastewater and the decanter cake. Such conditions are sources of food for methanogenic bacteria. The different HRTs have been considered as the potential factors for biogas and methane production. The results for anaerobic co-digestion show the significant impact of the HRT on anaerobic digestion (Kaosol and Sohgrathok, 2014). The

best HRT is 10 d for anaerobic co-digestion between the wastewater from the block rubber factory and the decanter cake from the palm oil industry. The 10-d HRT can increase the organic substances in the form of the COD content. The amount of COD removal in the 10-d HRT reactor (R4) is the highest or close to the highest value among the 3 anaerobic co-digestion reactors (R2-R4). Therefore, from the results it can be concluded that co-digestion and the HRT can significantly affect the biogas and methane productions. The HRT affects the amount of methane produced.

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