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EFFECT OF COD LOADING RATE ON AN UPFLOW ANAEROBIC SLUDGE BLANKET REACTOR DURING ANAEROBIC DIGESTION OF PALM OIL MILL EFFLUENT WITH BUTYRATE

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Abstract. Palm oil Mill Effluent (POME) with concentrated butyrate was treated in a 4.5 l upflow anaerobic sludge blanket reactor (UASBR), run over a range of influent concentrations (16.5–46.0 g-COD l^{-1}), chemical oxygen demand (COD) loading rates (1.5–11.5 g-COD$l^{-1}d^{-1}$) and 11–4 days hydraulic retention time (HRT) at 37 °C by maintaining pH between 6.5–7.5. The process consistently removed 97–99% of COD at loading rates up to 1.5–4.8 g-COD $l^{-1}d^{-1}$ by varying HRT (11–7.2 days). Butyrate is an important intermediate in the anaerobic degradation of organic matter. In sulphate-depleted environment, butyrate in POME (BOD/COD ratio of 0.5) is β-oxidised to acetate and hydrogen, by obligate proton reducers in syntrophic association with hydrogen utilizing methanogens. The conversion of acetate to methane appeared to be rate limiting step. Maximum biogas (20.17 $ll^{-1}d^{-1}$) and methane production (16.2 $ll^{-1}d^{-1}$) were obtained at COD loading rate of 4.80 $gl^{-1}d^{-1}$ and HRT of 7.2 days. The biogas and methane production were higher in the presence of butyrate compared to control. The methane content of the biogas was in the range of 70–80% throughout the study while in control it was 60–65%. Finding of this study clearly indicates the successful treatment of POME with butyrate in UASBR.

Keywords: Anaerobic degradation, Palm oil mill effluent, Butyrate, Acetate, UASB reactor.

1. Introduction

Malaysia is the world's largest producer and exporter of crude palm oil (CPO). The total productions of CPO in the year 2008 and 2009 were 17,734,441 and 16,044,874 tonnes, respectively (MPOB 2008). POME is a slimy, viscous and reddish brown liquid with a lot of fine suspended solids, at pH ranging between 4 and 5 (Najafpour *et al.* 2006). POME is a highly polluted effluent due to its high values of COD and BOD. Direct discharge of POME into the environment can cause several pollution problems. Furthermore, with the introduction of effluent discharge standards imposed (BOD of 100 mg/l) by the Department of Environment in Malaysia, POME has to be treated before being released into the environment (DOE 1999).

Over the past 20 years, the techniques available for the treatment of POME in Malaysia, were based on biological treatment, consisting of anaerobic, facultative and aerobic pond systems (Faisal, Hajime 2008). Since the BOD/COD ratio of POME is 0.5, therefore, it can be treated easily by means of anaerobic process (Data for engineers: POME 2004). In anaerobic digestion of POME, complex organic pollutants are degraded to methane and carbon dioxide in discrete steps by the concerted action of several different metabolite groups of microorganisms (Demirel, Scherer 2008; Weiland 2010). Anaerobic digestion has been employed by most palm oil mills as their primary treatment of POME (Poh, Chong 2009). More than 85% of palm oil mills in Malaysia have adopted the ponding system due to its low capital cost (Tong, Jaafar 2004), while the rest opted for open digesting tank (Yeoh 2004; Yacob *et al.* 2005).

Among the high rate anaerobic reactor for the industrial effluent treatment, the use of an upflow anaerobic sludge blanket (UASB) process has gained popularity in recent years, with over 500 installations worldwide (Latif *et al.* 2011a). This is due mainly to the positive energy balance of anaerobic treatment processes and the development of an inexpensive and high rate treatment systems (Misevicius, Baltrenas 2011). In the process of POME degradation into methane, carbon dioxide and water, there is a sequence of reactions involved viz. hydrolysis, acidogenesis (including acetogenesis) and methanogenesis (Bitton 2005; Nwuche, Ugoji 2008, 2010), carried out by different microorganisms (Cote *et al.* 2006) to produce biogas to be used to generate electricity and to save fossil energy (Linke 2006; Ahmad *et al.* 2011a).

Butyrate is one of the major intermediates in the anaerobic degradation of complex organic pollutants (Sheridan *et al.* 2003; Hatamoto *et al.* 2008). During anaerobic treatment of soft-drink waste water, about 60% of glucose was converted to methane via butyrate

(Lau, Fang 1997) and in another case butyrate was mostly (over 80%) converted to methane within 2 and 5 days (Hatamoto *et al.* 2008), while Amani *et al.* (2010) reported that high concentration of butyrate could inhibit methanogenesis. Degradation of propionate and butyrate to methane is initiated by different microbial groups (Chauhan *et al.* 2006). The propionate consortium capable of degrading propionate to methane has been studied extensively in recent years because of energy partitioning among the three metabolic groups participating in methanogenesis. It has been found that none of the butyrate degrading acetogens can degrade propionate, while two independent studies reported that propionate-degrading granules can degrade butyrate (Mechichi, Sayadi 2005).

The present study was carried out to examine the startup performance of UASB reactor, treating POME with concentrated butyrate. The reactor was operated continuously over a period of 90 days and at twelve hydraulic retention times to assess substrate removal efficiency and the volume and composition of the gas produced.

2. Material and Methods

2.1. Experimental Setup

A 4.7 l UASB reactor, made up of plexiglass, was used for this study (Fig. 1). The reactor was equipped with gas collector, gas-biomass-liquid seperator, pH controller and a sampling port. The reactor was jacketed and operated at constant temperature of 37 °C. Biogas pipe was directly connected with gas chromatography (GC) to obtain individual gas contents.

2.2. Sample Collection

POME samples were collected from LHSC-Palm Oil Mill, situated in the state Pahang, Malaysia. It was sieved to remove coarse particles such as fibres, shells and stones. These samples were stored in a refrigerator at 4 °C. The features and composition of the POME used are summarized in Table 1, which shows the average values of five replicate analyses for each parameter and discharge limits for POME into water sources in Malaysia. Sodium bicarbonate ($NaHCO_3$) solution was used to adjust the pH value of POME between 6.5 to 7.5. Nitrogen and phosphorus were added in the form of NH_4Cl and KH_2PO_4 to the influent stream to give a ratio of C:N:P = 350:5:1 by wt. along with $CaCO_3$ (20 mgl^{-1}) to improve granule formation. Some nutrients (in mgl^{-1}) like $FeCl_2.4H_2O$, 5.6; $MnCl_2.4H_2O$, 0.15; $CoCl_2.6H_2O$, 2.3; $ZnCl_2$, 23; $NiCl_2.6H_2O$, 0.12; H_3BO_3, 0.08; $Na_2MoO_4.2H_2O$, 0.085; Yeast extract (100); $CuCl_2.2H_2O$, 0.17 were also added.

2.3. Seed Sludge Formation

Prior to this study, flocculant sludge was taken from commercial anaerobic digester of Feldah Palm Oil treatment plant, located at Lepas Hilir, Pahang in Malaysia. An UASB reactor was incubated with this sludge for one month at 35 °C, using glucose as organic substrate, and the biogas produced collected. During this period the reactor was fed daily with 155 ml of diluted POME. At the end of this period, about one litre quantity of this biomass containing 11,150 mgl^{-1} COD; 4,800 mgl^{-1} BOD; 3,246 mgl^{-1} TS (total solids), and 2,130 mgl^{-1} VSS (volatile suspended solids) was used to seed the experimental reactor. As one litre of seed sludge was introduced into the reactor, the corresponding sludge loading rate was 0.3 g-COD $g^{-1}VSSd^{-1}$.

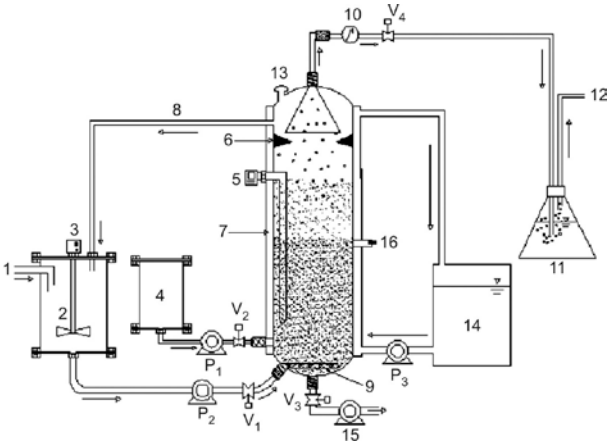

Fig. 1. Experimental setup of UASBR: 1 – Refill pipe, 2 – POME holding tank, 3 – Stirrer motor, 4 – $NaHCO_3$ dosing tank, 5 – pH & temperature indicator, 6 – Baffles, 7 – Water jacket, 8 – Overflow pipe, 9 – Liquid splitter, 10 – Biogas flow meter, 11 – Biogas collection, 12 – Methane gas holder, 13 – Pressure controller, 14 – Hot water tank, 15 – Drain pump, 16 – Sampling point $P_{1–3}$ Peristaltic pumps, $V_{1–5}$ Control valves

Table 1. Physico-chemical Properties of the POME used

Parameter	Concentration (mgl^{-1}) (Mean ± Standard deviation)	Discharge standard (1-1-1984 and thereafter)
pH	4.42 ± 0.12	5.0–9.0
BOD	33000 ± 2806	100
COD	62000 ± 7842	___
TSS	50,000 ± 654	400 as SS
VSS	42230 ± 2806	___
SCOD	37000 ± 1624	___
Oil & Grease	8563 ± 2560	50
TN	1312 ± 55	200*
NH_3-N	94 ± 9.165	150*

All parameters are in units of mgl^{-1} except pH

*****Value of filtered sample.

2.4. Reactor Operation: COD and HRT

The initial COD loading rate was 1.5 g $l^{-1}d^{-1}$, corresponding to influent concentration of 16.5 g-COD l^{-1} and HRT of 11 days. The influent concentration was increased stepwise from 16.5 to 17.5, 18.0, 19.5, 20.5, 23.5, 27.5, 31.5, 34.5, 38.5, 42.5, 46.0 g-COD l^{-1}. The COD loading rate was kept low at early stages, because overloading may cause acid accumulation in the digester. This results in "sour condition", resposible for the reduction of pH and treatment efficiency, while underloading leads to low gas production.

The pH of the reactor was maintained in the range of 6.5–7.5 by dosing sodium bicarbonate. The reactor was continously fed with the influent containing butyrate as a sole organic substrate by peristaltic pump, with a flow rate capacity of 4.8 lh^{-1}. During the experimental period the reactor was monitored for COD (total) and SCOD (soluble) removal efficiencies, biomass concentration, pH, methane production and volatile fatty acids (VFA) cocentration in the effluent. The loading rate of the reactor was enhanced by increasing the butyrate concentration in the influent (Table 4).

2.5. Chemical Analysis

The analyses of all samples were carried out in accordance with the American Public Health Association (APHA, 1995). COD was measured by direct digestion method using HACH-DR 5000 apparatus high range (435HR program), and the biogas yield with a wet gas meter (W-NK-O.SA, Shinagawa). Gas samples were obtained through an inverted funnel placed above baffles near the top of the reactor. Biogas composition was determined using a gas chromatograph (GC-8A, Shimadzu, Kyoto) with a thermal conductivity detector equipped with a steel column packed with WG-100 (GL Sciences, Tokyo) at 50 °C. Volatile fatty acids were determined with a gas chromatography (W-NK-O.SA, Shinagawa), equipped with a 2m × 4mm glass column packed with Suplocopor (100–120 mesh) coated with 10% Fluorad FC 431. The temperatures of the column, injection port and flame ionisation detector, were 130, 220 and 240 °C, respectively.

Effluent and biogas production rate were measured and analysed weekly, while biomass concentration was analysed bi-weekly for each loading rate.

3. Results

3.1. Characterization of control digester

Control treatment of POME was carried out in two control digesters. The loading rate of control digester was enhanced by increasing influent POME concentration (without infusing butyrate). COD removal efficiencies, biogas and methane production values used in this report were average of those from two control digesters (Table 2). Daily differences between the two digesters rarely exceeded 9% for these values.

3.2. Anaerobic degradation of POME by adding butyrate

3.2.1. COD Removal Efficiency

The COD and SCOD removal efficiencies were in the range of 73–99% and 61.42–87.18% (Table 3). These removal efficiencies were higher compared to control (70–96%, 58–79%). The COD and SCOD removal efficiencies were increased up to 97% and 77% during the first two weeks at COD loading rate of 1.5–1.59 $gl^{-1}d^{-1}$ and HRT of 11days but in the third week, the COD and SCOD removal efficiencies reduced to 17.8% and 16.38% at the COD loading rate of 1.64 $gl^{-1}d^{-1}$ and HRT of 11. Then it again started enhancing with the increase in COD loading rate and found to be maximum of 99% and 87.18% at the COD loading rate of 4.8 $gl^{-1}d^{-1}$ and HRT of 7.2 d from the day 71 to 74. When the COD loading rate was increased to 6.01 $gl^{-1}d^{-1}$, the COD and SCOD removal efficiency was sharply reduced to 82% and 72.3%. At loading rate of 7.33 $gl^{-1}d^{-1}$, the COD and SCOD removal efficiency again decreased to 73% and 68.42% but when the COD loading rate was increased 11.5 $gl^{-1}d^{-1}$, it again picked the level up to 85% and 73.56% and after that it became steady.

Table 2. Results of control experiment obtained at each loading after steady state condition during anaerobic treatment

Days	Influent COD Concentration (mgl^{-1})	COD loading rate ($g1^{-1}d^{-1}$)	HRT (days)	COD removal efficiency %	Biogas production ($ll^{-1}d^{-1}$).	Gas composition (CH_4 %).
1–4	16500	1.5	11	80.2 ± 0.05	1.98 ± 0.2	60
5–10	17500	1.59	11	82.7 ± 0.04	9.25 ± 0.2	63
11–21	18000	1.64	11	85.3 ± 0.07	10.19 ± 0.3	61
22–33	19500	1.77	11	91.6 ± 0.03	11.85 ± 0.3	60
34–50	20500	1.97	10.6	94.4 ± 0.07	12.03 ± 0.1	64
51–56	23500	2.22	10.4	96.0 ± 0.01	12.39 ± 0.2	65
57–65	27500	2.93	9.4	95.3 ± 0.07	12.01 ± 0.3	63
66–70	31500	3.67	8.6	89.1 ± 0.08	11.73 ± 0.2	60
71–74	34500	4.80	7.2	83.0 ± 0.07	9.18 ± 0.3	59
75–80	38500	6.01	6.4	79.7 ± 0.03	7.50 ± 0.2	57
81–85	42500	7.33	5.8	72.0 ± 0.08	6.97 ± 0.2	54
86–90	46000	11.5	4.0	70.2 ± 0.06	6.32 ± 0.2	52

Results are mean of 10 values ± standard error of the mean (SEM).

3.2.2. Volatile Fatty Acid

In this study VFA in digester was in the range of 905.45–1192 mg l^{-1} (Table 3) while in control digester VFA was found in low concentration (851–1050 mg l^{-1}). Since VFA concentrations increased gradually, therefore, no reduction in COD removal efficiency and biogas production was observed except at COD loading rate of 1.64. At this loading rate COD removal efficiency dropped from 97.8 to 80% with the 18.8% decrease in biogas production. During the first few weeks, when the biomass population was small, and the methanogenic activity minimal, a little fatty acid accumulation was observed in the lower part of the reactor. But from the 22 days onwards, with the increase in loading from 1.64–1.77 and HRT of 11 days, it gradually recovered and reached 98% and finally to a maximum of 99% at COD loading rate of 4.8 g-$CODl^{-1}d^{-1}$. Effluent VFA was in the range of 120–27 mgl^{-1}(Fig. 2). Figure 3 shows the reduction in effluent acetic acid and butyric acid during start up. Acetic acid in the effluent was found to be decreased from 44 to 10 mgl^{-1} while butyric acid from 40 to 05 mg l^{-1} with in the same period of time. At the same

time, the pH of the effluent gradually increased from 6.6 to 7.8 because of VFA reduction.

Table 3. Experimental results obtained at each loading after steady state condition during anaerobic treatment (POME with butyrate)

Days	A	B	C	D	E	F	G
1–4	905.45 ± 1.25	4992.32 ± 2	0.1814 ±0.01	73 ± 1	2.71 ± 0.3	97.0 ± 0.08	70.12 ± 0.08
5–10	926.24 ± 1.16	4997.26 ± 1	0.1854 ± 0.01	78 ± 1	9.25 ± 0.2	97.8 ± 0.07	77.80 ± 0.06
11–21	978.53 ± 1.15	4878.69 ± 1	0.2000 ± 0.01	70 ± 1	5.11 ± 0.2	80.0 ± 0.08	61.42 ± 0.07
22–33	1023.24 ± 1.10	4387.42 ± 2	0.2340 ± 0.01	72 ± 1	12.82 ± 0.3	98.0 ± 0.06	82.00 ± 0.06
34–50	1057.68 ± 2.12	4246.85 ± 3	0.2490 ± 0.01	74± 1	15.93 ± 0.2	97.6 ± 0.07	75.90 ± 0.08
51–56	1071.39 ± 2.08	4195.73 ± 1	0.2553 ± 0.01	75 ± 2	17.24 ± 0.2	98.1 ± 0.08	80.50 ± 0.07
57–65	1085.59 ± 1.16	4072.65 ± 3	0.2665 ± 0.01	75 ± 1	19.71 ± 0.2	98.3 ± 0.09	85.80 ± 0.06
66–70	1120.38 ± 2.06	3997.96 ± 4	0.2802 ± 0.01	80 ± 1	19.82 ± 0.3	98.7 ± 0.07	84.70 ± 0.06
71–74	1148.73 ± 1.12	3782.47 ± 3	0.3036 ± 0.01	77 ± 2	20.17 ± 0.2	99.0 ± 0.07	87.1± 0.09
75–80	1163.94 ± 2.19	3698.79 ± 1	0.3146 ± 0.01	76 ± 2	17.80 ± 0.2	82.0 ± 0.06	72.30 ± 0.08
81–85	1178.58 ± 2.16	3569.23 ± 1	0.3302 ± 0.01	73± 1	14.87 ± 0.3	73.0 ± 0.09	68.42 ± 0.07
86–90	1192.64 ± 2.15	3259.35 ± 2	0.3603 ± 0.01	71 ± 1	13.42 ± 0.2	85.0 ± 0.08	73.56 ± 0.09

Results are mean of 10 values ± standard error of mean (SEM)
(A): Total VFA concentration in UASBR (mgl^{-1}, as acetic acid).
(B): Alkalinity ($mgNaHCO_3\,l^{-1}$).
(C): TVFA/Alkalinity
(D): Gas composition (CH_4 %).
(E): Biogas production ($ll^{-1}d^{-1}$).
(F): COD removal efficiency %
(G): SCOD removal efficiency %

3.2.3. Alkalinity and VFA:Alk ratio fraction in UASBR

The alkalinity of the system was in the range of 3259–4993 mgl^{-1}, which fell in the range of 2,500–5000 mgl^{-1} (Patel, Madamwar 2002). The VFA:Alk fraction ratio of UASBR was found in the range of 0.1814–0.3603 from 11 to 4 days of HRT. The alkalinity and ratio fraction between VFA and alkalinity of UASBR at various HRT is outlined in Table 3. The alkalinity concentration of UASBR increased from 3259 mg-$NaHCO_3$ l^{-1} to 4992.32 mg-$NaHCO_3$ l^{-1} by HRT of 4 to 11 days. For control digester VFA:Alk was also found < 0.4 (data not shown). Thus, the VFA:Alk ratio was found to be on conserved trends as the VFA:Alk increased with the decrease of HRT.

3.2.4. TSS and VSS

There was a net increase in VSS concentrations in the reactor as shown in Table 4. The increase in VSS concentration indicates healthy sludge growth. During start up period, a small increase in concentration was due to sludge loss, afterwards a considerable increase in VSS was observed in the lower region of the reactor.

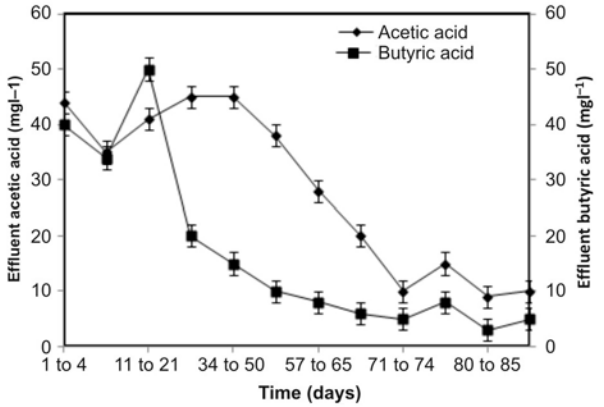

Fig. 2. Effluent acetic and butyric acid concentrations during the start-up period

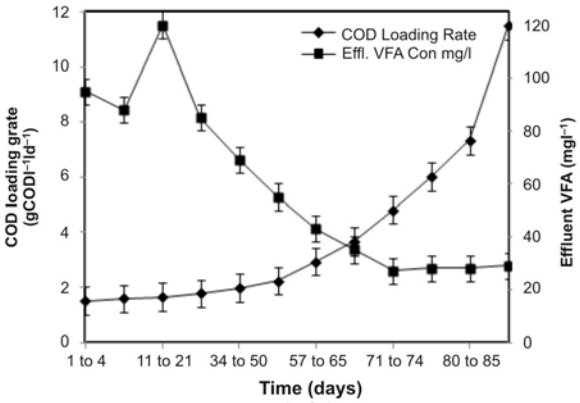

Fig. 3. Effect of COD loading rate on effluent VFA concentration

Maximum removal of TSS and VSS was obtained at COD loading rate of 4.80 $gl^{-1}d^{-1}$and HRT 7.2 days. A noticeable increase in VSS in the lower region of the reactor was observed only after the influent concentration increased to 16.5 gl^{-1} corresponding to a COD loading rate of 1.5 g COD gl^{-1} day^{-1}. The increase the influent concentration increased to 19.5 gl^{-1} corresponding to a COD loading rate of 1.7 g COD gl^{-1} day^{-1}. This value is very close to the optimum value of 0.6 g COD g^{-1} VSS^{-1} day^{-1} for biomass growth (Ahmad *et al.* 2011b). During start up, effluent total suspended solids were in the range of 1.38–1.72 gl^{-1} (Table 4) but as organic loading rate increased effluent TSS were also increased to 2.06 gl^{-1}, thus, showing that COD loading rate affects the TSS removal. Meanwhile, effluent VSS showed a similar removal tendency as TSS where, effluent VSS were 1.21–1.80 gl^{-1} at startup which further increased to 1.90 g/l till end of experiment.

3.2.5. Biogas and Methane Production

The biogas production and g-COD removal at the steady state were analysed every day and it was found that one kg-COD removed can produce 480 litres of biogas, 325 litres of methane. The course of biogas production with butyric acid reduction in the effluent is shown in Figure 4.

Table 4. Biomass quantities (VSS &TSS) in UASB reactor and effluent (POME with butyrate)

Days	Added butyrate concentration gl^{-1} POME	Influent COD Concentration (mgl^{-1})	COD loading rate ($g1^{-1}d^{-1}$)	HRT (days)	Sludge in digester (g VSS)	Effluent (g VSS l^{-1})	Effluent TSS (gl^{-1})
1–4	0.5	16 500	1.5	11	30.23 ± 2	1.21 ± 0.01	1.38 ± 0.03
5–10	0.5	17 500	1.59	11	33.45 ± 1	1.30 ± 0.03	1.45 ± 0.02
11–21	1.0	18 000	1.64	11	38.78 ± 1	1.38 ± 0.01	1.56 ± 0.02
22–33	1.5	19 500	1.77	11	40.30 ± 2	1.50 ± 0.02	1.72 ± 0.03
34–50	2.0	20 500	1.97	10.6	46.49 ± 1	1.80 ± 0.02	2.06 ± 0.01
51–56	2.5	23 500	2.22	10.4	48.72 ± 2	1.60 ± 0.02	1.91 ± 0.02
57–65	3.0	27 500	2.93	9.4	50.33 ± 2	1.68 ± 0.01	1.80 ± 0.02
66–70	3.5	31 500	3.67	8.6	53.08 ± 1	1.53 ± 0.03	1.72 ± 0.03
71–74	4.0	34 500	4.80	7.2	58.05 ± 2	1.05 ± 0.01	1.20 ± 0.02
75–80	5.0	38 500	6.01	6.4	60.56 ± 3	1.63 ± 0.02	2.23 ± 0.01
81–85	5.5	42 500	7.33	5.8	62.23 ± 1	1.59 ± 0.02	2.040.02
86–90	6.0	46 000	11.5	4.0	66.39 ± 2	1.90 ± 0.01	2.05 ± 0.02

Results are mean of 10 values ± standard error of the mean (SEM).

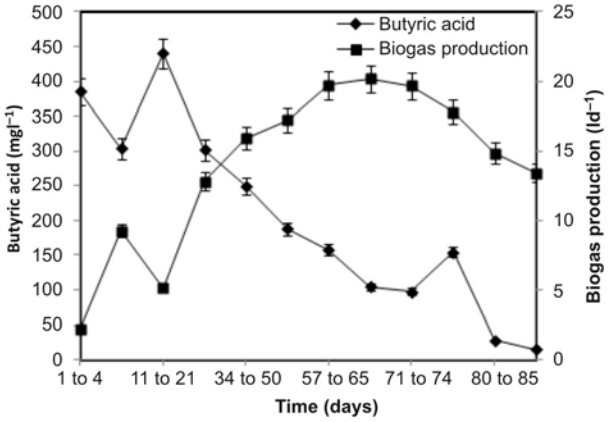

Fig. 4. Course of biogas production with butyric acid reduction in the effluent

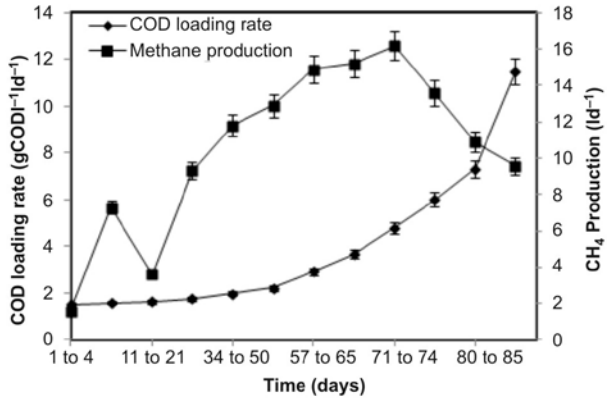

Fig. 5. Effect of COD loading rate on methane production with time

The methane content range was 70–80% throughout this study which was higher than that in control (52–65%) (Table 2). Figure 5 shows that volumetric methane production increased with the COD loading rate up to 4.80 $gl^{-1}d^{-1}$. Reduction in biogas was oberved at COD loading rate of 1.64 $gl^{-1}d^{-1}$ due to accumulation of volatile fatty acids during the second week of start up. Maximum biogas production was achieved at COD loading of 4.80 $gl^{-1}d^{-1}$ and HRT of 7.2 days and decreased by inreasing the COD loading rate to 11.5 $gl^{-1}d^{-1}$.

4. Discussion

4.1. COD Removal Efficiency

The COD removal efficiency of an UASB reactor is slightly affected by hydraulic retention time or insensitive to either HRT or COD level in the wastewater (Shin *et al.* 2001). It was, in general, dependent on the COD loading rate. The decline in the COD removal efficiency at COD loading rate of 6.01 $gl^{-1}d^{-1}$, was mainly due to the accumulation of acetate in the effluent. Butyrate was degraded by acetogenic bacteria into acetate (CH_3COO^-) and hydrogen (H_2) (eq. 1), with 1 gram of butyrate COD converting into 0.8 g acetate COD and 0.2 g H_2 COD. Acetate can be converted to CH_4 via acetoclastic methanogens (eq. 2) and hydrogen to combine with CO_2 to form CH_4 using hydrogenotrophic methanogens (eq. 3). The high concentration of acetate and absence of butyrate in the effluent seems to indicate that in the degradation of butyrate (Table 5), the conversion of acetate to methane is the rate-limiting step (Weathers, Parkin 2000). A similar observation was also reported by Ahring and Westermann (1987) for a continuous culture. The drop in COD removal efficiency with the increasing organic loading rate was also reported by Rajeshwari *et al.* (2000), Nadais *et al.* (2005) and Hampannavar, Shivayogimath (2010). Thus, with the controlled pH and temperature, a high COD reduction was achieved as compared to uncontrolled system (Rajeshwari *et al.* 2000).

Thus, the results obtained indicate that at the COD loading rate of 4.8 $gl^{-1}d^{-1}$, higher was the COD removal efficiency and lowest was the effluent VFA concentration along with the increase in biogas production.

Table 5. Reactions involved in anaerobic degradation of butyric acid

Acetogenesis

$CH_3CH_2CH_2COO^- + 2H_2O \longrightarrow 2CH_3COO^- + 2H_2 + 2H^+$

(ΔG_{37}^0 = +86.0 KJ/mol of butyrate) (1)

Methanogenesis

$2CH_3COO^- + 2H^+ \longrightarrow 2CH_4 + 2CO_2$

(ΔG_{37}^0 = –159.1 KJ/mol of butyrate) (2)

$2H_2 + 0.5\ CO_2 \longrightarrow 0.5CH_4 + H_2O$

(ΔG_{37}^0 = –63.0 KJ/ mol of butyrate) (3)

Overall Butyrate Degradation

$CH_3(CH_2)_2COO^- + H_2O + H^+ \longrightarrow 2.5CH_4 + 1.5\ CO_2$

(ΔG_{37}^0 = –136.1 KJ/mol of butyrate) (4)

4.2. Volatile Fatty Acid

VFA in the digester should be lower otherwise it would be toxic to the system. When VFA value increases drastically, indicates a slow conversion of VFA by methanogens (Basri *et al.* 2010), causes deterioration of the system. In this experiment VFA range was 905.45–1192 mg l^{-1} (Table 3). The result of fatty acid accumulation is typical to those, expected during the start up, where the response of the acid-producing fraction of the microbial consortium is always more rapid than that of the methanogens, due to step-wise increase in substrate loading (Mustapha *et al.* 2003). Several cases of reactor failures, in the studies of wastewater treatment, are due to accumulation of high concentration of volatile fatty acids. This causes a drop in pH, which inhibits methanogenesis (Parawira *et al.* 2006). It was found that digester could tolerate the concentration of acetic acid up to 4000 mgl^{-1} without inhibiting gas production (Latif *et al.* 2011a). In this study the acetic acid concentration was found up to 1193 mgl^{-1} which was suitable for digester. The pH range 6.5–7.5 was optimal for bacterial growth and COD removal efficiency (Poh *et al.* 2010). According to Lesile Grady *et al.* (1999), the sensitivity of methanogenic bacteria to the pH were coupled with the VFA, which are the intermediates of the anaerobic stabilization of organic matter, bring about the negative response by the anaerobic system. Thus, the concentration of volatile fatty acid is an important parameter to monitor and guarantee to the reactor performance (Buyukkamaci, Filibeli 2004).

4.3. Alkalinity and VFA:Alk ratio fraction in UASBR

In this study, the alkalinity was used in the terms of $NaHCO_3$, similar to Krisch and Sykes (1971), who recommended $NaHCO_3$ to control pH dissolving easily and providing bicarbonates directly to the system. However, it is expensive than other chemicals.

According to Zhao and Viraraghavan (2004) the proper ratio for volatile acid to alkalinity should range between 0.1 to 0.2 for anaerobic digestion process. In this study, the VFA:Alk ratio of UASBR was in the range of 0.1814–0.3603 from HRT of 11 to 4 days. The VFA:Alk ratio, for the stability of anaerobic digestion process, must be < 0.4, hence the digestion process was cosidered to operate without acidification risk (Rapso *et al.* 2004). As a result, the performance of UASBR could maintain methanogenic activity (by keeping low VFA concentration). Therefore, adequate alkalinity or buffer capacity was essential to maintain a stable pH in the digester for optimal biological activity (Agdag, Sponza 2005).

4.4. TSS and VSS

Since there was a net increase in VSS concentration in the reactor, as shown in Table 4, indicating the active biomass growth. A very high COD removal efficiency, shown by UASB reactor, was thought to be promoted by the rapid and stable production of an active biomass, which could be retained in the system due to its excellent settlement qualities. This was due to the fact of accumulation and retention of biomass in the reactor by showing high VSS concentrations, and finding low VSS concentrations in the effluent.

4.5. Biogas and Methane Production

It has been observed that increasing organic loading rates contribute to high biogas production (Basri *et al.* 2010). However, the gas production will increase with COD loading rate till a stage where methanogens could not work quick enough to convert acetic acid to methane (Latif *et al.* 2011a). Methane production increased linearly with the COD loading rate up to 1.77 to 4.80 $CODl^{-1}d^{-1}$. Tantrakarnap (2003) achieved 552 litres of biogas with one kg-COD, which was higher than this study. Methane production rate in the range of 79–80%, using liquid fraction of hen manure waste in UASB reactors, was reported by Kalyuzhnyi *et al.* (1998) and treating brewery wastewater in the range of 79–81% was reported (Latif *et al.* 2011b).

Thus, the methane content obtained by adding butyrate in POME was higher compared to control. The high content of methane in the biogas indicates the complete fermentation and the loss of CO_2 in the dissolved form in the effluent.

5. Conclusions

POME is always regarded as a highly polluting wastewater generated from palm oil mills. UASBR technology is capable of producing a higher quality effluent that can successfully meet the increasingly stringent effluent discharge standards set out in the Environmental Quality Act, 1974. The use of POME as a renewable energy resource can improve energy security while reducing the environmental burdens of waste disposal.The key findings are:

1. An upflow anaerobic sludge blanket (UASB) reactor resulted in successful treatment of POME with butyrate at 37 °C. Addition of butyrate in POME improved methane production compared to control.

2. COD loading rate was an important operating parameter that affected the COD removal. Influent concentration was increased step-wise after achieving the low VFA concentration in the reactor.

3. With the controlled pH and temp, more COD reduction and biogas production were achieved. Thus, anaerobic digestion of POME with butyrate in UASBR appeared an efficient treatment method by achieving 99% COD removal and 20.17 $l^{-1}d^{-1}$ biogas production at loading rate of 4.80 g-COD$l^{-1}d^{-1}$ and HRT of 7.2 days. In this respect, this technology shows a promising option to improve the effluent quality.

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SUVARTOJAMO ChDS POVEIKIS PALMIŲ ALIEJAUS GAMYBINIŲ NUOTEKŲ SU BUTIRATU ANAEROBINIO PŪDYMO PLOKŠTELINIAME REAKTORIUJE METU

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Santrauka

Palmių aliejaus gamybinės nuotekos (*POME*) su koncentruotu butiratu buvo apdorotos 4,5 *l* talpos aukštyn tekančio aerobinio dumblo plokšteliniame reaktoriuje (*UASBR*). Nuotekos tekėjo įvairių koncentracijų (16,5–46,0 g – ChDS 1^{-1}), cheminio deguonies suvartojimo (ChDS) normos (1,5–11,5 g – ChDS $1^{-1}d.^{-1}$). Hidraulinio sulaikymo trukmė (*HRT*) nuo 11 iki 4 dienų, kai temperatūra 37 ^{o}C, pH palaikant 6,5–7,5. Vykstant procesui nuolat buvo pašalinama 97–99 % ChD, kai tiekimo ir pakrovimo sparta 1,5–4,8 g – ChDS $1^{-1}d.^{-1}$ kintant *HRT* (11–7,2 d.). Butiratas yra svarbus tarpininkas organinių medžiagų anaerobinio skilimo procese. Sulfatas iš aplinkos, butiratas iš *POME* (BDS/ChDS santykis 0,5) yra acetato ir vandenilio β oksidatoriai, priverčiantys protonų reducentus sintrofinės sąveikos su vandeniliu metu utilizuoti metanogenus. Acetato virtimas metanu pasirodė esąs greitį ribojantis veiksnys. Daugiausia biodujų (20,17 *l* 1^{-1} $d.^{-1}$) ir metano (16,2 *l* 1^{-1} $d.^{-1}$) susidarė tada, kai suvartojamo ChD tiekimo greitis buvo 4,80 g $1^{-1}d.^{-1}$, o *HRT* – 7,2 dienos. Daugiau biodujų ir metano susidarė dalyvaujant butiratui, palyginti su kontroliniu pavyzdžiu. Biodujose metano kiekis tyrimo metu svyravo 70–80 %, o kontroliniame buvo 60–65 %. Šis tyrimas aiškiai parodė, kad *POME* su butiratu *UASB* reaktoriuje apdorojamas sėkmingai.

Reikšminiai žodžiai: anaerobinis skilimas, palmių aliejaus gamybinės nuotekos, butiratas, acetatas, *UASB* reaktorius.

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