CHAPTER 4

RESULTS AND DISCUSSION

4.1 Palm Oil Mill Effluent (POME) Characteristics

In this study, the POME wastewater mainly contains high content of degradable organic matter with the characteristics is shown in Table 4.1.

Table 4.1: Characteristics of palm oil mill effluent (POME).

Parameter	Concentration range (mg/L)	Mean (*)
pH	4.25 – 4.48	4.34 ± 0.09
COD	75000 – 80000	77500 ± 3535.53
SCOD	37500-40000	38750±1767.77
BOD	20000-23400	21059±1028.29
VFA(as acetic acid)	8500 – 10000	9360 ± 581.33
Alk	5000 – 5500	5260 ± 150.55
TS	40000-43550	42050±1119.52
TVS	32500-38700	35460±2161.38
SS	26250-28920	27924±1948.86
O&G	3167 – 5193	4424 ± 1097.85
NH_3-N	400 – 490	436 ± 35.62

Unit for all parameter is mg/l except pH. * Each value obtained is an average of ten replicates. ± shows standard deviations among replicates.

4.2 Acclimatization Phase of SCAR

In this research study, pH, microbial growth, COD of effluent, COD removal efficiency, VFA, Alk, biogas production rate and biogas composition were used as the indicators that supply complimentary information of the anaerobic degradation process in the acclimatization phase of SCAR.

4.2.1 pH Variation during the Acclimation Process of SCAR

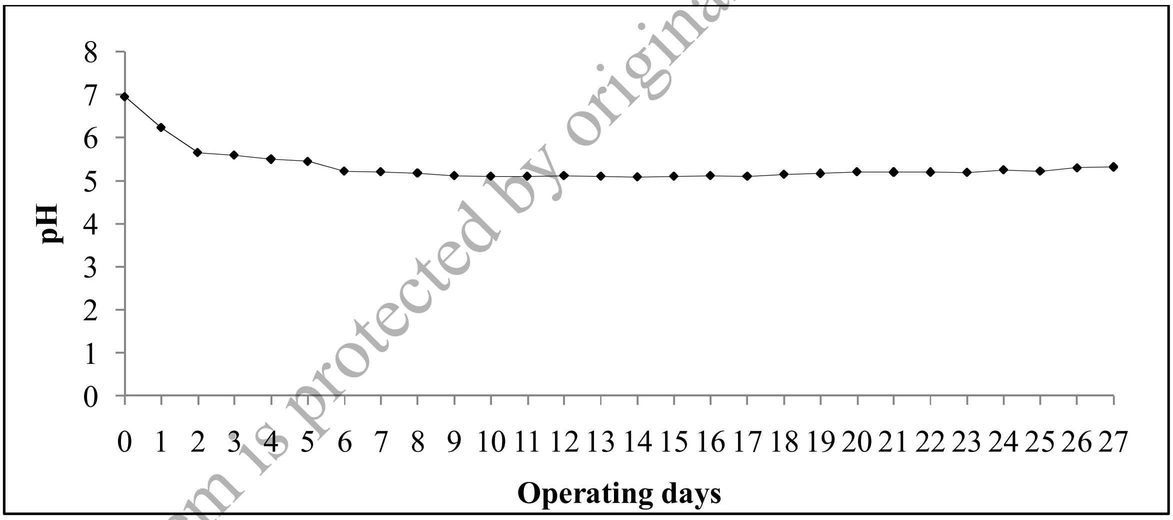

Figure 4.1: pH variation of suspended closed anaerobic reactor (SCAR) during the acclimation phase

The pH variation during the acclimation process is illustrated in Figure 4.1. The initial pH of the anaerobic digested POME wastewater from anaerobic pond was at 6.95. Throughout this acclimation process, the SCAR was loaded at 6.25-6.67 kg COD/m^3/day, which corresponds to HRT of 12 days.

According to Figure 4.1, the pH drop showed a distinct trend towards acidification. The pH decreased from 6.95 to 5.11 in the case of HRT of 12 days of 6.25-6.67 kg COD/m^3 day on operation days between 0 and 10 days, which is similar with the findings (pH drop from 6 to 4.3 for wastewater) reported in the literature (Venkata Mohan, S. *et al*., 2008). The pH shift towards acidic side in anaerobic microenvironment was an index of VFAs generation in alliance with the existing buffering capacity (Alk) of the system (Irene, S. and Charles, B., 2005). At the same time, this indicates that the acidogenesis phase had occurred in the SCAR because of the pH drop from 6 to 5 was generally considered as an optimum range for both effective functioning of acidogenic bacteria and inhibition of the methanogenic bacteria activity (Ginkel, S.V. and Logan, B., 2005). For the next 17 days, the pH values showed fluctuation between 5.09 and 5.32 within the optimum pH range for the growth of acidogenic bacteria. Fang and Liu (2002) had stated that the optimum range for all acidogenic bacteria was below 6.0 pH. Hence, this can prove that the SCAR had already reached steady state of the anaerobic digestion process and the acidogenic activity had started to proceed optimally within this pH range.

4.2.2 Microbial Growth Variations during Acclimation Process of SCAR

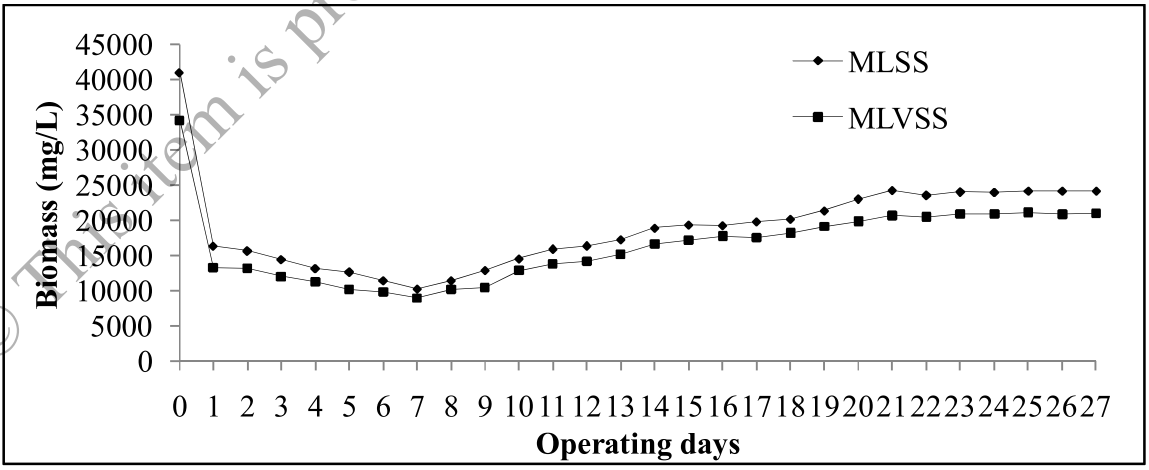

Figure 4.2: Microbial growth of the SCAR during acclimation process.

The mixed liquor volatile suspended solid (MLVSS) inside the SCAR was analyzed as the microbial growth or biomass concentration. In the meantime, the mixed liquor suspended solids (MLSS) was also measured for investigation of fraction ratio between

MLVSS and MLSS. The microbial growth variation during the acclimation process is illustrated in Figure 4.2. The initial MLVSS and the VSS:SS ratio of the anaerobic digested POME wastewater from anaerobic pond were 34190 mg/L and 0.8, respectively. After 7 days of operation, the MLVSS concentration decreased to 8940 mg/L. This is because the pH of the SCAR was reduced due to VFAs production. It is known that VFAs can cause microbial stress if present in high concentrations, resulting in a depletion of buffering capacity and a depression of pH to levels that also inhibit the hydrolysis and acidogenesis phase as mentioned at Section 2.5 (Palmisano, A.C. and Barlaz, M.A., 1971). Moreover, Van den Heuvel, J.C. (1992) had stated that inhibition of the fermentative bacterial population by its main product VFAs when using glucose as the main substrate as stated at Section 2.7. At the same time, the VSS:SS increased to 0.87 in the reactor.

From the 7th until 21st days of operation, the biomass increased progressively from 8940 mg/L to 20680 mg/L whereas the VSS:SS ratio decreased from 0.87 to 0.85. The gradually increase of biomass was due to the presence of acidogenic bacteria in the mixed liquor which started to slowly acclimatize to the new environment since the pH of SCAR was in the range of 5.09 and 5.21. This is because the reactor was operated at a pH of below 6.0 to facilitate the proliferation of acidogenic (Ginkel, S.V. and Logan, B., 2005). For the next 6 days, the biomass concentration fluctuated between 20480 mg/L and 21100 mg/L. This value was lower than those (28402.4 mg/L) reported in the study of anaerobic bench scale reactor (Wong, Y.S. *et al.*, 2009). Meanwhile, the VSS:SS ratio was constant at 0.87 during this period. Therefore, the acclimatization period of SCAR had accomplished.

4.2.3 COD Variations during Acclimation Process of SCAR

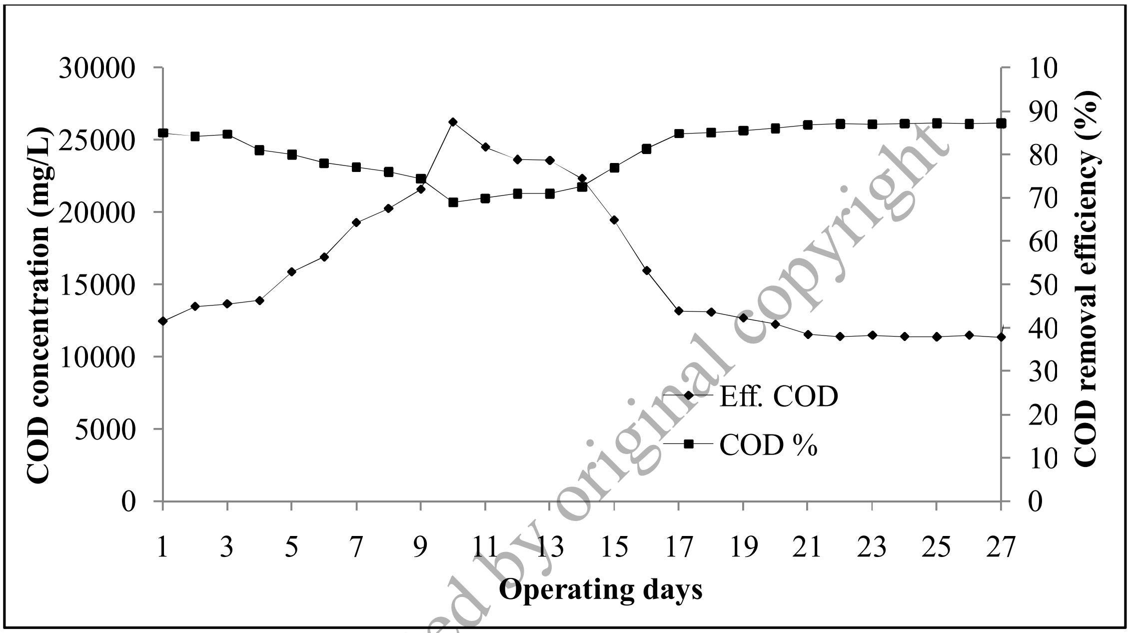

Figure 4.3: COD concentration of effluent and removal efficiency of SCAR during acclimation process.

The SCAR effluent COD concentration and removal efficiency during the acclimation process are demonstrated in Figure 4.3. During this study, the COD concentration of influent POME wastewater was between the range of 75000 mg/L to 80000 mg/l. Throughout this acclimation process, the SCAR was loaded at 6.25-6.67 kg COD/m^3/day, which corresponded to hydraulic retention time (HRT) of 12 days. Based on Figure 4.3, the effluent COD sharply increased from 12475 mg/L to 26250 mg/L during the operation of 1st to 10th days. Meanwhile, the COD removal efficiency gradually reduced from 84.93% to 68.93 % between 1st and 10th. This is because the VFAs concentration of the SCAR was steeply increased during this period as mentioned in Section 4.2.4. George, T *et al.* (1993) have stated that the COD of wastewater will increase significantly during the acidogenesis phase because of the dissolution of the VFAs in the wastewater. Besides that, a number of inorganic constituents and essential nutrients will be solubilized during the acidogenic phase due to the low pH values in the wastewater (George, T., Hilary, T. and

Samuel V., 1993). It is known that VFAs can cause a depletion of buffering capacity and a depression of pH to levels that inhibit the hydrolysis/acidogenesis phase if present in high concentrations as mentioned in Section 2.7 (Palmisano, A.C. and Barlaz, M.A., 1971). Moreover, it had been reported that even though process pH was fixed at the optimal range, the accumulation of VFAs may contribute to a reduced rate of hydrolysis of the solid organic substrate as stated in Section 2.7 (Banks, C.J. and Wang, Z., 1999).

From 10th until 22nd day of operation, the effluent COD rapidly reduced to 11400 mg/L. However, the COD removal efficiency was progressively increased to 87 %. This condition shows that the acidogenic bacteria inside SCAR growth well since the pH of SCAR was in the range of 5.09 and 5.21. The optimum pH range for the acidogenic bacteria growth well was below pH 6 (Ginkel, S.V. and Logan, B., 2005). The system reached its stability from the 22nd to 27th day of operation with the fluctuating of the effluent COD between 11375 mg/L and 11500 mg/L and COD removal efficiency between 86.93 % and 87.19 %. This SCAR had shown that the COD removal efficiency under HRT of 12 days was between 86.93 % and 87.19 %, which was approximately identical with COD removal efficiency (around 80 %) from the extracted sunflower flour wastewater by a mesophilic anaerobic fluidized-bed reactor (Rafael, B. et al., 2001). Furthermore, this value was consistent with the findings (<95 % at HRT of 13 days) of the studies of Yacob, S. *et al.* (2006b) for the POME.

4.2.4 Volatile Fatty Acid (VFA) and Alkanity (Alk) Variations during Acclimation Process

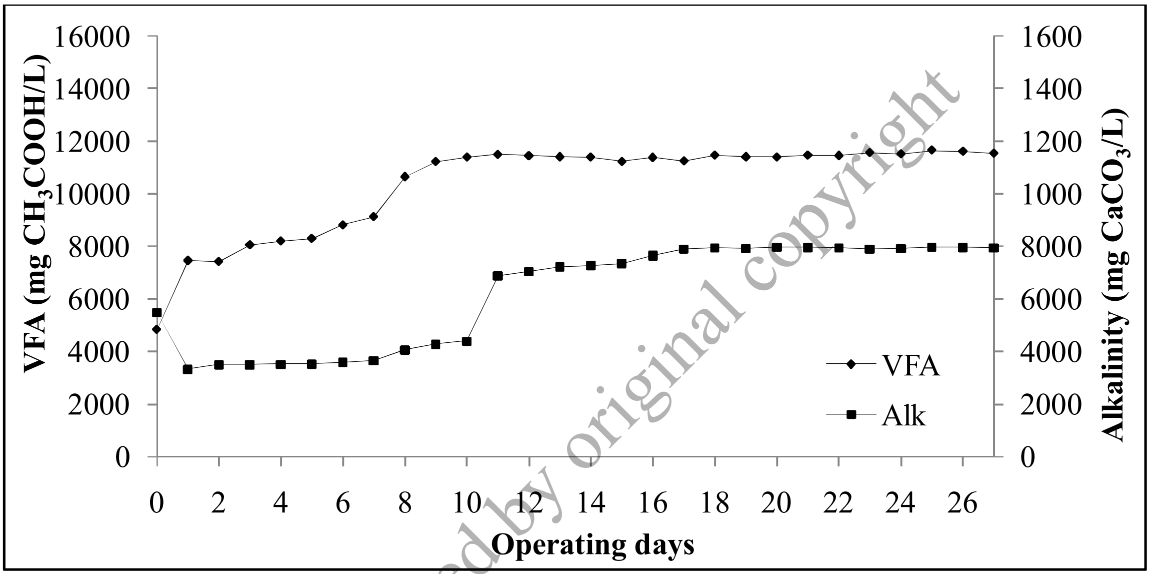

Figure 4.4: Volatile fatty acid (VFA) and Alkanity (Alk) of SCAR during acclimation process.

The concentration of VFA is a main consideration for high-quality performance of an anaerobic digestion process, hence it is essential to examine optimum conditions and the efficiencies of digesters by examining VFA. The Alk represents the buffering capacity of anaerobic degradation system. Figure 4.4 depicts VFA as acetic acid and Alk produced during the acclimation operation. For 11 days of operation, VFA concentration increased sharply from 4834 mg CH_3COOH/L to 11485.71 mg CH_3COOH/L. These steep increases of VFA concentration inside SCAR showed that the complex organic materials of POME were being hydrolyzed and fermented by rapidly growing and pH-insensitive acidogenic bacteria into VFAs as discussed in Section 2.7 (Siegrist, H. *et al.*, 1993).

After one day of operation, the Alk decreased rapidly from 5480 mg $CaCO_3/L$ to 3330 mg $CaCO_3/L$ due to VFAs production. It is known that VFAs can cause a depletion of buffering capacity as mentioned in Section 2.7 (Palmisano, A.C. and Barlaz, M.A., 1971).

After 9 days of operation, the Alk gradually increased from 3330 mg $CaCO_3$/L to 4390 mg $CaCO_3$/L. In addition, the Alk increased steeply from 4390 mg $CaCO_3$/L to 6880 mg $CaCO_3$/L for the next 1 day of operation. For the next 7 days of operation, the Alk continuously increases to 9750 mg $CaCO_3$/L. This is the result of the system alkalinity which acts as a buffer to sustain the anaerobic performance in the presence of VFA production (Venkata Mohan, S. *et al*., 2007).

For the remaining days of the operation, the VFA concentration fluctuated between 11228.57 mg CH_3COOH/L and 11648.57 mg CH_3COOH/L. However, this VFA concentration was higher than those (600 mg CH_3COOH/L) reported in the literature (Yacob, S. *et al*., 2006b). Though the Alk oscillated between 9710 mg $CaCO_3$/L and 9770 mg $CaCO_3$/L for the remaining days of the operation, however, this Alk concentration was lower than those (13333 mg $CaCO_3$/L) stated in the literature (Wong, Y.S. et al., 2009). In addition, this steady condition denotes that the system had reached its stable state.

4.2.5 Biogas Production Rate Variations during Acclimation Process

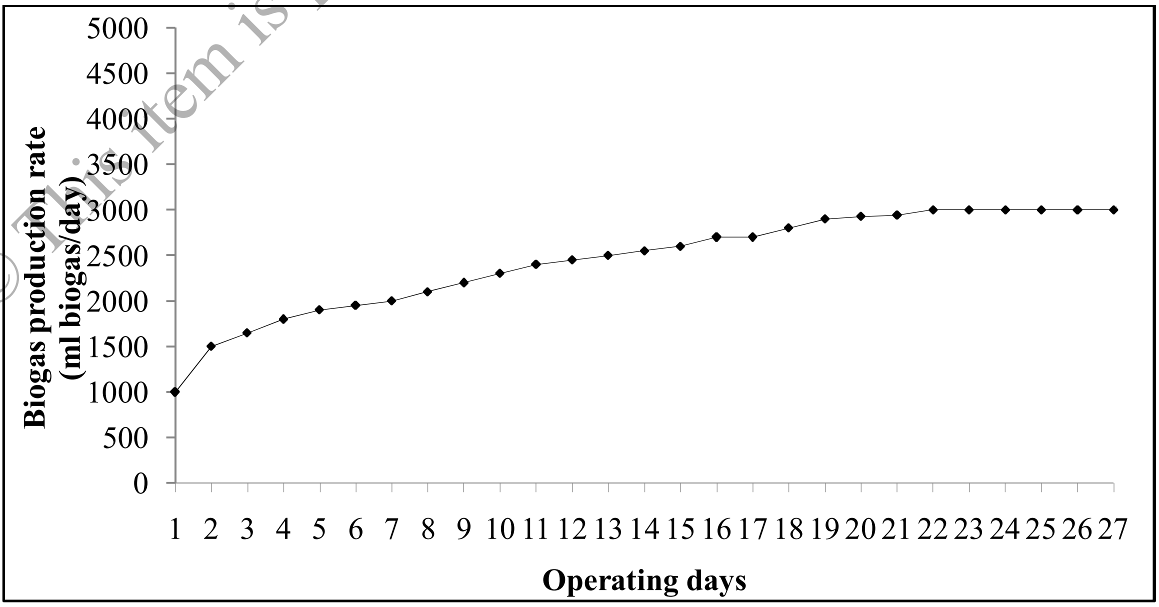

Figure 4.5: Biogas production rate of SCAR during acclimation process.

Figure 4.5 shows the biogas production rate during the acclimatization period. During the initial period of acclimatization, there was a gradual rise in biogas generation till the 22th day of operation. This may be due to the characteristic of palm oil effluent being a complex substance requires adequate time for degradation to occur, which was stated by Krishnan V. and Desa A. (2006). In addition, this clearly shows that the microbes are adapted to degrade the POME. For the remaining days of start-up period, the biogas generations were almost consistent (3000 ml biogas/day). Hence, it can be concluded that the reactor is in a stable operating condition.

4.2.6 Biogas Contents Variations during Acclimation Process

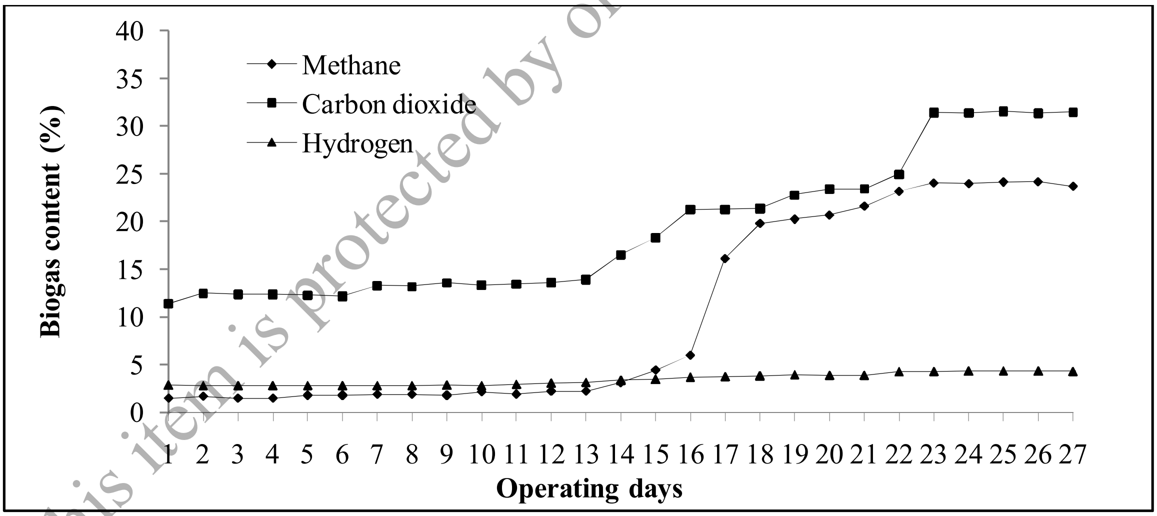

Figure 4.6: Biogas composition of SCAR during acclimation process.

Figure 4.6 illustrates biogas contents during the acclimation operation of the reactor. At initial period of acclimation, the CH_4 and CO_2 contents were also nearly consistent until 13rd day of operation whereas the H_2 content was almost constant until 9th day of operation. Meanwhile, Figure 4.6 shows that the CO_2 and H_2 contents were higher than CH_4 content. At this stage, it is believed that the colony of acidogenic bacteria was more than the methanogenic bacteria to convert the monomers resulting from hydrolytic bacteria into

VFAs, CO_2 and H_2 as mentioned in Section 2.3.1 (Toerien, D.F. and Hattingh, W.H.J., 1969).

A steep increase in the CH_4 and CO_2 contents from 2.21 % to 24.08 % and from 13.96 % to 31.44 %, respectively are observed for the next 10 days of operation. Nevertheless, the H_2 content gradually increased from 3.17 % to 4.31 % from 10th until 23rd day of operation. Increased of CO_2 and H_2 contents was the consequence of fermentation (acidogenesis) of the monomers of proteins, carbohydrates and lipids resulting from hydrolytic bacteria as discussed in Section 2.3.1 (Toerien, D.F. and Hattingh, W.H.J., 1969). As COD removal efficiency increased as shown at Figure 4.3, methane production rate increased causing an increase in methane content. These findings are also in agreement with those stated in the literature (Hikmet, T., 1994). At the same moment, Figure 4.6 shows that the CH_4 and CO_2 contents were higher than the H_2 content. Therefore, it is a clearly noted that the methanogenesis phase which can convert acetate acids and H_2 into CH_4 and CO_2 had started to occur in the SCAR as stated in Section 2.3.3 (Jeris, J. and McCarty, P.L., 1965).

The CH_4, CO_2 and H_2 contents were approximately steady within the range of 23.72 %– 24.23 %, 31.36 %– 31.58 % and 4.31% – 4.38 %, respectively for the remaining days of acclimation period, thus it can be considered that the SCAR had reached stability condition. These findings are contradictory with those (CH_4 and CO_2 contents from POME treatment were 36 % and 64 %) reported by Yacob, S. *et al*. (2005).

4.3 Performance of SCAR at Different Hydraulic Retention Times (HRTs).

The steady-state operation parameters of SCAR at different HRTs are shown in Table 4.2. Included in the data are the mean values of five steady state values for POME feed flow rate, organic loading rate (OLR), pH, influent COD, effluent COD, COD removal efficiency, effluent VFA, VFA, Alk, MLVSS, MLSS, biogas production rate, biogas productivity, biogas compositions, CH_4 volume and methane yield within each HRT. The standard deviation of five steady state values for each parameter within each HRT is also included. In addition, Table 4.3 illustrates performance of various anaerobic treatment methods on POME treatment.

In this research study, the vital parameters in Table 4.2 are COD removal efficiency, VFA, biogas production rate and biogas composition, thus, the detailed information of these parameters would be discussed in the following sections at each batch of HRT.

Table 4.2: Steady state operation parameters of SCAR at the different HRTs.

Parameter	Hydraulic retention time (HRT, Days)					
	12	10	8	6	4	2
POME Feed flow rate (L $POME_{fed}$/day)	0.38±0.00	0.45±0.00	0.56±0.00	0.75±0.00	1.13±0.00	2.25±0.00
OLR (kg COD/m^3/day)	6.67±0.01	7.60±0.00	9.45±0.22	12.96±0.19	19.87±0.37	38.29±0.27
pH in SCAR	5.26±0.05	5.36±0.01	5.54±0.05	5.53±0.04	5.34±0.01	5.20±0.01
MLVSS in SCAR (mg/L)	20958±92.84	30368±409.54	31246±1447.99	30012±115.84	35144±96.07	43226±53.20
MLSS in SCAR (mg/L)	24116±92.09	32276±97.37	34904±341.51	34032±66.11	41026±327.15	48212±309.06
Influent COD (mg/L)	80000±89.44	76000±1225.56	75560±1761.53	77760±1132.7	79480±1461.85	76580±540.37
Effluent COD (mg/L)	11420±64.71	27590±51.84	29370±325.19	34340±207.36	35370±189.08	40230±700.54
COD removal efficiency (%)	87.08±0.11	63.87±0.26	58.10±0.08	54.30±0.22	48.18±0.04	38.20±0.02
Effluent VFA (mg CH_3COOH/L)	9822.86±86.66	12440.57±253.3	14407.43±400.34	15503.91±82.08	15787.6±27.56	16199.69±15.91
VFA in SCAR (mg CH_3COOH/L)	11569.71±58.57	13546.68±9.19	15754.29±18.63	16314.29±28.57	16542.86±30.30	16956.00±16.85
Total Alkalinity in SCAR (mg $CaCO_3$/L)	5902±55.41	6620±15.81	6650±13.42	6728±32.71	7492±24.9	7712±8.37
Biogas production rate (ml biogas/day)	3000±0.00	1550±0.00	838±10.95	714±8.94	644±8.94	604±5.48
Biogas productivity (ml biogas/ml $POME_{fed}$)	8±0.00	3.44±0.00	1.46±0.02	0.95±0.01	0.55±0.04	0.27±0.00
Methane (%)	24.05±0.20	18.64±0.05	16.65±0.03	14.14±0.04	12.22±0.07	10.64±0.03
Carbon dioxide (%)	31.45±0.08	34.33±0.03	36.17±0.04	37.63±0.03	38.65±0.01	39.63±0.03
Hydrogen (%)	4.35±0.03	4.75±0.01	4.95±0.03	6.15±0.03	7.15±0.01	8.15±0.03

Methane volume (L CH_4/day)	0.72±0.01	0.29±0.00	0.14±0.00	0.1±0.00	0.08±0.00	0.06±0.00
Methane yield (L CH_4/g $COD_{removed}$)	0.025±0.00	0.013±0.00	0.006±0.00	0.003±0.00	0.002±0.00	0.001±0.00
CH_4:CO_2	0.76±0.01	0.54±0.00	0.46±0.00	0.38±0.00	0.32±0.00	0.27±0.00

*Values are the averages of determinations taken at steady-state period of each HRT. ± shows standard deviations.

**All gas data normalized to STP (0°C, 1 atm).

Table 4.3: Performance of various anaerobic treatment methods on POME treatment

Type of reactor	Influent COD (mg/L)	HRT (days)	COD removal efficiency (%)	Biogas productivity (ml biogas/ml $POME_{fed}$)	Methane composition (%)	Methane yield (L CH_4/g $COD_{removal}$)	Reference
Anaerobic pond	56000	40	97.8	0.008	54.40	N/A	Yacob, S. *et al.*, 2006a
Open anaerobic digester	43200	20	80.7	0.030	36.00	N/A	Yacob, S. *et al.*, 2005
UASFF	34740	3	97	N/A	71.90	0.310	Najafpour, G.D. *et al.*, 2006
CSTR	59940	18	80	N/A	62.50	N/A	Tong, S.L. and Jaafar, A.B., 2006)
SCAR	88560	12	87.08	8.00	24.05	0.025	This study

* SCAR – present study

* N/A – data unavailable

* The theoretical methane yield – 0.50 L CH_4/ g $COD_{removal}$ at STP (Hikmet, T., 1994).

* The theoretical methane yield which was predicted by Buswell and Muller – (0.47 L CH_4/ g $COD_{removal}$) (Francis, J.P., 1998).

* The methane yield at standard conditions – 0.35 L CH_4/ g $COD_{removal}$ (Jerry, L.H. and Douglas, D.B., 1998).

4.3.1 Variation in COD Removal Efficiency of SCAR at Different Hydraulic Retention Times

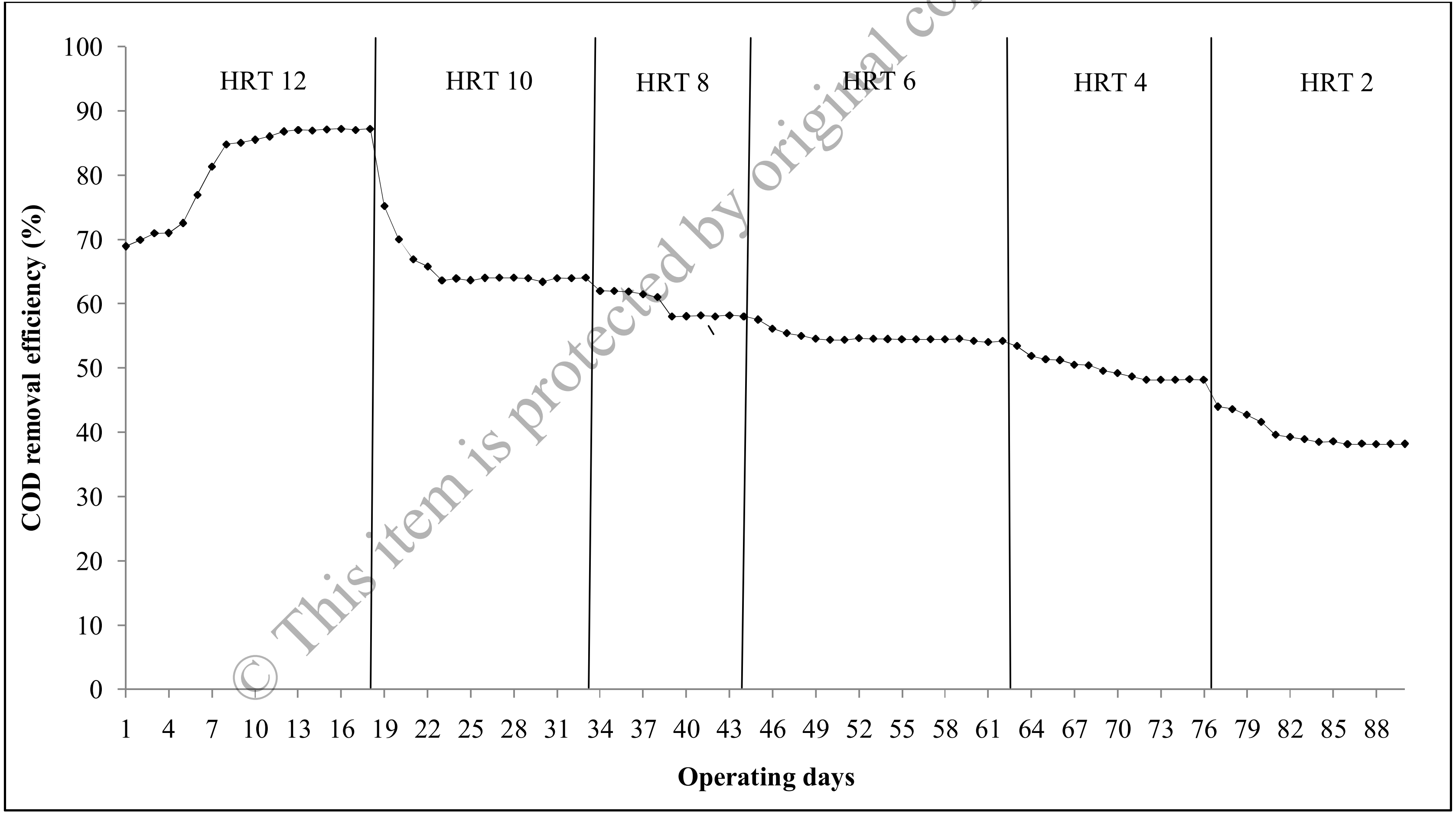

Figure 4.7: Variation in COD removal efficiency of SCAR on various hydraulic retention times.

In Figure 4.7, COD removal efficiency for SCAR operation and cycle period showed a steady increase in the effluent COD concentration before reaching the steady state with the function of cycle period with all the HRTs studied except HRT 12 days. This is due to the wash-out phase of the reactor which was caused by the higher OLR or lower HRT. Hence, the system stressed to obtain a maximum COD loading rate in a short period of time (Wong, Y.S. et al., 2009). Except for the higher HRT (12 days), the COD removal efficiency of HRT of 12 days showed a steady decrease in the effluent COD concentration before reaching the steady state. This was because higher HRT would increase the time of contact between substance and biomass.

The performance of the reactor with respect to substrate removal (COD removal) was found to be influenced by the HRT. From Table 4.2, the COD removal efficiency decreased from 87.08 % to 38.2 % as HRT decreased. These findings are consistent with those stated in the journalism (Sanchez, E. *et al*., 2005). Besides that, various studies have confirmed that lower HRTs will decrease COD removal efficiency in wastewater treatment systems as stated in Section 2.5.7 (Sanchez, E. *et al*., 2005). This is because soluble biodegradable material in the effluent increases with the rise of OLR or decrease of HRT. Moreover, such an increase in the effluent COD (or a decrease in the COD removal efficiency) was paralleled by a similar increase in the effluent VFA, as seen in Table 4.2. This was due to the COD will increase drastically during the acidogenesis phase by the dissolution of VFAs in the wastewater (George, T. *et al*., 1993). In addition, it is known that VFAs can cause a depletion of buffering capacity and a depression of pH to levels that inhibit the hydrolysis/acidogenesis phase if present in high concentrations as mentioned in Section 2.7 (Palmisano, A.C. and Barlaz, M.A., 1971). Moreover, it had been reported that even when process pH was fixed at the optimal range, the accumulation of VFAs may contribute to a reduced rate of hydrolysis of the solid organic substrate as stated in Section 2.7 (Banks, C.J. and Wang, Z., 1999).

Based on the results obtained from Table 4.2, the steady value of COD removal efficiency was directly proportional to the steady value of CH_4 content but inversely proportional to the steady value of CO_2 formation rate. Hikmet, T. (1994) has stated that the

CH_4 formation rate decreased and the CO_2 production rate increased when COD removal efficiency decreased. Furthermore, Table 4.3 shows that a comparison of the performance of the SCAR in the present study with other anaerobic treatment methods. The best COD removal efficiency of 87.08 % was achieved with an HRT of 12 days in the SCAR. This result was higher than those observed with the open anaerobic digester (Yacob, S. *et al*., 2005) as well as the finding from the CSTR (Tong, S.L. and Jaafar, A.B., 2006). This also clearly shown that the SCAR required low HRT in order to achieve high COD removal efficiency if compared with the open anaerobic digester (Yacob, S. *et al*., 2005) and the CSTR (Tong, S.L. and Jaafar, A.B., 2006). However, the COD removal efficiency of the present SCAR was lower than those findings with the anaerobic pond (Yacob, S. *et al*., 2006a) which required HRT of 40 days and the UASFF (Najafpour, G.D. *et al*., 2006) which required HRT of 3 days.

4.3.2 Variation in Volatile Fatty Acid (VFA) of SCAR at Different Hydraulic Retention Times

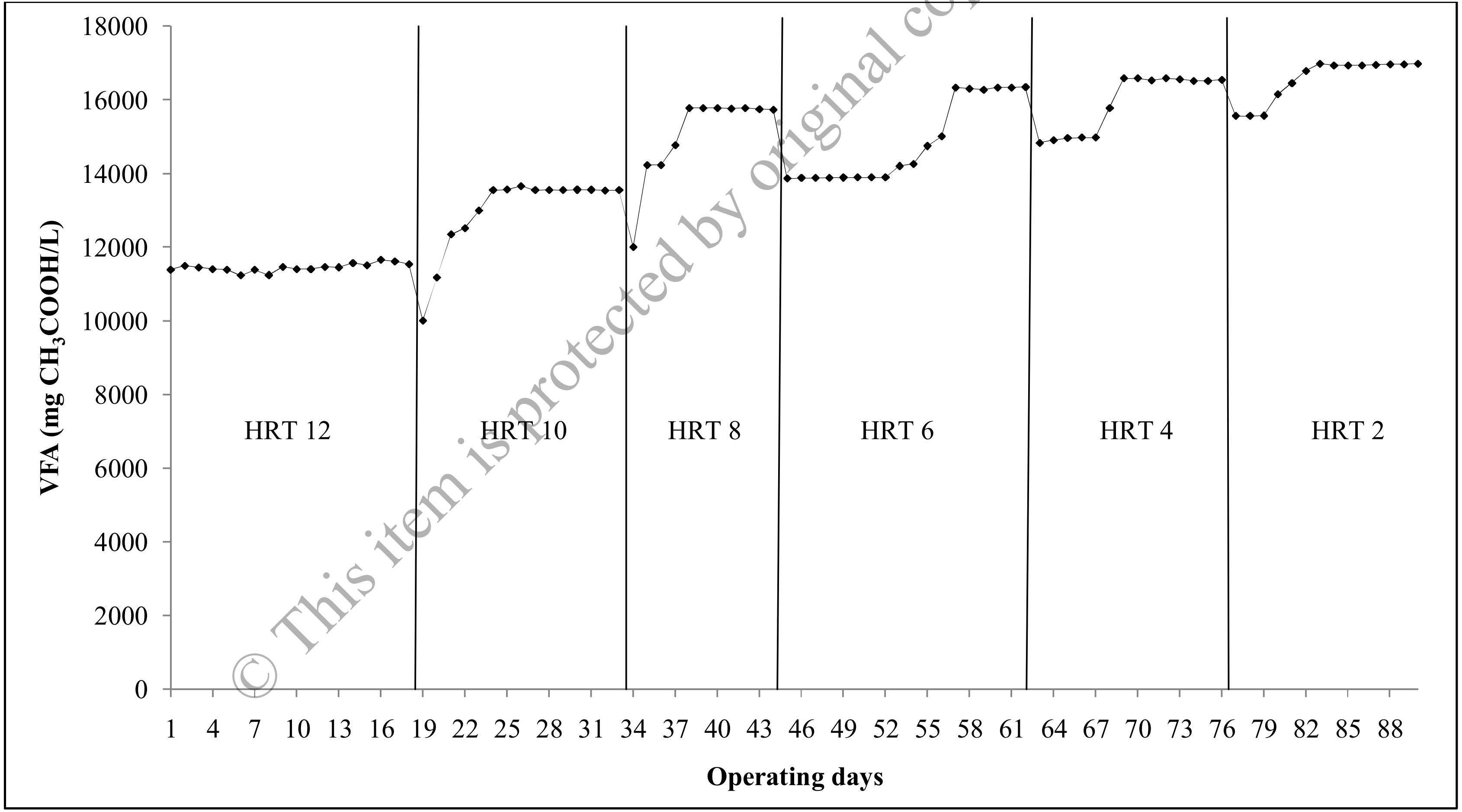

Figure 4.8: Variation in volatile fatty acid (VFA) of SCAR on various hydraulic retention times.

Figure 4.8 depicts VFA as acetic acid produced during the reactor operation. It can be observed from the data that VFA production varied consistently with different HRTs. Relatively lower VFA concentrations were recorded with HRT of 12 days. VFA concentration showed a steady increase from 11382.86 mg CH_3COOH/L to 11562.86 mg CH_3COOH/L before attaining the steady state. In the case of HRT of 10 days, VFA production increased from 10000 mg CH_3COOH/L and approached 13542.86 mg CH_3COOH/L before reaching the steady state. The VFA concentration increased from 12000 mg CH_3COOH/L to 15771.43 mg CH_3COOH/L before reaching the steady state in the case of HRT of 8 days. In the case of HRT of 6 days, VFA production increased from 13857.14 mg CH_3COOH/L and approached 16328.57 mg CH_3COOH/L before reaching the steady state. The VFA concentration increased from 14828.57 mg CH_3COOH/L to 16585.71 mg CH_3COOH/L before reaching the steady value in the case of HRT of 4 days. Relatively higher VFA concentrations were recorded with HRT of 2 days. VFA concentration showed a steady increase from 15557.14 mg CH_3COOH/L to 16971.43 mg CH_3COOH/L at before reaching the steady state. This is because the conversion rate of organic matter to VFA exceeded the conversion rate of VFA to CH_4 in the acidogenic phase (Morel, E. *et al.,* 2006).

In addition, the VFA concentration increased from 11569.71 mg CH_3COOH/L to 16956.00 mg CH_3COOH/L with a decrease in HRT as mentioned in Table 4.2. This is because low OLR causes low level concentration of VFA at longer HRT, whereas shorter HRT with high OLR causes accumulation of VFA (Faisal, M. and Unno H., 2001). Moreover, an increase in the VFA was paralleled by a similar increase in the effluent COD (or a decrease in the COD removal efficiency), as demonstrated in Table 4.2. George T. et al. (1993) have stated that the VFAs can increase COD of the wastewater during acidogenesis phase. Besides that, Table 4.2 shows that the biogas production rate was inversely proportional to the VFA in the SCAR. This is because methanogens are unable to work fast enough to convert acetic acid to CH_4 as a result of accumulation of VFAs.

4.3.3 Variation in Biogas Production Rate of SCAR at Different Hydraulic Retention Times

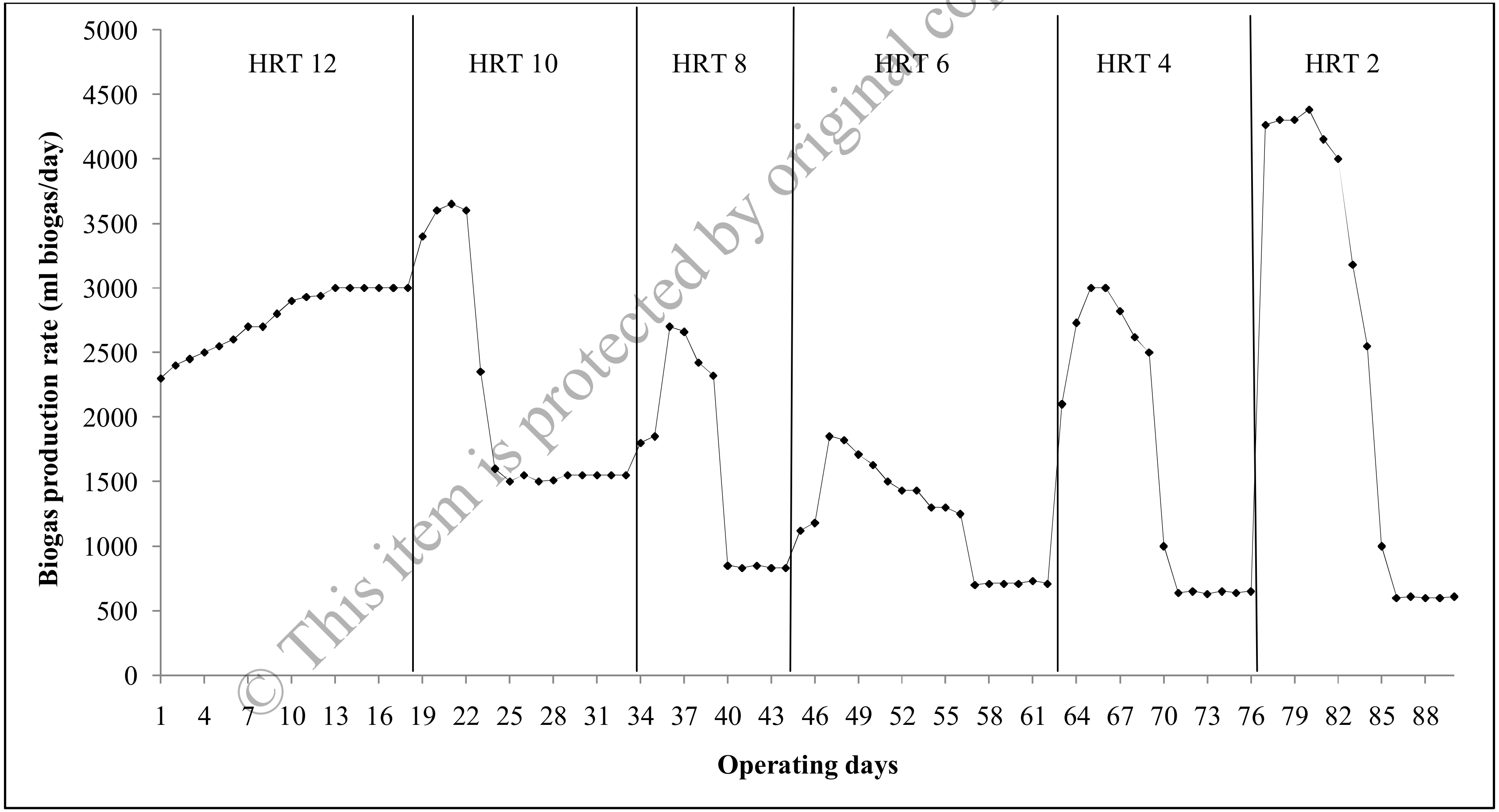

Figure 4.9: Variation in biogas production rate of SCAR on various hydraulic retention times.

The daily biogas productions observed at different HRTs from the SCAR are illustrated in Figure 4.9. At HRT of 12 days, there was a sharp increase of biogas production from 1st day until 10th day followed by a gradual increase before reaching a steady-state of biogas production at the 13rd day. At HRT of 10 days, there was an intense production of biogas from 18th day until 21st day followed by a gradual drop from 21st to 22nd day. Upon reaching steady state, a sharp decrease of biogas production can be observed at the 24th day. Whereas for HRT of 8 days, the biogas production rate sharply increased from 33rd day until 36th day followed by a steady drop from 36th to 37th day and decrease substantially reaching steady state values below 850 ml biogas/day at the 40th day. Meanwhile, at HRT of 6 days, we notice the biogas production rate quickly rose from 44th day until 47th day followed by a gradual drop from 47th to 56th day and then a sharp decrease of biogas production reaching steady state values below 730 ml biogas/day at the 57th day. Whereas for HRT of 4 days, the biogas production rate sharply increased from 62nd day until 65th day followed by a steady drop from 66th to 70th day and a rapid decrease of biogas production rate upon reaching steady state values below 650 ml biogas/day at the 72nd day. Besides that, at HRT of 2 days, the biogas production rate quickly rose from 76th day until 77th day followed by a gradual increase from 77th to 80th day and then a sharp decrease of biogas production to reach steady state values below 610 ml biogas/day at the 86th day. The reduction in the biogas production rate was due to inhibition caused by accumulation of VFAs. The steady-state results of VFA, biogas production rate, biogas productivity and composition obtained from the SCAR at different HRTs are summarised in Table 4.2.

As indicated the biogas productivity and production rate of the SCAR was directly proportional to the HRT. The biogas productivity and production rates of the SCAR were decreased from 8 ml biogas/ml $POME_{fed}$ to 0.27 ml biogas/ml $POME_{fed}$ and from 3000 ml biogas/day to 604 ml biogas/day, respectively as the HRT decreased from 12 days to 2 days. From Table 4.2, VFA concentration was 11569.71 mg CH_3COOH/L for the SCAR at HRT of 12 days. However, for the SCAR at HRTs of 10, 8, 6, 4 and 2 days, VFA concentration increased to 13546.68 mg CH_3COOH/L, 15754.29 mg CH_3COOH/L, 16314.29 mg CH_3COOH/L, 16542.86 mg CH_3COOH/L and 16956.00 mg CH_3COOH/L, respectively.

This accumulation of VFA in the SCAR at HRTs of 10, 8, 6, 4 and 2 days were mainly due to the fact that methanogens could not convert all the acetic acid to CH_4 in the SCAR. Excess VFA built up in the digester causing inhibition of the methanogenesis process. Therefore, the biogas productivity and production rate decreased. The optimum biogas productivity (8 ml biogas/ml $POME_{fed}$) and biogas production rate (3000 ml biogas/day) with 24.05 % of CH_4, 31.45 % of CO_2 content and 4.35% of H_2 content were achieved at a HRT of 12 days. Based on Table 4.3, The optimum biogas productivity (8 ml biogas/ml $POME_{fed}$) in this study was higher than those reported in the anaerobic pond (0.008 ml biogas/ml $POME_{fed}$) [8] and the open anaerobic digester (0.030 ml bigas/ml $POME_{fed}$) (Yacob, S. *et al*., 2005).

4.3.3 Variation in Biogas Composition of SCAR at Different Hydraulic Retention Times

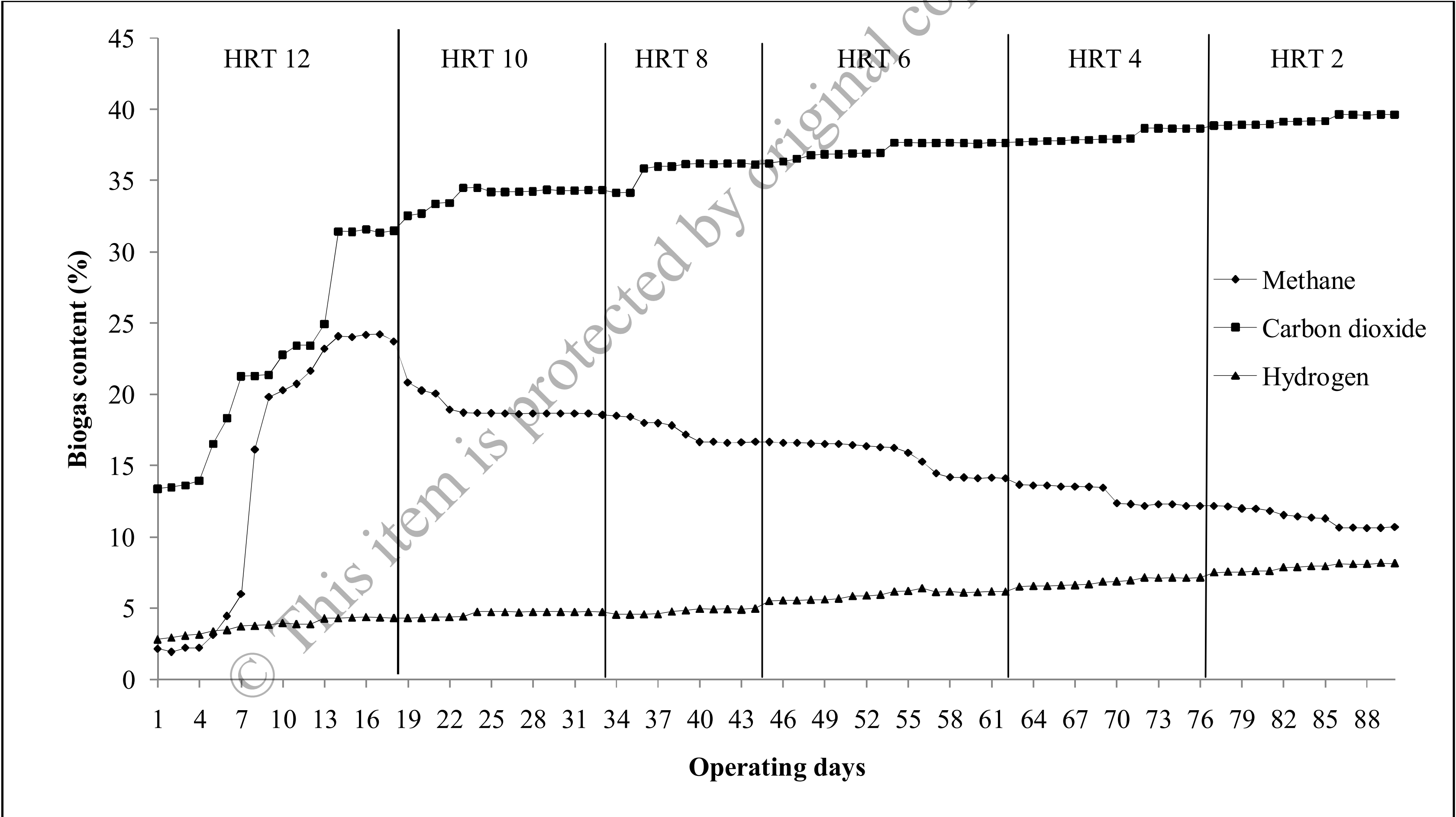

Figure 4.10: Variation in biogas composition of SCAR on various hydraulic retention times.

At higher HRT (12 days), the CH_4 and CO_2 contents were almost consistent during the initial period followed by an intense production of CH_4 and CO_2 from 4th day until 14th after that the CH_4 and CO_2 contents reached the steady state. Meanwhile, the H_2 content gradually increased upon reaching the steady state during HRT of 12 days period. The elevation in the CH_4 content during HRT of 12 days is because of CH_4 production rate increased with increased COD removal efficiency as mentioned in Figure 4.7. These findings are also consistent with those that are reported in the literature (Hikmet, T., 1994). Meanwhile, the elevation of CO_2 and H_2 contents during HRT of 12 days is the consequence of the fermentation (acidogenesis) of the monomers of proteins, carbohydrates and lipids as discussed in Section 2.3.1 (Toerien, D.F. and W.H. J. Hattingh., 1969). Moreover, Figure 4.10 also shows that biogas compositions for SCAR operation and cycle period demonstrated a steady reduction in the CH_4 content, a steady increase in the CO_2 content and a steady rise in the H_2 content before reaching the steady state with the function of cycle period with all the HRTs studied except HRT of 12 days. The reduction of CH_4 content is due to the persistence of acidophilic conditions due to presence of VFA [84], whereas the elevation of CO_2 and H_2 are due to fermentation (acidogenesis) of the monomers of proteins, carbohydrates and lipids which can produce the H_2 and CO_2 gases became more active as discussed at Section 2.3.1 (Toerien, D.F. and Hattingh, W.H.J., 1969).

The contents of the CH_4, CO_2 and H_2 produced during the steady-state period at different HRTs are shown in Table 4.2. The steady state CH_4 percentage was decreased from 24.05 % to 10.64 % with decrease of HRT. The optimal CH_4 percentage of 24.05 % was obtained with the highest HRT (12 days). A decrease in the steady value of CH_4 content is caused by an increase in the VFA and decrease in the COD removal efficiency as mentioned in Table 4.2. This is because high OLR was characterized by high concentration of VFA at the lower HRT, which can explain why the methanogenic process which can produce CH_4 gas was inhibited. Besides that, Hikmet, T. (1994) has stated that the CH_4 content decreased when COD removal efficiency and HRT decreased.

According to the literature, the highest CH_4 content (24.05 %) with HRT of 12 days was lower than those observed in anaerobic pond (54.4 %) which required HRT of 40 days (Yacob, S. *et. al*., 2006a), anaerobic digester (36.0 %) which required HRT of 20 days (Yacob, S. *et. al*., 2005), UASFF (71.9 %) which required HRT of 3 days (Najafpour, G.D. *et al*., 2006) and CSTR (62.5 %) which required HRT of 18 days (Tong, S.L. and Jaafar, A.B., 2006) as mentioned in Table 4.3. The lower CH_4 content found in this study may be attributed to the two explanations. The first explanation is due to the persistence of acidophilic conditions as a consequence of presence of VFA (Venkata Mohan, S. *et al*., 2008). The second may be due to the extraction of H_2 gas formed during acidogenic process which is essential for CH_4 formation in methanogenic step (Venkata Mohan, S. *et al*., 2008). Meanwhile, Table 4.3 shows that the highest methane yield (0.025 L CH_4/g $COD_{removal}$) with HRT of 12 days was lower than the finding of UASFF (0.31 L CH_4/g $COD_{removal}$) which required HRT of 3 days (Najafpour, G.D. *et al*., 2006), the theoretical methane yield which was 0.50 L CH_4/g $COD_{removal}$ at STP (Hikmet, T., 1994), the theoretical methane yield (0.47 L CH_4/g $COD_{removal}$) which was predicted by Buswell and Muller (Francis, J.P., 1998) and the methane yield (0.35 L CH_4/g $COD_{removal}$) that is stated in the literature (Jerry, L.H. and Douglas, D.B., 1998). In this research study, CH_4 production per unit of organic matter destroyed was less than the theoretical values, this is due to a fraction of the organic matter is converted to new bacterial cells (Hikmet, T., 1994).

In addition, the steady state CO_2 and H_2 contents were increased from 31.45 % to 39.63 % and from 4.35 % to 8.15 %, respectively with a decrease in HRT. The optimal CO_2 and H_2 percentages of 39.63 % and 8.15 %, respectively, were obtained with the lowest HRT. Besides that, such an increase in the CO_2 and H_2 contents were paralleled by a similar increase in the VFA, as illustrated in Table 4.2. These are because of the fermentation (acidogenesis) process which can produce VFAs, CO_2, H_2 and some lactic acid becaming more active at the low HRT if compared with high HRT. Additionally, the steady value of CO_2 content was inversely proportional to the steady value of COD removal efficiency as mentioned in Table 4.2. This finding is consistent with the statement of other journalism whereby the CO_2 content increased as COD removal efficiency decreased (Hikmet, T., 1994). Furthermore, CO_2 is the principal gas generated during the acidogenesis phases and smaller amounts of H_2 gas will also be produced (George, T. *et al.,* 1993).

Table 4.2 also demonstrates that the CH_4:CO_2 fraction was reduced from 0.76 to 0.27 with a decrease in HRT. This is because of the fermentation (acidogenesis) process can actively produce VFAs and CO_2 at the low HRT if compared with the high HRT. At the same time, the VFAs produced from the fermentation inhibited the methanogenic process which could release CH_4.