CHAPTER IV
RESULTS AND DISCUSSION

4.1 Two-stage for Hydrogen and Methane Production

Hydrogen and methane are produced from alcohol wastewater by using two-stage upflow anaerobic sludge blanket reactors (UASB). The alcohol wastewater was fed with an initial feed COD of 51,600 mg/l. For hydrogen production step, the first 4-L UASB reactor was operated at different COD loading rate (5, 10, 20, 48, 60, 120, 180 and 270 kg/m^{3}d), pH 5.5 and a recycle ratio of feed-to-effluent from methane-producing stage of 1:1. For methane production step, a second 24-L UASB unit was fed by the effluent from the first UASB. Both UASBs were operated in mesophilic condition (37°C).

4.2 Gas Production Rate

The gas production rate performance of each UASB unit as a function of COD rate is shown in Figure 4.1. The gas production rate was daily measured by gas meter in term L/d in steady condition. As COD loading rate increased from 5 to 48 kg/m^{3}d, the gas production rate from both the first and second UASB increased from 2.3 to 28.5 l/d and 5.7 to 39.6 l/d, respectively and then decreased at further increasing COD loading rate from 60 to 270 kg/m^{3}d. The maximum gas production rates of 28.5 l/d and 39.6 l/d in the first UASB unit and the second UASB unit was found at the same COD loading rate of 48 kg/m^3 d. The results can be explained that a high COD loading rate provided higher substrates available for microbes to convert into higher quantities of gaseous products (Intanoo *et al.*, 2012). However at a very high COD loading rate, gas production rate decreased due to the microbial cells were washed out from the system as a result of the increasing toxicity from the VFA accumulation in the system which will be discussed later.

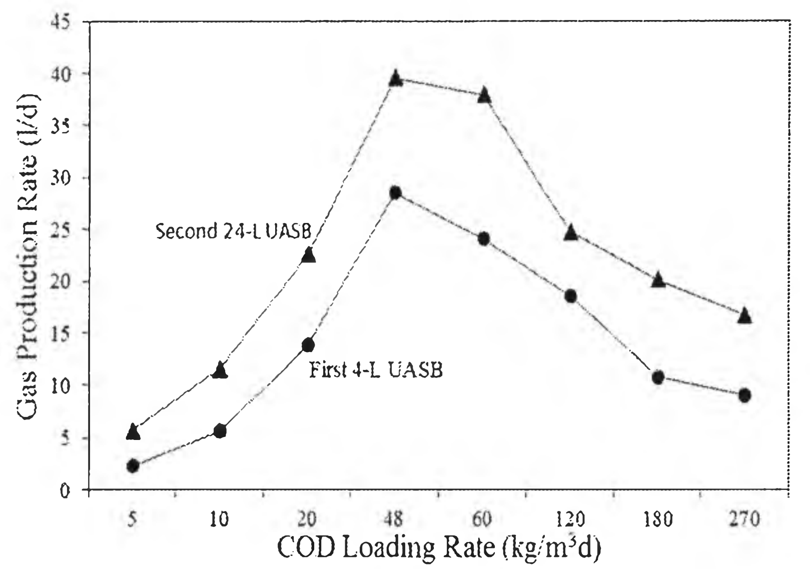

Figure 4.1 Effect of COD loading rate on gas production rate in two-stage UASB.

4.3 Gas Composition

The produced gas composition was analysed by gas chromatograph. From Fig.4.2, for the hydrogen production step, the produced gas contained only methane and carbon dioxide at a low COD loading rate varying from 5 to 120 kg/m^{3}d. When the COD loading rate increased from 180 to 270 kg/m^{3}d, hydrogen gas was detected. For the methane production step, the gas composition mainly consisted of methane and carbon dioxide without hydrogen in the whole studied rang of COD loading rate. For both hydrogen and methane production steps, the methane content increased with increasing COD loading rate and reached a maximum at a COD loading of 48 kg/m^{3}d contained 64.4% CH_4 and 84.8% CH_4, respectively. With further increasing COD loading rate from 60 to 270 kg/m^{3}d, the methane content units slightly decreased for both UASBs whereas the hydrogen content in the produced gas from the first UASB unit increased from 0.9 to 22.1% with increasing COD loading rate 180 to 270 kg/m^{3}d. The results can be explained by the fact that high COD loading rates result in wash-out of methanogen from the system, causing the dominance of hydrogen-producing (Chen *et al.*, 2001). Liu found that HRT longer than 2 day, the methanogen could still grow and utilize hydrogen as substrate (Liu et al., 2008).

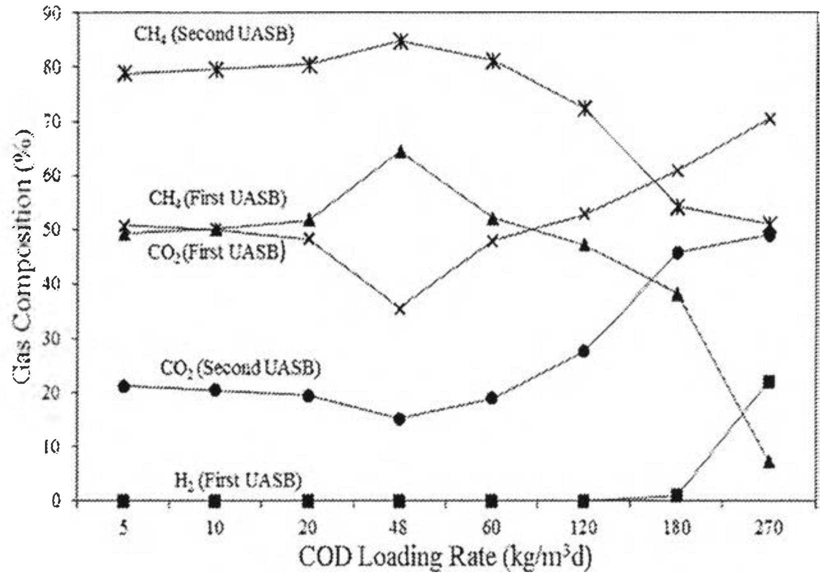

Figure 4.2 Effect of COD loading rate on gas composition in two-stage UASB.

4.4 Hydrogen and Methane Yield

The yields of produced hydrogen and methane production are defined as a ratio of the amount of produced hydrogen or methane to the amount of organic substrates consumed in the unit of L/kg COD removed. Figure 4.3 showed the hydrogen and methane yield at different COD loading rate. The methane yield for either first or second UASB increased with increasing COD loading rate and reached the maximum methane yield of 164.23 and 427.53 l CH_4/kg COD removed, respectively at COD loading rate of 48 kg/m^{3}d. Interestingly, at a COD loading rate of 270 kg/m^{3}d, the first UASB unit provided the highest hydrogen yield of 2.31 l H_2/kg COD. When the COD loading rate increased from 60 to 270 kg/m^{3}d, the yield of methane decreased because of the high concentration of volatile fatty acids in the reactor, resulting in the high toxicity to the microbes.

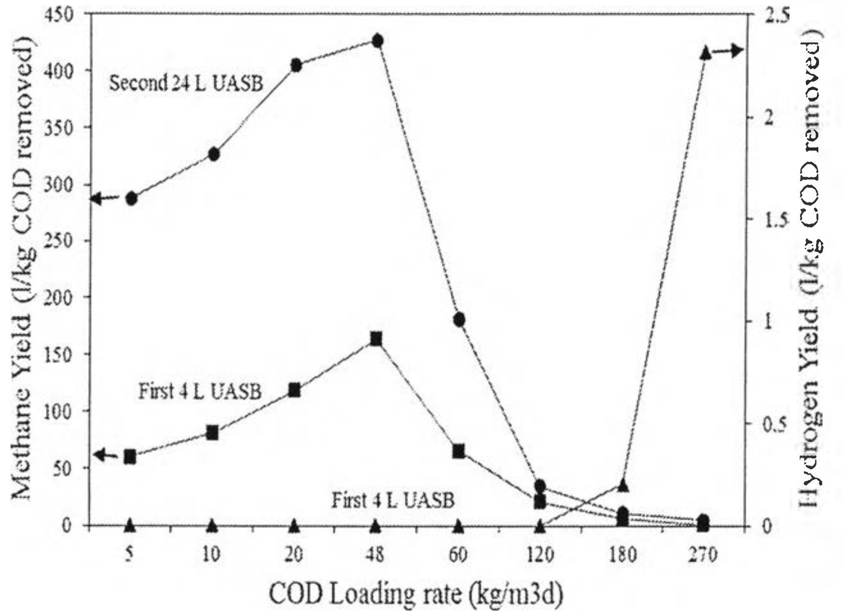

Figure 4.3 Hydrogen and methane yield versus COD loading rate in two-stage UASB.

4.5 Specific Hydrogen and Methane Production Rate

Specific hydrogen and methane production rate is defined as the hydrogen or methane production rate per unit weight of the microbial cells in the reactor. Figure 4.4 showed the specific hydrogen and methane production rate of the first and second UASB unit at different COD loading rate. The results showed that with increasing COD loading rate, the specific methane production rate for both the first and second UASB increased and reached a maximum value of 229 l CH_4/kg MLVSS d and 51 l CH_4/kg MLVSS d, respectively. When the system was operated higher than 48 kg/m^3d, the specific methane production rate was decreased. At COD loading rate of 270 kg/m^3d, a maximum specific hydrogen production rate was 22 l H_2/kg MLVSS d.

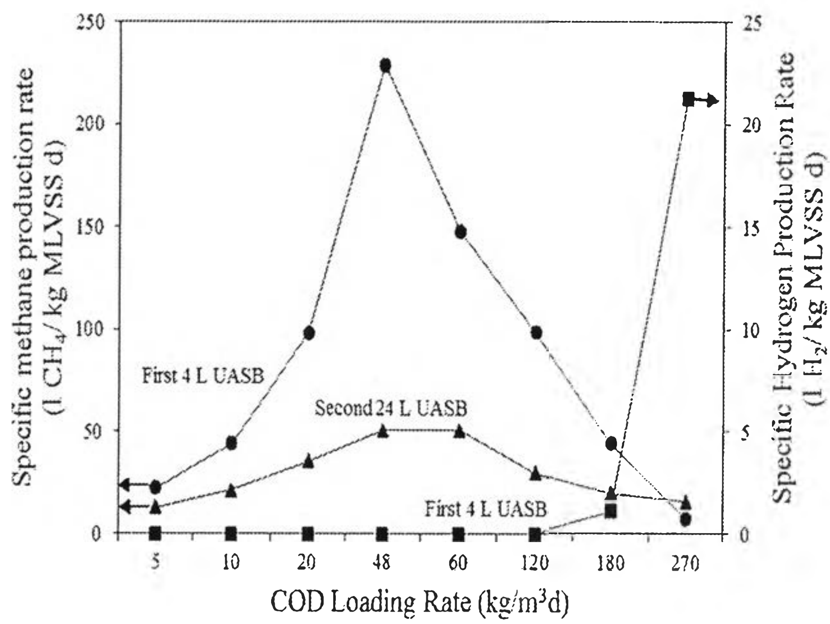

Figure 4.4 Specific hydrogen and methane production rate versus COD loading rate in two-stage UASB.

4.6 COD Removal

The effect of COD loading rate on the COD removal is shown in Figure 4.5. The COD removal increased with increasing COD loading rate and to reach the maximum value of 41.7% and 64.9 % for the first and second UASB units, respectively at a COD loading rate of 48 kg /m^3d which well corresponded to the methane production rate. After that, the COD removal decreased with further increasing COD loading rate. The results can be explained by the fact that in the COD loading rate range of 5-48 kg/m^3d, an increase in COD loading rate directly increased substrates available for microbes, leading to both higher COD removal and gas production rate whereas, in the COD loading rate range of 48-270 kg/m^3d, the decreasing COD removal with increasing COD loading rate resulted from the increase in toxicity from the VFA accumulation. The result also indicated that a two-stage concept that hydrogen production step was followed by methane production step could maximize COD removal efficiency. Zhu et al. (2010) reported a COD removal rate of 19% in hydrogen production step whereas 51% of COD removal was in methane production step from potato waste using two-stage anaerobic digestion process.

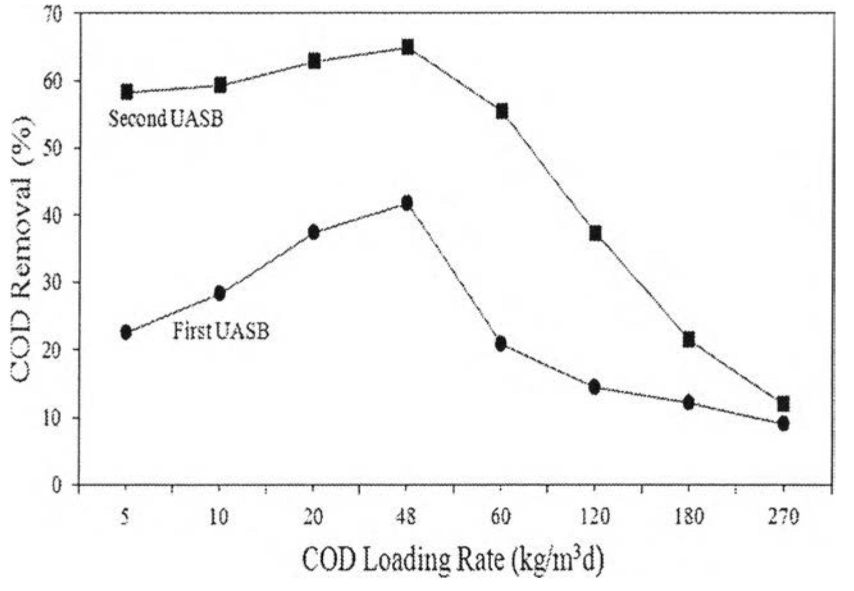

Figure 4.5 COD removal efficiency versus COD loading rate in two-stage UASB.

4.7 Microbial Concentration

The microbial concentration (MLVSS) was a parameter used for determining the capability of the microorganism of growing in the bioreactor and the microbial concentration (VSS) was washed out. Figure 4.6 and 4.7 showed the effect of COD loading rate on MLVSS and VSS in the first and second UASB unit, respectively. For both hydrogen and methane production step, the MLVSS increased with increasing COD loading rate whereas VSS decreased with increasing COD loading rate from 5 to 48 kg/m^3d. With further increasing COD loading rate higher than 48 kg/m^3d, the MLVSS of first UASB unit slightly increased while the MLVSS of second UASB unit decreased. The VSS in both hydrogen and methane production step increased at higher COD loading rate than 48 kg/m^3d. This explained that the increase in microbial growth was due to high amount of organic compounds in the reactor, at a high COD loading rate. However, the decrease in microbial growth with increase COD loading rate higher than 48 kg/m^3d because of acid accumulation toxicity to stop the hydrogen and methane producing bacteria growth.

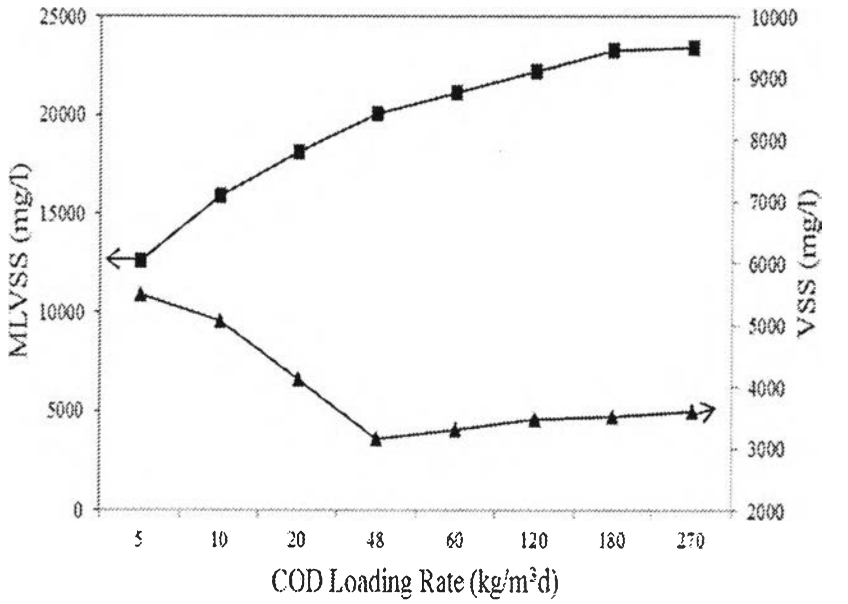

Figure 4.6 MLVSS and effluent VSS versus COD loading rate in a first UASB.

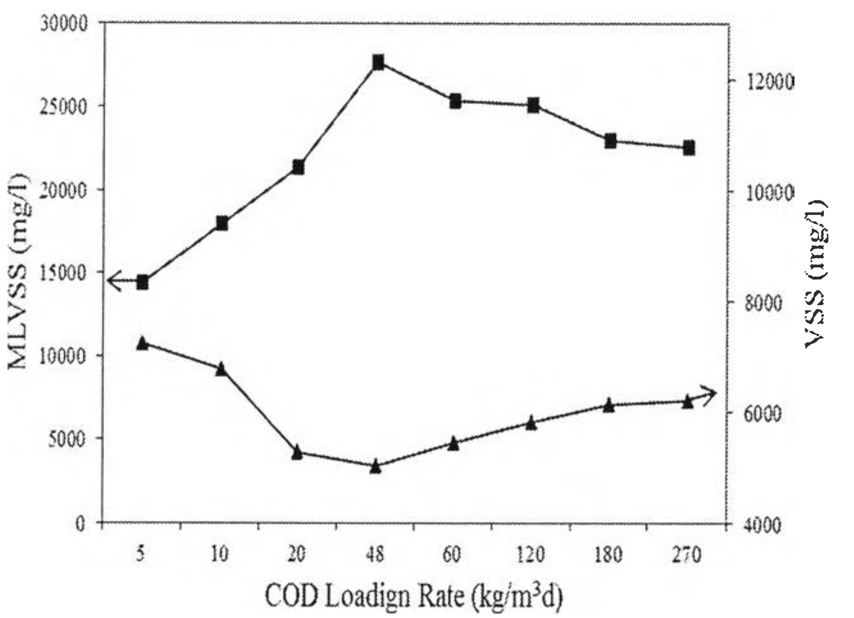

Figure 4.7 MLVSS and effluent VSS versus COD loading rate in a second UASB.

4.8 Volatile Fatty Acid (VFA) for Hydrogen and Methane Production

The total VFA concentration in the effluent of either first UASB or second UASB unit was quantified as acetic acid by using distillation-titration method as a standard method (Eaton *et al.*, 2005). Figure 4.8 showed the effect of COD loading rate on total of VFA in first UASB unit. The total VFA concentration increased with increasing COD loading rate. At the COD loading rate from 5 to 48 kg/m^3 d, the methane gas can be produced because produced VFA were utilized for methane generation. For higher COD loading rate (>48 kg/m^3d), the lower methane yield obtained and hydrogen was observed at 270 kg/m^3 d. The result was due to the persistence of acidophilic condition due to presence of VFA (Mohan *et al.*, 2008).

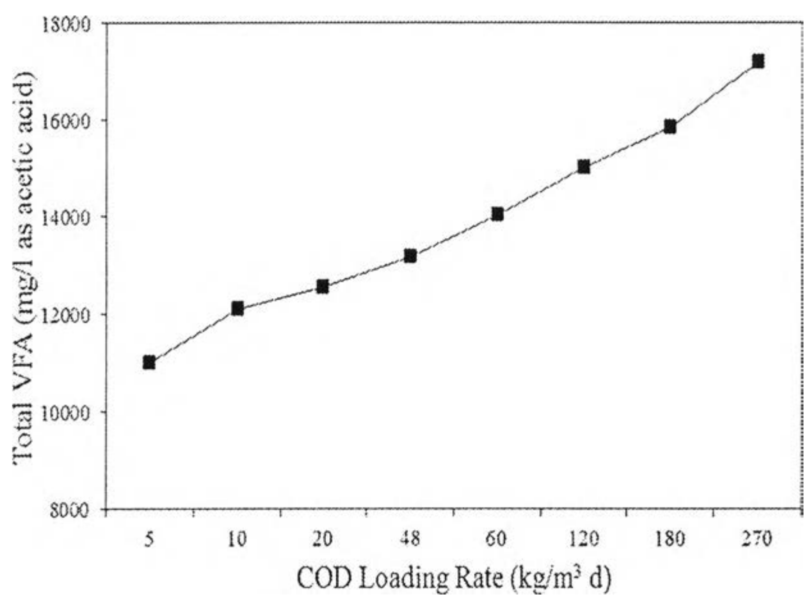

Figure 4.8 The amount of volatile fatty acid as a function of COD loading rate in a first UASB.

Aside from the produced gas, the main liquid products were VFA, which useful parameters for monitoring hydrogen production (Yang *et al.*, 2006). The main components of VFA were acetic acid, propionic acid, butyric acid, and valeric acid. Figure. 4.9 showed the concentration of VFA and ethanol, the results show that the butyric acid was the most abundant species in the effluent. The maximum of butyric acid was 5002.66 ml/g at COD loading rate 270 kg/m^3d which was hydrogen produced. The result indicated that the hydrogen production phase was butyric acid type fermentation, according to Equation 4.2. Another pathway of hydrogen production was when acetic acid was the end product, a theoretical maximum of 4 moles hydrogen per mole glucose is produced according to Equation 4.1. However, for mesophilic condition, hydrogen yield was less than 2 mole hydrogen per mole glucose whereas hydrogen reached the theoretical maximum of 4 mole hydrogen per mole glucose at extreme- thermophilic condition (70 °C) (Van Niel *et al.*, 2002).

Acetic acid production: $C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$ (4.1)

Butyric acid production: $C_6H_{12}O_6 \rightarrow CH_3(CH_2)_2COOH + 2CO_2 + 2H_2$ (4.2)

The cumulated propionic acid concentation resulted in low hydrogen becasuse propionic acid formation usually consumes the produced hydrogen according to Equation 4.3 From the results, propionic acid slightly decreased with increasing COD loading rate. Therefore, to maximize the hydrogen production rate at COD loading rate 270 kg/m^3d, the propionic acid was minimum.

Propionic acid production: $C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O$ (4.3)

Ethanol concentration increased with increasing COD loading rate from 5 to 270 kg/m^3 d. At a COD loading rate 270 kg/m^3 d, the highest ethanol concentration of 3,806 mg/l was archived by the hydrogen production. From the result can be explained that the produced ethanol can accordingly improve the efficiency of hydrogen production, according to Equation 4.4.

Ethanol production: $C_6H_{12}O_6 + H_2O \rightarrow C_2H_5OH + CH_3COOH + 2H_2 + 2CO_2$ (4.4)

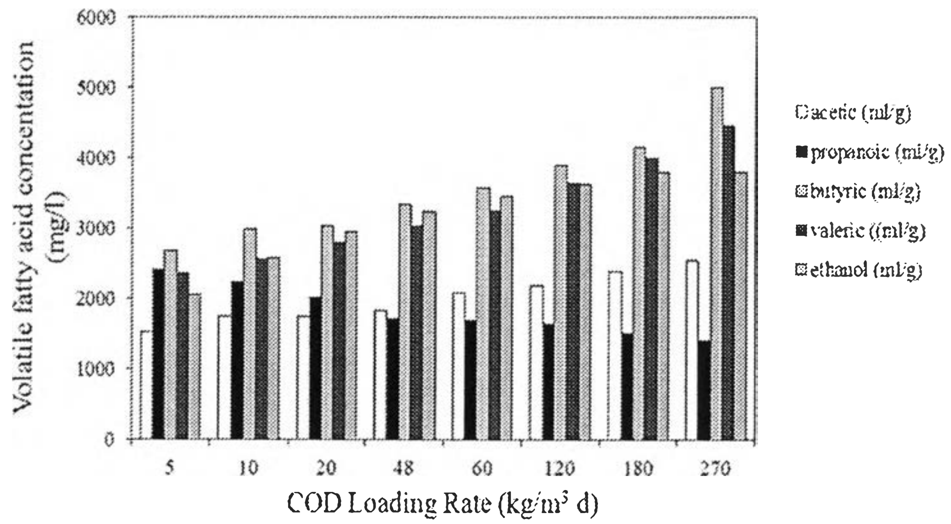

Figure 4.9 The volatile fatty acid concentration as a function of COD loading rate in a first UASB.

Figure 4.10 showed the effect of COD loading rate on the total VFA concentration in the second UASB unit. The total VFA concentration slightly changed with increasing COD loading rate in the range of 5-48 kg/m^{3}d.With further increasing COD loading rate beyond 48 kg/m^{3}d, it increased dramatically. The VFA results suggest that the toxicity level to the methanogens is approximately around 500 mg/l. The minimum total VFA concentration was 2173.04 mg/l as acetic acid at COD loading rate of 48 kg/m^{3}d which was maximum methane content because methane was produced in this step which consumes hydrogen and VFA generated from the primary acidogenesis step, according to the Equation 4.5-4.8. (Mohan et al., 2008).

$$CH_3COOH \rightarrow 2H_2+CO_2 \quad (4.5)$$

$$CH_3CH_2CH_2COOH+2H_2O \rightleftharpoons CH_3COOH+2H_2 \quad (4.6)$$

$$CH_3CH_2CH_2CH_2COOH+2H_2O \rightleftharpoons CH_3CH_2COOH^-+CH_3COOH^-+2H_2 \quad (4.7)$$

$$4H_2+CO_2 \rightarrow CH_4+2H_2O \quad (4.8)$$

Figure 4.11 showed the concentration of VFA and ethanol concentration in methane production step. Both ethanol and VFA concentration decreased with increasing COD loading rate from 5 to 48 kg/m^{3}d and then increased with further increasing COD loading rate from 48 to 270 kg/m^{3}d. The lowest VFA and ethanol concentration were at COD loading rate of 48 kg/m^{3}d. The result shows that VFA concentration and ethanol produced from hydrogen production step can be recovered to produce methane.

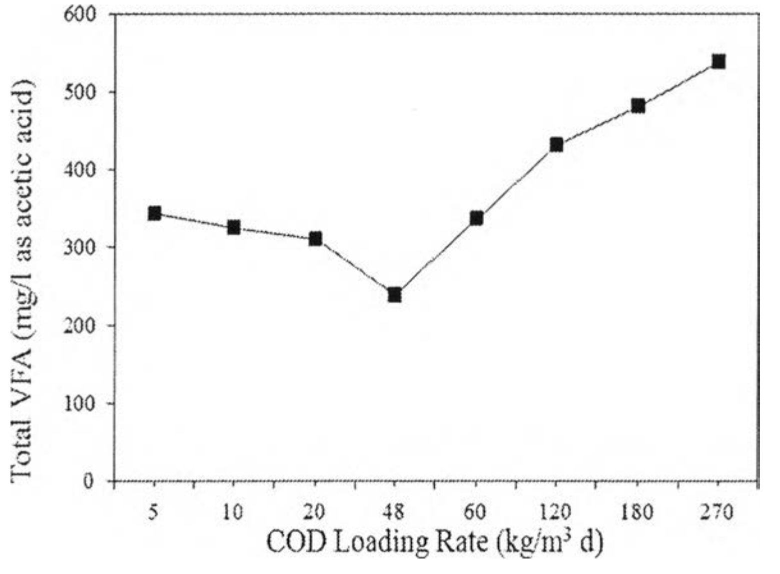

Figure 4.10 Total volatile fatty acid (VFA) versus COD loading rate in a second UASB.

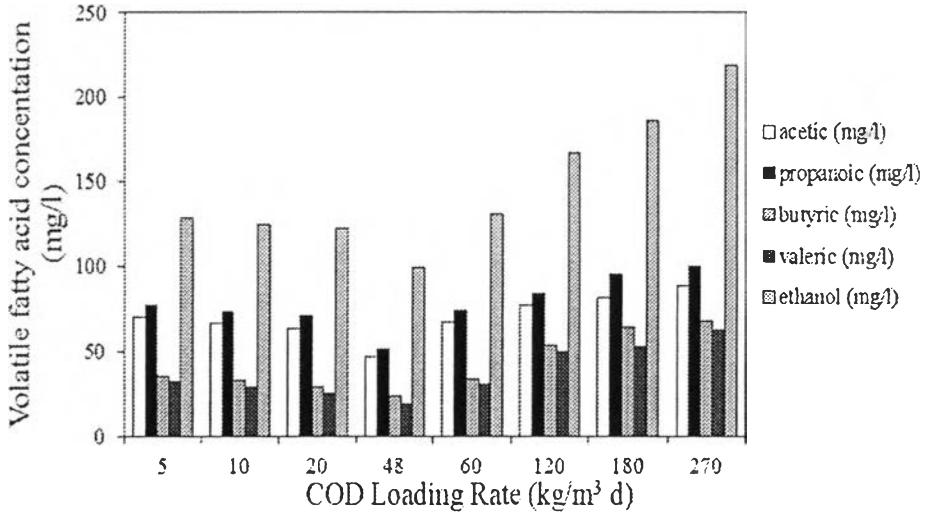

Figure 4.11 The volatile fatty acid concentration as a function of COD loading rate in a second UASB.