CHAPTER IV
RESULTS AND DISCUSSION

4.1 Biohydrogen Production

The upflow anaerobic sludge blanket reactor (UASB) was operated with cassava wastewater at various different COD loading rates from 10 to 30 kg/m^{3}d under mesophilic temperature (37°C). The mixed culture with the selectively enriched hydrogen producing bacteria, by boiling it before being added to the reactor, was used. The pH in the reactor was maintained at 5.5±0.4 in order to sustain acidogenic (hydrogen-producing bacteria) activity. The effect of COD loading rate on the biohydrogen production was investigated to obtain an optimum condition.

4.1.1 Gas Production Rate

The gas production rate was daily measured by gas counter in L/d. The effect of COD loading rate on the gas production rate at steady state is presented in Figure 4.1. The gas production rate rapidly increased with increasing COD loading rate from 5.9 L/d at a COD loading rate of 10 kg/m^{3}d to 29.5 L/d at a COD loading rate of 30 kg/m^{3}d. This can be explained in that high amount of organic compounds in the reactor at a high COD loading rate can be more digested to gaseous products. Although the higher COD loading rate provided high gas production rate, a COD loading rate higher than 30 kg/m^{3}d was not studied due to the decrease in hydrogen production rate and yield, as shown later.

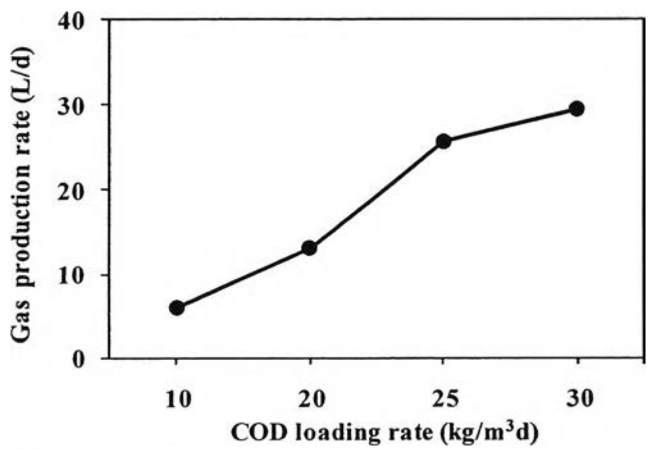

Figure 4.1 Effect of COD loading rate on gas production rate at 37°C and pH 5.5.

4.1.2 Gas Composition

The composition of produced gas was determined by the gas chromatograph equipped with TCD (GC-TCD). The produced gas mainly consisted of hydrogen and carbon dioxide at high COD loading rates of 25 and 30 kg COD/m^3d (or short hydraulic retention time), as shown in Figure 4.2. On the other hand, methane could be detected at low COD loading rates of 10 and 20 kg COD/m^3d. From the results, the maximum hydrogen percentage of 36.42% was obtained at a COD loading rate of 25 kg/m^3d.

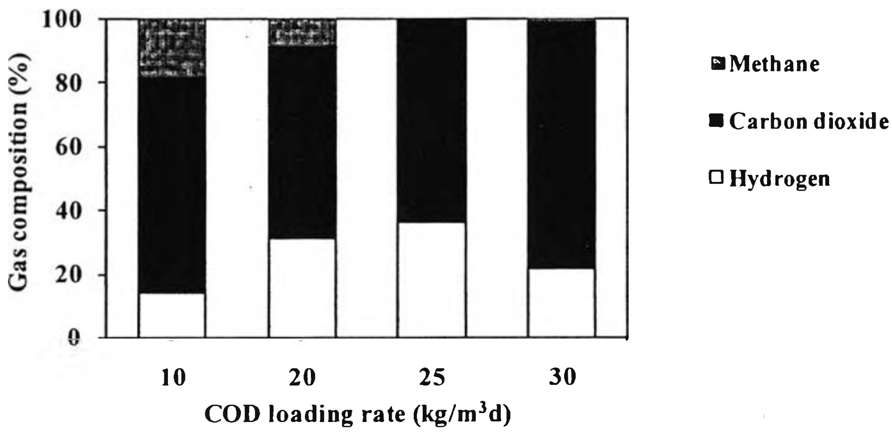

Figure 4.2 Effect of COD loading rate on gas composition at 37°C and pH 5.5.

4.1.3 Hydrogen Production Rate

The effect of COD loading rate on hydrogen production rate is shown in Figure 4.3. The hydrogen production rate greatly depends on both the gas production rate and the hydrogen composition. The hydrogen production rate continuously increased from 0.81 L/d at a COD loading rate of 10 kg/m^3d to 9.36 L/d at a COD loading rate of 25 kg/m^3d and then decreased with further increasing COD loading rate up to 30 kg/m^3d due to the decrease in the hydrogen percentage.

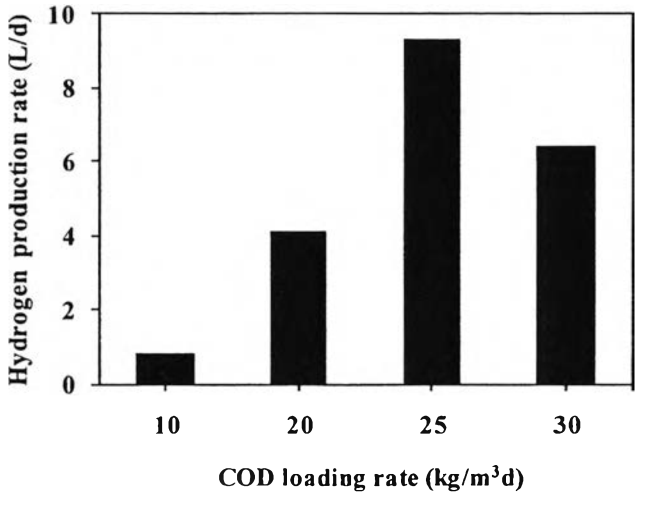

Figure 4.3 Effect of COD loading rate on hydrogen production rate at 37°C and pH 5.5.

4.1.4 Hydrogen Yield

Yield of hydrogen production is defined as the ratio of the amount of produced hydrogen to the amount of organic substrates consumed in the wastewater in the unit of L/kg COD removed. Figure 4.4 shows that the yield of hydrogen rapidly increased with increasing COD loading rate from 15.82 L/kg COD removed at 10 kg COD/m^{3}d to 39.83 L/kg COD removed at 25 kg COD/m^{3}d. However, at 30 kg COD/m^{3}d, the yield of hydrogen adversely decreased because both the percentage of hydrogen and the COD removal (as shown later) decreased.

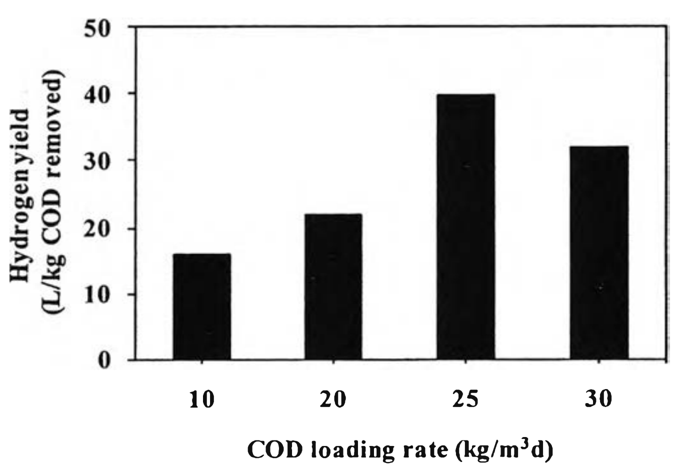

Figure 4.4 Effect of COD loading rate on hydrogen yield at 37°C and pH 5.5.

4.1.5 Specific Hydrogen Production Rate

Specific hydrogen production rate is defined as the hydrogen production ability from the fermenter in unit of L of produced hydrogen per kg of volatile fatty acid per day. The experimental results shown in Figure 4.5 indicated that the maximum specific hydrogen production rate was 10.4 L/kg MLVSS d at a COD loading rate of 25 kg/m^3 since the produced hydrogen amount from the consumed organic substrates in the reactor (hydrogen yield) was dominated. On the other hand, the decrease in specific hydrogen production rate at lower COD loading rates of 10-20 kg COD/m^{3}d and higher COD loading rate of 30 kg/m^{3}d may result from hydrogen-producing microorganism wash-out (Chang and Lin, 2004), as shown later by the effluent VSS.

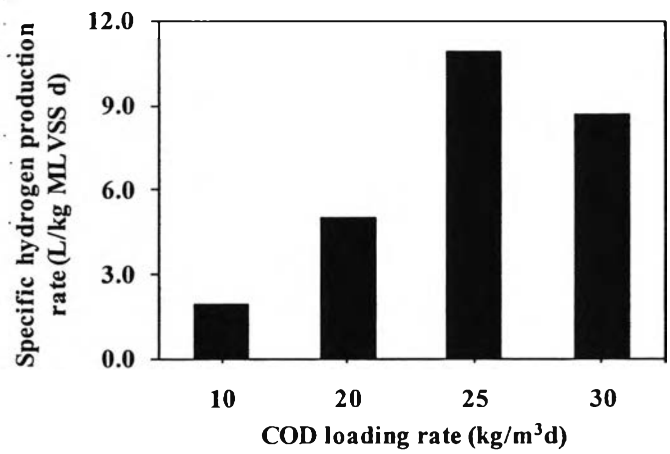

Figure 4.5 Effect of COD loading rate on specific hydrogen production rate at 37°C and pH 5.5.

4.1.6 COD Removal

The effect of COD loading rate on the COD removal is shown in Figure 4.6. The results show that the percentage of COD removal increased with increasing COD loading rate and reached the maximum value of 43.83% at 25 kg COD/m^{3}d. After that, the percentage of COD removal decreased to 30.58% at 30 kg COD/m^{3}d. At the too high COD loading rate, the system has low hydraulic retention time (HRT), at which microorganisms have a too short time for digesting the organic compounds. This indicates that a well-balanced COD loading rate is required to achieve the maximum COD removal, simultaneously with high gas production rate.

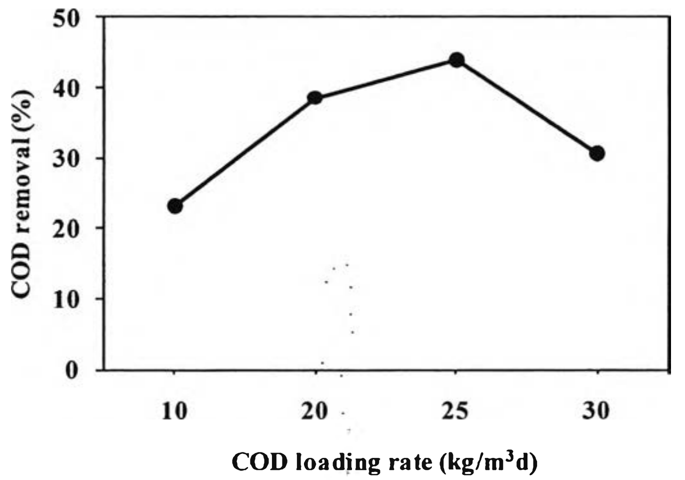

Figure 4.6 Effect of COD loading rate on percentage of COD removal at 37°C and pH 5.5.

4.1.7 Volatile Fatty Acids (VFA) Concentration

VFA concentration in the effluent at the steady state is quantified approximately as acetic acid by using the distillation-titration method as a standard method (Greenberg *et al.,* 1992). The experimental data on VFA concentration shown in Figure 4.7 reveal that the VFA concentration decreased with increasing COD loading rate. The lowest organic acid concentration in the effluent of 8,220 mg/L at 25 kg COD/m^{3}d was found. The results integrated that the increase in the hydrogen was accompanied with low VFA concentration.

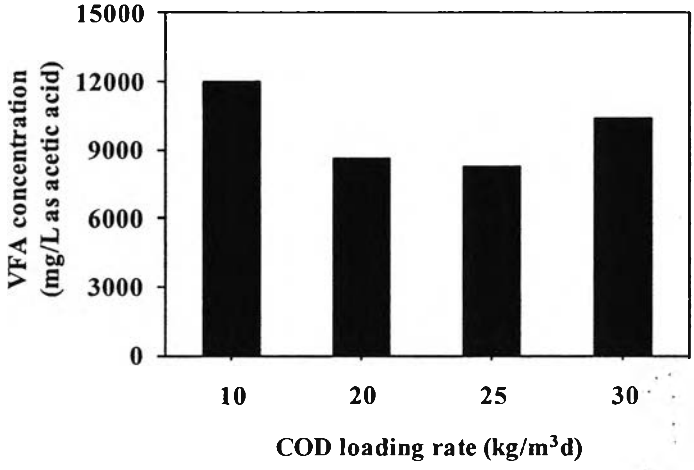

Figure 4.7 Effect of COD loading rate on percentage of COD removal at 37°C and pH 5.5.

4.1.8 VFA Composition

The major volatile fatty acids in the liquid effluent were acetic acid, propionic acid, butyric acid, and valeric acid with average concentrations of 700-1180, 660-1360, 3100-6450, and 1510-4050 mg/L, respectively, as shown in Figure 4.8. At the optimum 25 kg COD/m^{3}d, the volatile fatty acid concentrations were 47% butyric acid, 25% valeric acid, 18% acetic acid, and 10% propionic acid. Moreover, the lowest butyric acid-to-acetic acid ratio of 2.63 was obtained at the optimum condition, as shown in Figure 4.9. In general, the production of acetic and butyric acids is favorable when hydrogen production is dominant, according to Equations 4.1 and 4.2 (Mohan *et al.*, 2008).

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

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

In addition, the production of valeric and propionic acids was also important in affecting the consumption of hydrogen initially produced, according to Equations 4.3-4.6 (Mohan *et al.*, 2008 and Zhao and Yu, 2008).

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

Valeric acid production:

$$CH_3CH_2COOH + CH_3(CH_2)_2COOH \rightarrow CH_3(CH_2)_3COOH + CH_3COOH \quad (4.4)$$

$$CH_3CH_2COOH + CH_3COOH + H_2 \rightarrow CH_3(CH_2)_3COOH + 2H_2O \quad (4.5)$$

$$CH_3CH_2COOH + 2CO_2 + 6H_2 \rightarrow CH_3(CH_2)_3COOH + 4H_2O \quad (4.6)$$

The theoretically maximum hydrogen production is 4 mole of hydrogen per 1 mole of acetic acid produced; however, the production of valeric acid from the initially produced propionic, acetic, or butyric acids also decreased the efficiency of hydrogen production. At a COD loading rate of 30 kg/m^{3}d, the highest acetic acid concentration was obtained. This possibly pointed out that acetic acid was produced with no either hydrogen produced or hydrogen consumed, as shown in Equations 4.7 and 4.8 (Gavala *et al.*, 2006).

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH \quad (4.7)$$

$$4H_2 + 2CO_2 \rightarrow 2CH_3COOH + 2H_2O \quad (4.8)$$

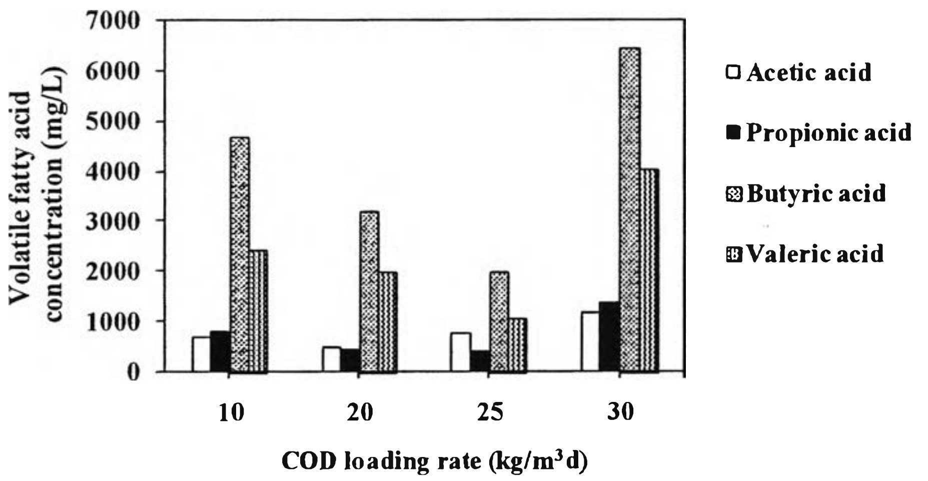

Figure 4.8 Effect of COD loading rate on composition of volatile fatty acid at 37°C and pH 5.5.

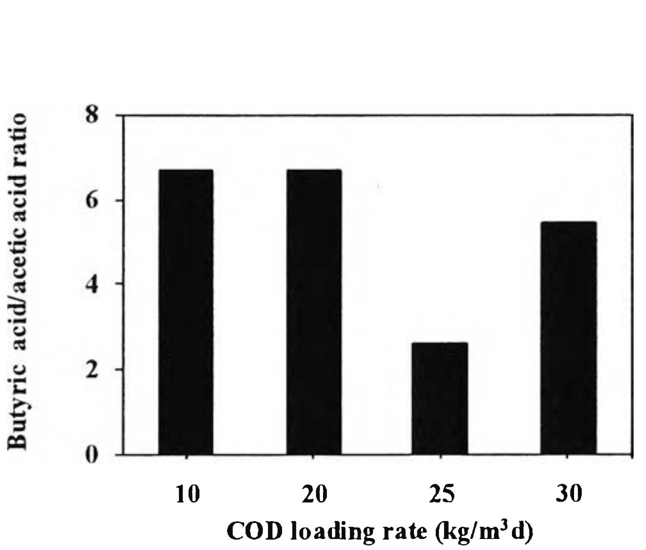

Figure 4.9 Effect of COD loading rate on the ratio of butyric acid-to-acetic acid ratio at 37°C and pH 5.5.

4.1.9 Microbial Growth and Effluent Suspended Solids

The microbial growth is a parameter used for determining the capability of the microorganism of growing and degrading the organic compounds present in the bioreactor. In this study, the microbial growth was examined in terms of mixed liquid volatile suspended solids (MLVSS), and the wash-out of microorganism from the bioreactor in the effluent was examined in terms of volatile suspended solids (VSS) at the steady state of the operation. Figure 4.10 shows the effect of COD loading rate on both the MLVSS and the effluent VSS. The results showed that with increasing COD loading rate from 10 to 25 kg/m^{3}d, the MLVSS increased to reach a maximum (35,740 mg/L), but the effluent VSS decreased to reach a minimum (94 mg/L). After that, the increase in the COD loading rate higher than 25 kg/m^{3}d resulted in the decreased in the MLVSS, but the increase in the effluent VSS. This point out that at the optimum COD loading rate of 25 kg/m^{3}d, the microbial growth in the bioreactor was the highest, accompanying with the least loss of the microbes from the bioreactor.

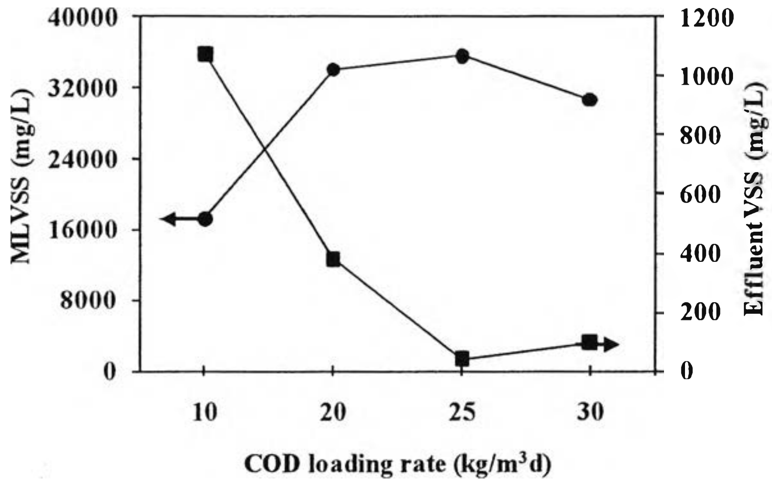

Figure 4.10 Effect of COD loading rate on MLVSS and effluent VSS at 37°C and pH 5.5.

4.2 Biomethane Production

The effluent from the biohydrogen reactor at the optimum condition, which was operated a COD loading rate of 25 kg/m^{3}d, was further fed into the biomethane production reactor. The methane production was operated without pH control and at the mesophilic temperature (37°C) to obtain the maximum methane production.