CHAPTER VI

OPTIMIZATION OF HYDROGEN AND METHANE FROM CASSAVA WASTEWATER USING TWO STAGE UPFLOW ANAEROBIC SLUDGE BLANKET REACTOR (UASB) UNDER THERMOPHILIC OPERATION

(will be submitted to Biofuel Bioproduct and Biorefinering)

6.1 Abstract

The objective of this study was to investigate the separate hydrogen and methane productions from cassava wastewater by using a two-stage upflow anaerobic sludge blanket (UASB) system under thermophillic operation (55 °C). The recycle ratio of the effluent from the methane bioreactor-to-the feed flow rate was fixed at 1:1 and the pH of the hydrogen UASB unit was maintained constant at 5.5. The two-stage UASB system was operated at different COD loading rates. At an optimum COD loading rate of 90 kg/m^{3}d based on the feed COD, feed flowrate and hydrogen UASB volume or 15 kg/m^{3}d based on the feed COD, feed flowrate and methane UASB volume, the produced gas from the hydrogen UASB unit contained 40 % H_2, 52 % CO_2 and 8 % CH_4 and the system provided a maximum hydrogen yield and specific hydrogen production rate of 80.25 ml H_2/g COD removed and 520 ml H_2/l d, respectively. At the same optimum COD loading rate, the produced gas from the methane UASB unit contained 65 % CH_4 and 35 % CO_2 without hydrogen and the system provided a maximum methane yield and specific methane production rate of 183.31 ml CH4/g COD removed and 650 ml CH_4/l d, respectively. The toxic levels of total volatile organic acids (VFA) to hydrogen-producing bacteria and methane-producing bacteria were 10,000 and 400 mg/l as acetic acid, respectively. The recycle of the effluent of the methane UASB unit to the hydrogen UASB unit could minimize the use of NaOH for pH control in the hydrogen UASB unit.

Keywords: Hydrogen and methane production; Cassava wastewater; Upflow anaerobic sludge blanket reactor (UASB); Thermophilic operation

6.2 Introduction

Currently, biogas technology has been widely applied to several industrial wastewaters and animal wastes economically [1]. It does not only produce combustible biogas which is widely used to substitute fuel oil for steam generation in industry but also reduces treatment cost. Several industrial wastewaters can be used to produce biogas such as food wastewater [2], cassava wastewater [3], and cornstalk waste [4]. Apart from gaining the combustible biogas, anaerobic digestion offers several benifits; for example, it can be operated at a high organic loading rate under ambient conditions, reduces the overall treatment cost, decreases the emission of greenhouse gases, and eliminates odorous problems [5]. However, the anaerobic processes require a rather large size of bioreactor because of their slow rates. One of interesting techniques for the improvement of biogas production from wastewaters is a use of two-stage processes [6].

The two-stage anaerobic process consists of two sequential steps of hydrogen and methane production units [7]. In the first unit, the organic compounds in wastewater are hydrolyzed and converted anaerobically to hydrogen, carbon dioxide, and volatile fatty acids (VFA) by acidogenic bacteria. Next, the effluent liquid from the first unit is continuously fed to the second unit to further produce methane by methanogenic bacteria. The two-stage anaerobic processes can produce a higher methane production rate and yield due to a better balance between the rates of VFA production and consumption as compared to a single process [8]. Sarada and Joseph [9] reported that a two-stage anaerobic system operated at a temperature of 30 °C, a HRT of 24 d and an organic loading rate of 4.5 kg/m^{3}day gave 50 % increase in the gas production rate and 40 % increase in the methane yield when being compared with a single-stage anaerobic process.

Temperature is another of important factors, affecting the process performance of anaerobic fermentation. A two-stage process operated under thermophilic temperature (55 °C) gave a higher biogas production rate than that operated at a low temperature (35-37 °C) because under the high temperature, the reaction rate is faster than that under the low temperature [8]. Luo et al., [10] reported that the hydrogen and methane yields in a two-stage thermophilic CSTR of cassava stillage were 55 ml H_2/g VS and 94 ml CH_4/g VS, respectively which were higher than those of two-stage mesophilic fermentation of food waste [11]. In this research, spontaneous hydrogen and methane productions from cassava wastewater were investigated by using a two-stage UASB process at a constant high temperature of 55 °C. The first hydrogen UASB unit was controlled at a constant pH 5.5. The effluent from the hydrogen bioreactor was further fed to the methane UASB bioreactor to produce methane without pH control. The two-stage UASB unit was operated at different COD loading rates ranging from 5, 10, 15, 20 and 25 kg/m^3d based on the feed COD and methane UASB unit or 30, 60, 90, 120 and 150 kg/m^3d based on the feed COD and hydrogen UASB unit. The recycle ratio of the effluent flow rate from the methane UASB bioreactor-to-the feed flow rate was fixed at 1:1 in order to minimize the use of NaOH for pH adjustment in the hydrogen UASB unit. It was hypothesized that both hydrogen and methane production efficiency could be achieved by the combination of two-stage process, the pH control at 5.5 for the hydrogen UASB unit and the effluent recycle operation as well as a use of thermophilic operation for both UASB units.

6.3 Materials and Methods

6.3.1 Substrate Preparation

The cassava wastewater used in this study was obtained from Ubon Bioethanol Co., Ltd., Ubon Ratchathani, Thailand. It was sieved to remove any large solid particles before use. The cassava wastewater used in the present work had a chemical oxygen demand (COD) value of 14,500 mg/l and a ratio of COD:nitrogen:phosphorous of 100:1.98:2.03, indicating that the studied cassava wastewater had sufficient amounts of both nutrients for anaerobic degradation (the theoretical ratio of COD:nitrogen:phosphorous is 100:1:0.4 for anaerobic decomposition for biogas production [12])

6.3.2 UASB Operation

The upflow anaerobic sludge blanket (UASB) reactors used in the study were constructed from borosilicate glass with a 4 and 24 L working volume for hydrogen and methane UASB bioreactors, respectively. The temperatures inside both bioreactors were controlled constant at 55 °C by circulating water through a water jacket of each bioreactor using a circulating/heating bath. The cassava wastewater was fed continuously to the bottom of the hydrogen UASB bioreactor (in upward direction) at any desired flow rate by using a peristaltic pump to obtain different COD loading rates (30, 60, 90, 120, and 150 kg/m^{3}d based on feed flow rate, feed COD and the hydrogen UASB working volume or 5, 10, 15, 20 and 25 kg/m^{3}d based on feed flow rate, feed COD and the methane UASB working volume). The pH of the hydrogen UASB unit was maintained at 5.5 by using a pH controller. The effluent from the hydrogen UASB unit was directly pumped into the methane UASB unit by a peristaltic pump with a level control probe. The pH of the methane UASB unit was not controlled. In order to minimize the consumption of NaOH for the pH control of the hydrogen UASB unit, a recycle ratio of the methane UASB effluent flow rate-to-feed flow rate of 1:1 was used in this study. The schematic of the two-stage UASB unit is shown in Figure 6.1. At any given COD loading rate, the two-stage UASB system was operated to reach steady state before taking effluent and produced gas samples for analysis and measurement. For each studied COD loading rate, the two-stage UASB system was operated around 4 weeks to reach steady state condition. The steady state was justified when both of the gas production rates and the effluent COD values of both hydrogen and methane UASB units did not change with time.

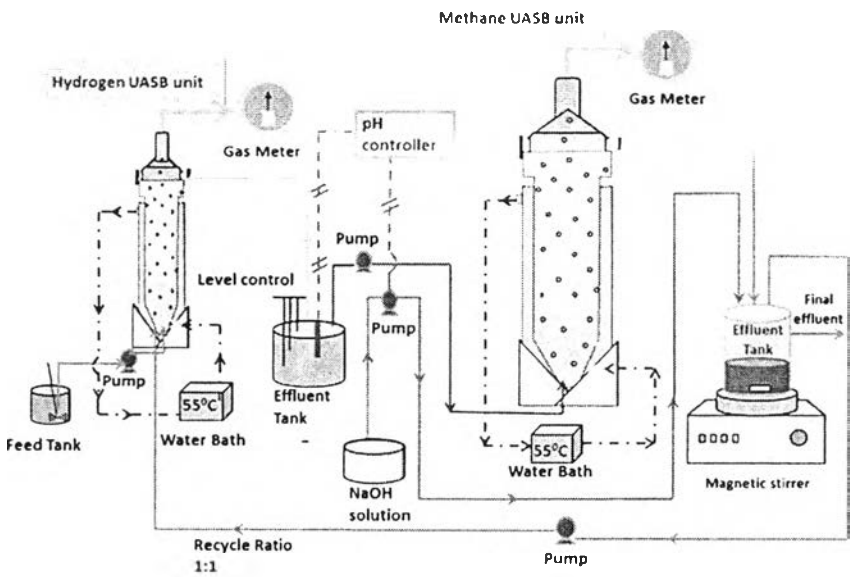

Figure 6.1 The schematic of the two-stage Upflow Anaerobic Sludge Blanket Reactor (UASB) unit.

6.3.3 Measurement and Analytical Methods

The volumes of produced gases from both UASB bioreactors were recorded daily by the wet gas meters (Ritter, TGO5/5). The compositions of both produced gas samples were determined by a gas chromatograph (Auto System GC, Perkin-Elmer) equipped with a thermal conductivity detector (TCD) and a packed column (stainless-steel 10'x 1/8' x .085" HayeSep D 100/120 mesh, Altech) and the analysis conditions were given elsewhere [12]. The chemical oxygen demand values (COD) in the feed and effluent samples were quantified by the dichromate method using a COD reactor and a spectrophotometer (HACH, DR 2700). The mixed liquor volatile suspended solid (MLVSS) was measured by taking the whole sludge in each bioreactor at the end of operation for any studied COD loading rate to represent the microbial concentration in each UASB unit. The effluent volatile suspended solid (effluent VSS) representing the microbial washout from each UASB unit was measured according to the standard methods [13]. The total amount of volatile fatty acids in mg as acetic acid per liter was determined by the distillation-titration method [13]. The samples obtained from the steam distillation were additionally taken for the determination of organic acid compositions by using another gas chromatograph (PR

2100, Perichrom) equipped with a flame ionization detector (FID) and the analysis conditions were given elsewhere [12]. Nitrogen analyses (in terms of organic nitrogen measured by the diazotization, cadmium reduction method, and inorganic nitrogen measured by the salicylate method) in the feed and effluent samples were carried out with the TNT persulfate digestion. The total phosphorous contents in the feed and effluent samples were determined by the molybdovanadate method with acid persulfate digestion (Hach Company) [14]. Moreover, the effluent samples of both hydrogen and methane bioreactors were measured for pH and alkalinity according to the standard methods [15]. The sodium concentrations in the effluents of both hydrogen and methane UASB units were measured using an atomic absorption spectrophotometer (AAS) (SpectrAA 300, Varian). The average values of all analysis and measurements (with less than 5 % standard deviation) were used to access the process performance of the two-stage UASB system.

6.4 Results and Discussion

6.4.1 Hydrogen Production Performance Results

6.4.1.1 COD Removal and Gas Production Rate

Figure 6.2a shows the effects of COD loading rate on COD removal and gas production rate of the hydrogen UASB unit operated at 55 °C and pH 5.5. Since the constant recycle ratio of 1:1 was used to operate the two-stage UASB system, actual COD loading rate calculated from the COD values of both feed and recycle effluent was also presented for a comparison. The COD removal increased with increasing COD loading rate and attained a maximum value of 35 % at a COD loading rate of 90 kg/m^{3}d. Beyond the COD loading rate of 90 kg/m^{3}d, it decreased with further increasing COD loading rate. The gas production rate also shows a similar trend to the COD removal. The maximum gas production rate (5.5 l/d) was found at the same COD loading rate of 90 kg/m^{3}d. The cassava wastewater contains a high organic content in terms of a COD value of 14,500 mg/l. Hence a higher COD loading rate simply provided a higher organic compound amount available for microbial activity, leading to both increases in COD removal and gas production rate. However, with further increasing COD loading rate from 90 to 150 kg/m^{3}d, the decreases in both COD removal and gas production rate resulted from the increasing toxicity from organic acid accumulation which will be discussed latter.

6.4.1.2 Hydrogen Production Efficiency

The gas composition and hydrogen production rate of the hydrogen UASB unit as a function of COD loading rate are shown in Figure 6.2b. The produced gas of the hydrogen UASB bioreactor mainly contained hydrogen and carbon dioxide with a small amount of methane. The methane content decreased steadily with increasing COD loading rate, corresponding to a reduction of hydraulic retention time (HRT) from 12 h at a COD loading rate of 30 kg/m^{3}d to 2.4 h at a COD loading rate of 150 kg/m^{3}d [15]. The hydrogen content increased with increasing COD loading rate from 30 to 90 kg/m^{3}d and then decreased with further increasing COD loading rate from 90 to 150 kg/m^{3}d. The maximum values of both hydrogen content and hydrogen production rate were 40 % and 2.2 l/d, respectively at the same COD loading rate of 90 kg/m^{3}d. The first increase in hydrogen production rate with increasing hydrogen content resulted from the increase in organic loading available for the microbial activity. However, the decreases in hydrogen production rate and content with further increasing COD loading rate from 90 to 150 kg/m^{3}d resulted from the increasing toxicity from increasing VFA in the system, as mentioned before [16]. The CO_2 concentration in the produced gas showed an opposite trend to the H_2 concentration.

The specific hydrogen production rate (SHPR) is used to indicate the ability of microbes to produce hydrogen from organics of any particular wastewater per unit volume of reactor or per unit dried weight of microbes, in which is very useful for scaling up a bioreactor. Both SHPR values increased with increasing COD loading rate from 30 to 90 kg/m^{3}d and then decreased with further increasing COD loading rate from 90 to 150 kg/m^{3}d (Figure 6.2c). Both maximum SHPR values found at the same COD loading rate of 90 kg/m^{3}d were 197.17 ml H_2/g MLVSS d and 530 ml H_2/l d which were consistent with the maximum values of hydrogen production rate, hydrogen content, and COD removal.

In addition, hydrogen yield used to indicate the efficiency of conversion of organic compounds to hydrogen by microbes in terms of ml H_2/g COD applied or ml H_2/g COD removed was also determined in this study. They showed the similar trend to the SHPR values (Figures 6.2c and 6.2d). The maximum hydrogen yield of 80.25 ml H_2/g COD removed (or 54.22 ml H2/g COD applied) was found at the same COD loading rate of 90 kg/m^{3}d which corresponded to the highest SHPR and hydrogen production performance. The higher hydrogen production efficiency resulted from the higher organic loading in the system to provide more food for the microorganisms to produce more hydrogen. Again, the SHPR and hydrogen yield sharply decreased when the COD loading rate increased beyond 90 kg/m^{3}d due to the toxicity from the VFA accumulation. In our previous work using anaerobic sequencing batch reactor to produce hydrogen from alcohol wastewater under a constant pH of 5.5 at 55 °C without effluent recycle [12], the maximum hydrogen yield of 130 ml H_2/g COD removed (or 30 ml H_2/g COD applied) was found at a COD loading rate of 68 kg/m3d under a constant pH 5.5. The hydrogen yield values obtained from the present work are comparable to those of the previous work. The hydrogen yield from cassava wastewater under the two-stage thermophilic UASB process of the present study is about 50 % higher than that under the two-stage mesophilic UASB process (12.82 ml H_2/g COD removed) [17].

As shown in Figure 6.2f, the alkalinity of the hydrogen UASB unit slightly increases with increasing COD loading rate and reaches at a maximum level at a COD loading rate of 90 kg/m^{3}d. With further increasing COD loading rate from 90 to 150 kg/m^{3}d, the system alkalinity slightly decreased. The decrease in alkalinity resulted from the increase in VFA in the system. It should be mentioned that the alkalinity range in the hydrogen UASB unit was considerably low because of the low system pH of 5.5.

6.4.1.3 Volatile Fatty Acid (VFA) and VFA Composition

The effects of COD loading rate on total VFA concentration and VFA composition in the hydrogen UASB unit are shown in Figure 6.3. The total VFA concentration increased markedly with increasing COD loading rate from 30 to 120 kg/m^{3}d but it slightly increased with further increasing COD loading rate beyond 120 kg/m^{3}d. The maximum total VFAs concentration (16,000 mg/l as acetic acid) was at the highest COD loading rate of 150 kg/m^{3}d. As compared the results shown in Figures 2 and 3, it can be concluded that the toxic level of VFA was around

10,000 mg/l as acetic acid for the cassava wastewater under the studied conditions to the hydrogen-producing bacteria which is consistent to our previous work [12].

As shown in Figure 6.3, the main components of VFA are butyric acid (HBu), valeric acid (HVa), acetic acid (HAc), and propionic acid (HPr). All produced organic acids had a similar trend to that of the total VFA concentration except the propionic acid concentration slightly increased with increasing COD loading rate. In this study, the butyric acid concentration was the highest while propionic acid concentration was the lowest, in which contributed to the system having high hydrogen production performance [18-19]. According to the microbial metabolic pathway, all organic acids are produced in conjunction with the production of hydrogen while the consumption of hydrogen results in the formation of propionic acid [20], as shown in the following equation.

$$CH_3COOH + H_2 \longrightarrow CH_3CH_2OH + H_2O \qquad (1)$$

Another component that also shows a negative effect to the efficiency of hydrogen production is the formation of ethanol. One mole of ethanol is produced by consuming one mole of hydrogen under anaerobic condition [21]. However, in this study, there was a very small amount of produced ethanol and the ethanol concentration remained almost unchanged throughout the COD loading rate range of 30 - 150 kg/m^{3}d. Therefore, the effect of produced ethanol can be negligible for this study.

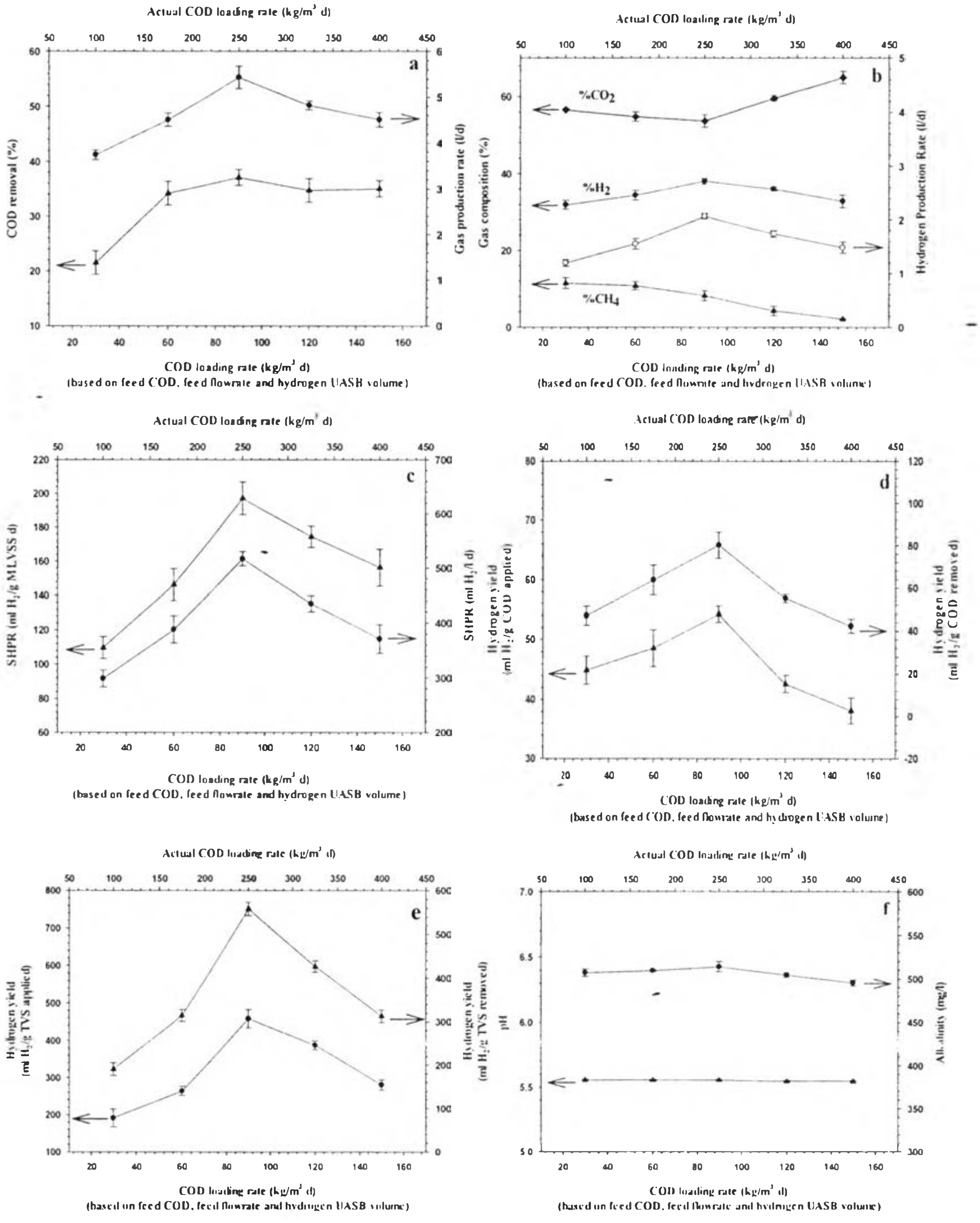

Figure 6.2 Effects of COD loading rate on (a) COD removal and gas production rate, (b) gas composition and hydrogen production rate, (c) specific hydrogen production rates, (d) hydrogen yield of the hydrogen UASB unit (e) hydrogen yield of the hydrogen UASB unit in terms of ml H_2/g TVS and (f) pH and alkalinity.

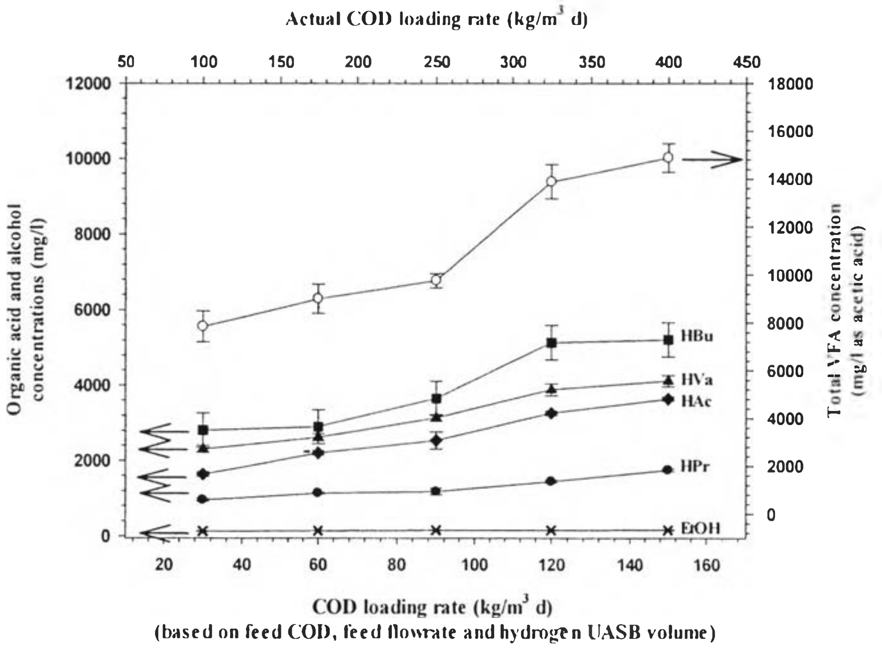

Figure 6.3 Total VFA, and VFA composition versus COD loading rate of the hydrogen UASB unit.

6.4.2 Methane Production Performance Results

6.4.2.1 COD Removal and Gas Production Rate

As described before, the liquid effluent from the hydrogen UASB unit was directly fed to the methane UASB unit for further producing methane. The methane bioreactor was also operated under thermophilic temperature (55 °C) without pH control. Figure 6.4a shows the COD removal at different COD loading rates (based on either the feed COD loading and methane UASB volume or the actual incoming COD loading and methane UASB volume). The COD removal increased with increasing COD loading rate and reached a maximum value of 72 % at a COD loading rate of 15 kg/m^{3}d (based on the feed COD, feed flowrate and methane UASB volume). Beyond the optimum COD loading rate of 15 kg/m^{3}d, the COD removal slightly decreased with further increasing COD loading rate. The gas production rate showed a similar trend to the COD removal. Interestingly, the gas production rate of the methane UASB unit was about 4 times higher than that of hydrogen UASB unit, corresponding to the sizes of both bioreactors.

6.4.2.2 Methane Production Efficiency

The composition of produced gas from the methane UASB unit mainly contained methane and carbon dioxide with a very small amount of hydrogen (less than 0.5 %) (Fig.6.4). Both methane content and methane production rate increased with increasing COD loading rate from 5 to 15 kg/m3d but they decreased with further increasing COD loading rate from 15 to 25 kg/m3d (Fig.4b). In contrast, the CO2 content in the produced gas showed an opposite trend. The maximum methane content and methane production rate of 68 % and 16 l/d, respectively were found at a COD loading rate of 15 kg/m3d, corresponding to the optimum COD loading rate of 90 kg/m3d (based on the feed COD, feed flowrate, and hydrogen UASB volume) for the maximum hydrogen production performance.

Figures 6.4c-d show the specific methane production rates (SMPR) and methane yields, as a function of COD loading rate. They increased with increasing COD loading rate and then decreased with further increasing COD loading rate from 15 to 25 kg/m^{3}d. The maximum values of SMPR (650 ml CH_4/l d or 356.31 ml CH_4/g MLVSS d) and methane yield (183.31 ml CH_4/g COD removed or 98.87 ml CH_4/g COD applied) were at a COD loading rate of 15 kg/m^{3}d. Hence, the COD loading rate of 15 kg/m^{3}d was considered to be an optimum organic loading rate for both production of hydrogen and methane by the two-stage thermophilic UASB system. The maximum methane yield of 840 CH_4/g TVS applied found in this study (Figure 4e) was about 100 % higher than that from household solid waste using one-stage process at 37 °C (413 ml CH_4/g TVS applied) [22-23].

The pH and alkalinity of the methane UASB unit increased with increasing COD loading rate and reached at maximum level at a COD loading rate of 15 kg/m3d (Fig.6.4f). With further increasing COD loading rate from 15 to 25 kg/m3d, the system pH and alkalinity sharply decreased. The sharp decreases in pH and alkalinity resulted from the increase in VFA in the system. The decrease in pH from 6.65 to 6.04 in the methane UASB unit affected the activity of methane-forming bacteria, causing the decrease in methane production performance because of the toxicity from the VFA accumulation [25-26], as indicated latter.

6.4.2.3 Volatile Fatty Acid (VFA) and VFA Composition

Figure 6.5 shows the effect of COD loading rate on total volatile fatty acid (VFA) concentration and composition in the methane UASB unit. The total VFA concentration increased steadily with an increase in COD loading rate. The maximum total VFA concentration of 780 mg/l as acetic acid was at the highest COD loading rate of 25 kg/m^{3}d. From the results of COD removal, gas production rate and total VFA, the toxic level of VFA to the methane-producing bacteria is around 400 mg/l. Similar to the organic acids produced in the hydrogen UASB unit, the methane UASB unit also only generated acetic acid, propionic acid, butyric acid and valeric acid and all produced organic acids also increased gradually when the COD loading rate increased. At any given COD loading rate, the concentration of acetic acid was the highest followed by propionic acid, butyric acid, and valeric acid, respectively. The highest acetic acid concentration resulted from the further degradation of both propionic acid and butyric acid, according to equations 2 and 3 [27]. The production of methane mainly resulted from the two basic bioconversion reactions of hydrogenotrophic and acetotrophic pathways, as shown in equations 4 and 5 [27-28].

$$CH_3CH_2CH_2COOH + 2H_2O \longrightarrow 2CH_3COOH + 2H_2 \quad (2)$$

$$CH_3CH_2COOH + 2H_2O \longrightarrow CH_3COOH + CO_2 + 3H_2 \quad (3)$$

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

$$CH_3COOH \longrightarrow CH_4 + CO_2 \quad (5)$$

6.4.3 Microbial Concentration and Microbial Washout Results

As shown in Figure 6.6. the microbial concentration (MLVSS) in each UASB bioreactor decreases with increasing COD loading rate whereas the microbial washout (effluent VSS) from each UASB unit shows an opposite trend. The results of both steady increases in hydrogen and methane production efficiency with decreasing microbial concentration in the studied COD loading rate range of 5-15 kg/m^{3}d (based on the feed COD, feed flowrate and methane UASB volume) suggest that an increase in COD loading rate simply increases in organic loading available for microbial activities to produce more both gases and the increases in microbial washout from both UASB bioreactors probably indicate that the only inactive microbes were washed out. However, the results showing the decreases in both production performance of hydrogen and methane with further increasing COD loading rate from 90 to 150 kg/m^{3}d based on the feed COD, feed flowrate and hydrogen UASB volume or 15 to 25 kg/m^{3}d based on the feed COD, feed flowrate and methane UASB volume can be explained by the fact that the increasing organic acid concentration greater than 10,000 and 400 mg/l increased the toxicity to the microbes in the hydrogen UASB unit and the methane UASB unit, respectively, causing increasing washout of active microbes from both UASB bioreactors. As a consequence, the microbial activities in of both hydrogen and methane productions of both UASB units decreased with further increasing COD loading rate in the mentioned range.

In this study, sodium hydroxide used to adjust pH in the hydrogen UASB unit could affect the microbial activity in both UASB bioreactors, depending on its concentration [29]. A low concentration of sodium in the range of 230-350 mg/l is known to serves as an essential element to stimulate the activity of methanogenic bacteria [29]. However, a high content of sodium greater than 16,000 mg/l reportedly exhibits toxicity to anaerobic microbes [30]. In this study, the sodium content in both studied UASB units was in the range of 150-220 mg/l in which is much lower than the sodium toxic level to anaerobic microbes. This low sodium level in the two-stage UASB system resulted from the effluent recycle operation.

6.4.4 Nitrogen and Phosphorous Uptakes and Transformation

Figure 6.7 shows the nitrogen and phosphorous uptakes and nitrogen compound transformation in both steps of acidogenesis and methanogenesis. Both of nitrogen and phosphorous uptakes for the acidogenic and methanogenic steps increased with increasing COD loading rate. The higher the COD loading rate, the higher the nutrient uptakes. The utilization of nitrogen by microbes can come from different nitrogen sources: ammonium-nitrogen, nitrate-nitrogen, nitrite-nitrogen, and organic-nitrogen [31]. The concentrations of ammonium-nitrogen, and nitrate-nitrogen from both steps decreased slightly with increasing COD loading rate whereas the organic-nitrogen concentration decreased drastically, suggesting that the nitrogen uptakes of both steps mostly came from organic-nitrogen compounds [10]. At the optimum COD loading rate for both UASB units, the ratio of COD removal:N uptake:P uptake in methane UASB unit was found to be 100:2.59:1.96, which is slightly higher than that in hydrogen UASB unit (100:2.20:1.31). Both N and P uptakes were much higher than the theoretical nutrient requirement for anaerobic decomposition for methane production in mesophilic temperature (COD:N:P = 100:1.0:0:2). This is because the system was operated under thermophilic temperature in which reportedly requires higher nutrients [12-13].

6.4.5 Overall Performance

Figure 6.8 shows the overall performance on both hydrogen and methane production of the two-stage UASB system under the thermophilic temperature of 55 °C at different COD loading rates. The two-stage UASB system was considered to be as a single reaction unit and both produced gas streams were combined to calculate the production performance of the mixed gas. This two-stage UASB process operated at a total COD loading rate of 12.9 kg/m^{3}d (based on total volume of both UASB units, feed COD and feed flowrate) provided a maximum total hydrogen yield of 458.63 ml H_2/g TVS applied and a maximum total methane yields of 510.61 ml CH_4/g TVS applied (Figure 8g) which was higher than those of two-phase thermophilic CSTR process at an organic loading rate of > 10 g VS/ L d (hydrogen yield 56.6 ml H_2/g VS applied and methane yield 249 ml H_2/g VS applied) [10]. The mixed gas produced from both UASB units, so-called hythane, contained 7 %H_2, 59.8 %CH_4 and 32.7 %CO_2 at the optimum COD loading rate. The H_2/CH_4 ratio (1:8.5) of the mixed gas produced from this study was higher than that of two-phase thermophilic CSTR process (1:4.4) [10]; because the continuously stirred tank reactor (CSTR) is a low rate anaerobic digester that causes both substrate and microorganisms passing through the digester quickly. The degradation efficiency including lower the conversion of substrate to biogas of a CSTR system has been reported to be lower than that of a UASB system [27.32]. The higher heating value (HHV) and the lower heating value (LHV) of the mixed gas (hythane) obtained from the optimum COD loading rate are 23.62 and 21.14 MJ/m^3 [33]. The biogas produced from a single-stage UASB unit typically contains 70 % CH_4 and 30 % CO_2 without H_2. The HHV and LHV of the biogas are 22.70 and 20.43 MJ/m^3, respectively. Hence, it can be concluded that a use of two-stage anaerobic process can provided a higher heating value of produced gas as compared to a single-stage anaerobic process based on gas volume.

6.5 Conclusions

In this study, separate production of hydrogen and methane from cassava wastewater using two-stage upflow anaerobic sludge blanket reactor (UASB) process under thermophilic temperature (55 °C) was optimized by recycling the methane UASB effluent to the hydrogen UASB unit at a constant recycle ratio of 1:1 and by controlling the hydrogen UASB unit at pH 5.5. The highest hydrogen production performance in terms of the highest hydrogen percentage (40 %), the highest hydrogen production rate (2.2 l/d), the highest hydrogen yield (54.22 ml H_2/g COD applied) and the highest SHPR (197.17 ml H_2/g MLVSS d) and the highest COD removal (35 %) was achieved at a COD loading rate of 90 kg/m^{3}d (based on the feed COD, feed flowrate and hydrogen UASB volume) corresponding to the optimum COD loading rate of 15 kg/m3d (based on the feed COD, feed flowrate and methane UASB volume) in which also provided the maximum process performance of the methane UASB (in terms of the highest methane percentage of 68 %, the highest methane production rate of 16 l/d, the highest methane yield of 164.87 ml CH_4/g COD applied, and the highest SMPR of 356.31 ml CH_4/g MLVSS d, and the highest COD removal of 72 %. The sodium concentrations of feed (138 mg/l) and the final effluent (150-220 mg/l) were not significantly different, indicating that the use of effluent recycle could reduce the NaOH consumption for the pH adjustment in the hydrogen UASB unit.

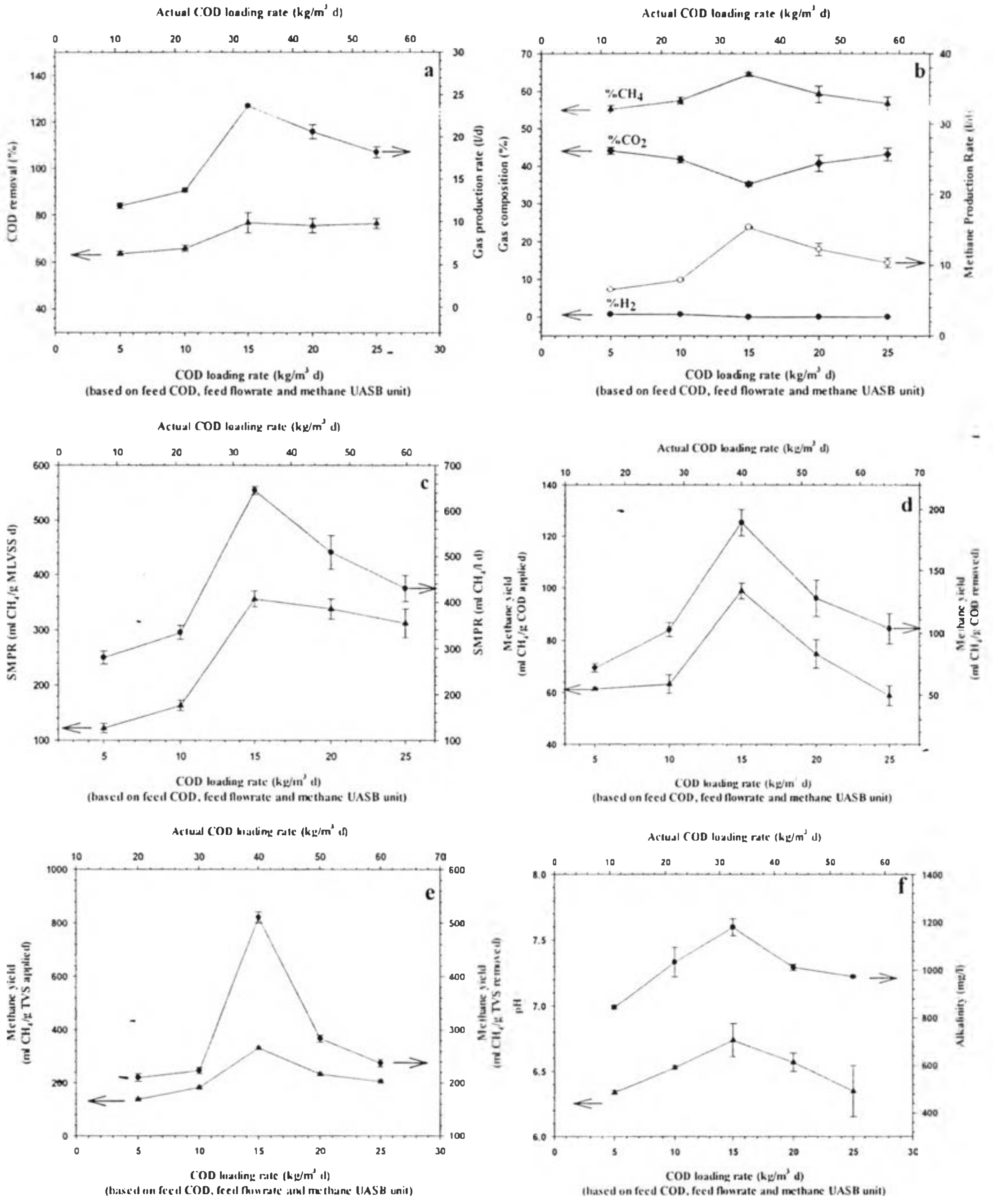

Figure 6.4 Effects of COD loading rate on (a) COD removal and gas production rate, (b) gas composition and methane production rate, (c) specific methane production rates, (d) methane yield of the methane UASB unit (e) methane yield of the hydrogen UASB unit in terms of ml CH_4/g TVS and (f) pH and alkalinity.

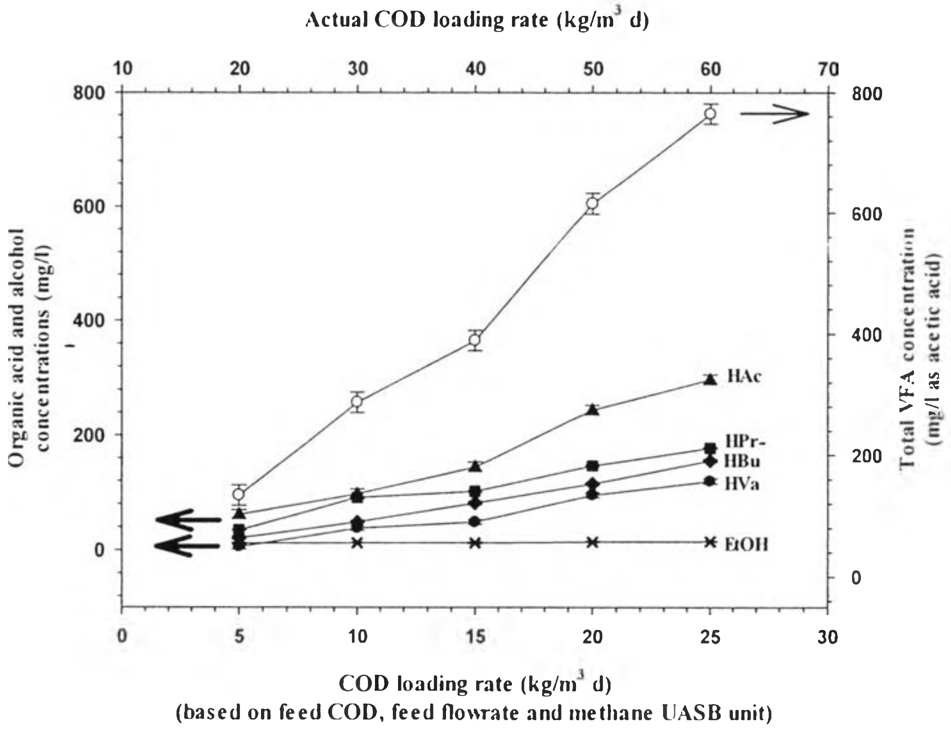

Figure 6.5 Total VFA, and VFA composition versus COD loading rate of the methane UASB unit.

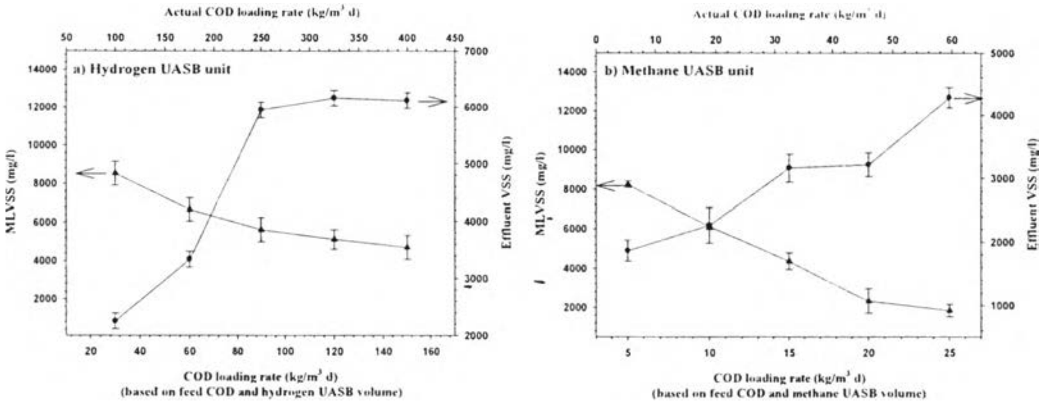

Figure 6.6 MLVSS and effluent VSS versus COD loading rate (a) for the hydrogen UASB unit, (b) for the methane UASB unit.

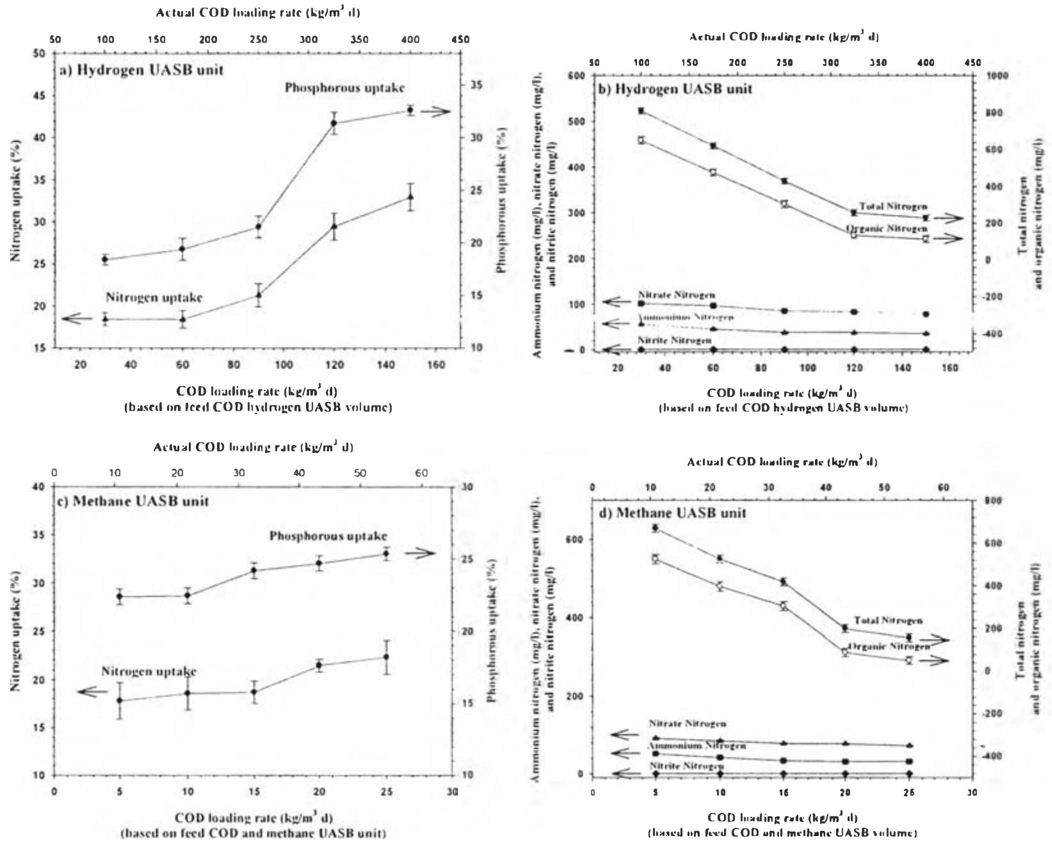

Figure 6.7 Effects of COD loading rate on (a) nitrogen and phosphorous removal of the hydrogen UASB unit, (b) total nitrogen, organic nitrogen and inorganic nitrogen concentrations of the hydrogen UASB unit, (c) nitrogen and phosphorous removal of the methane UASB unit and (d) total nitrogen, organic nitrogen and inorganic nitrogen concentrations of the methane UASB unit.

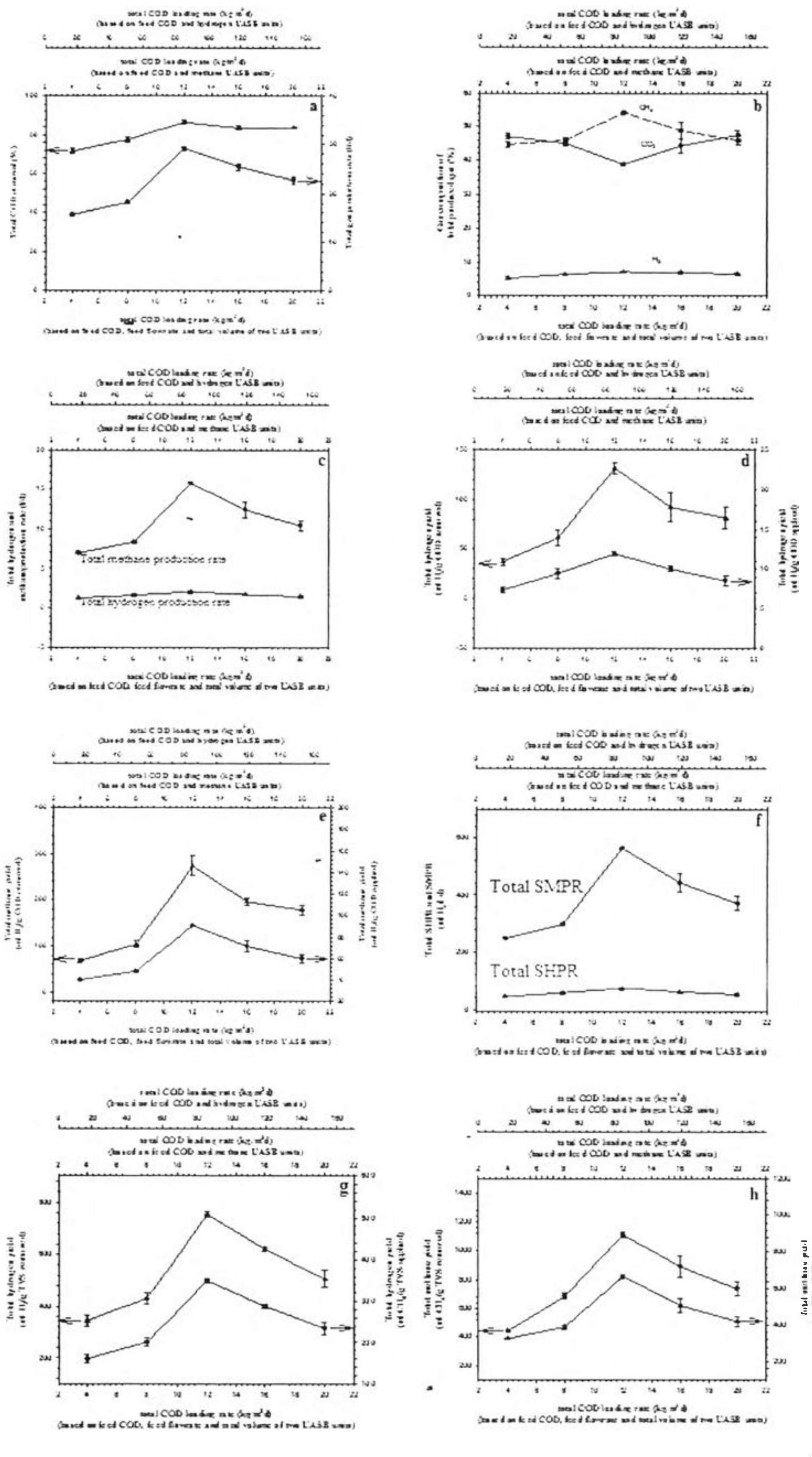

Figure 6.8 Overall performance of two-stage UASB process at 55 °C

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