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APPENDICES

Appendix A Calibration Curves

Table A1 Calibration curve for hydrogen (H_2)

Volume of hydrogen (ml)	Peak area
0.02	16,313
0.04	58,770
0.08	180,674
0.1	226,743
0.2	427,198
0.4	778,509

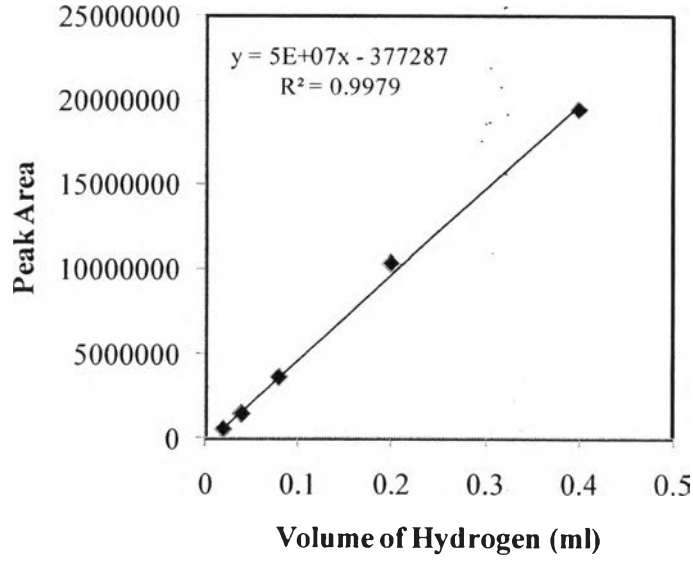

Figure A1 The relationship between volume of hydrogen (H_2) and peak area.

Equation

$$\text{Amount of hydrogen} = \frac{\text{Peak area} + 377287}{5 \times 10^7}$$

Table A2 Calibration curve for nitrogen

Volume of nitrogen (ml)	Peak area
0.02	34,210
0.04	128,767
0.08	305,287
0.1	393,916
0.2	809,433
0.4	1,602,475

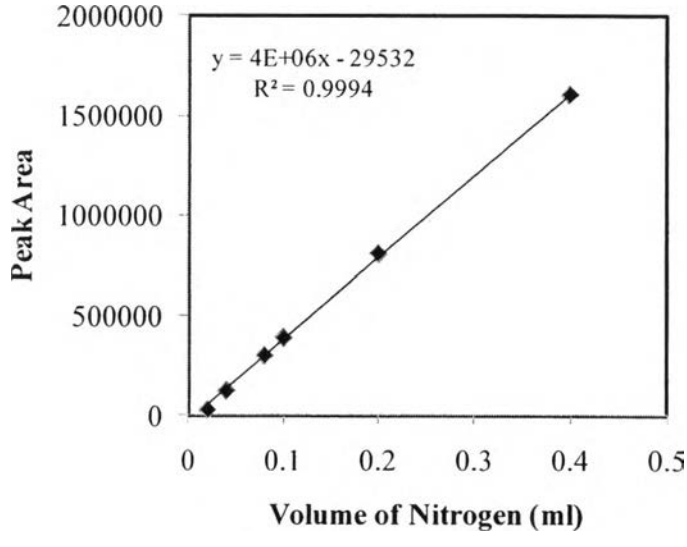

Figure A2 The relationship between volume of nitrogen (N_2) and peak area.

Equation

$$\text{Amount of nitrogen} = \frac{\text{Peak area} + 29532}{4 \times 10^6}$$

Table A3 Calibration curve for oxygen

Volume of oxygen (ml)	Peak area
0.02	12,286
0.04	43,995
0.08	104,342
0.1	135,546
0.2	280,220
0.4	562,001

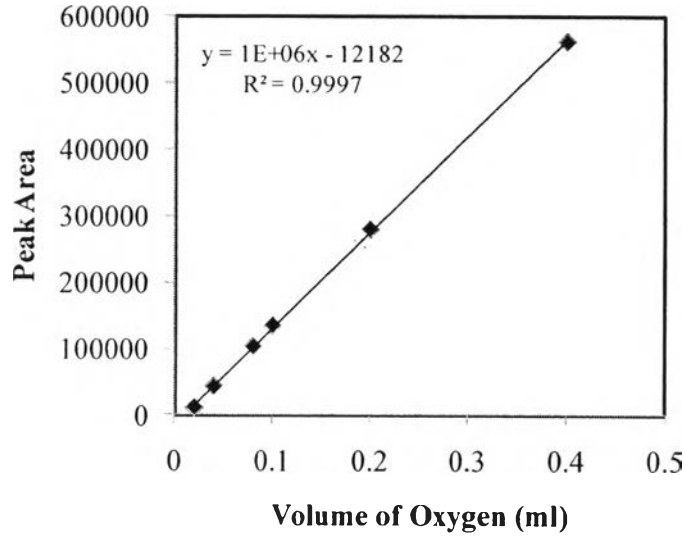

Figure A3 The relationship between volume of oxygen (O_2) and peak area.

Equation

$$\text{Amount of oxygen} = \frac{\text{Peak area} + 12182}{1 \times 10^6}$$

Table A4 Calibration curve for methane (CH_4)

Volume of methane (ml)	Peak area
0.02	92,517
0.04	381,106
0.1	1,293,552
0.2	2,674,654

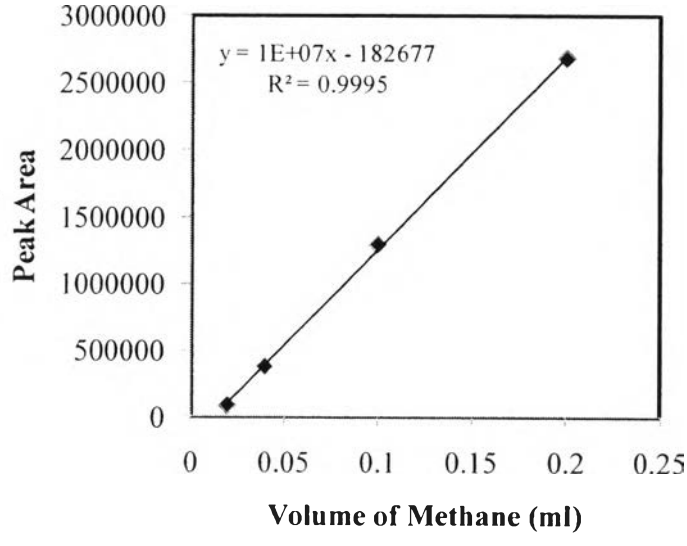

Figure A4 The relationship between volume of methane (CH_4) and peak area.

Equation

$$\text{Amount of methane} = \frac{\text{Peak area} + 182677}{1 \times 10^7}$$

Table A5 Calibration curve for carbon dioxide (CO_2)

Volume of carbon dioxide (ml)	Peak area
0.02	26,118
0.04	97,539
0.08	220,122
0.2	596,414
0.4	1,315,885

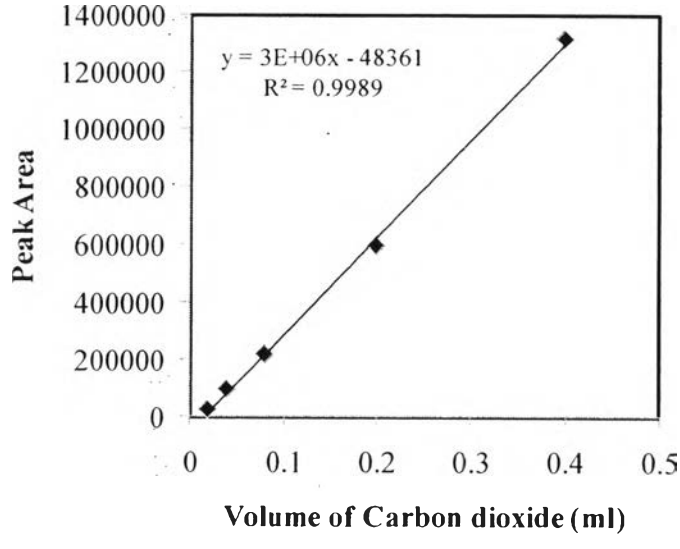

Figure A5 The relationship between volume of carbon dioxide (CO_2) and peak area.

Equation

$$\text{Amount of carbon dioxide} = \frac{\text{Peak area} + 48361}{3 \times 10^6}$$

Appendix B Preparation of 5 wt./vol.% NaOH Solution for pH-Controlled System

Preparation of NaOH at concentration of 5 wt./vol.%

$$= \frac{5}{100}\frac{g}{ml} = 50\frac{g}{l}$$

Appendix C Volatile Fatty Acids (VFA) Quantification by Distillation Method

C 1. Acetic Acids Stock Solution Preparation for Recovery Factor (f) Determination

Concentration of fresh acetic acid (liquid) = 99.7%

Density of acetic acid = 1.07 g/ml

Molecular weight of acetic acid = 60

Determination of fresh acetic acids concentration in term of molar

$$= \frac{0.997 \text{ L of acetic acid}}{\text{L of solution}} \text{ x } \frac{1.07 \text{ g of acetic acid}}{\text{mL of acetic acid}} \text{ x } \frac{1 \text{ mol of acetic acid}}{60 \text{ g of acetic acid}}$$

= 17.78 M

Preparation of acetic acid at concentration of 2,000 mg/L

$$= 2.000 \frac{\text{mg of acetic acid}}{\text{L of solution}} \text{ x } \frac{1 \text{ mole of acetic acid}}{60 \text{ g of acetic acid}}$$

= 0.0333 M

Dilution of acetic acid

$N_1V_1 = N_2V_2$

$V_1 = N_2V_2/N_1$

$= (0.0333x1)/17.78$

$= 1.873x10^{-3}$ L

C 2. Standard Sodium Hydroxide (0.1 M) Preparation

Concentration of fresh NaOH (solid) = 99%

Molecular weight of acetic acid = 40

Preparation of acetic acid at concentration of 0.1 M

$$= \frac{0.1\,\text{mol}}{1\,\text{L}} \text{x} \frac{40\,\text{g}}{1\,\text{mol}} x \frac{100}{99}$$

$$= 4.04\ \text{g}$$

C 3. Recovery Factor (f) Determination

Distill 150 ml of 0.0333 M of acetic acid in distillation apparatus

Calculate the recovery factor

$$f = \frac{a}{b}$$

where

a = volatile acid concentration recovered in distillate, mg/L

b = volatile acid concentration in standard solution used, mg/L

Find volatile acid concentration recovered in distillate by titration with 0.1 M of NaOH (MW of acetic acid = 60.5)

1) Distillate 50 ml NaOH 11.7 ml

Used NaOH	=	$11.7x10^{-3}x0.1$	
	=	$1.17x10^{-3}$	mol
Acetic acid in distillate	=	$1.17x10^{-3}$	mol
	=	$1.17x10^{-3}$ x 60.5	
	=	0.07	g
Concentration of acetic acid in distillate			
	=	0.07/50	
	=	$1.405x10^{-3}$	g/ml
	=	1,405	mg/l

2) Distillate 25 ml NaOH 5.7 ml

Used NaOH	=	$5.7x10^{-3}x0.1$	
	=	$5.7x10^{-4}$	mol
Acetic acid in distillate	=	$5.7x10^{-4}$	mol
	=	$5.7x10^{-4}$ x 60.5	
	=	0.034	g

Concentration of acetic acid in distillate

= 0.034/25

= 1.368×10^{-3} g/ml

= 1,368 mg/l

Average = 1,387 mg/l

Recovery factor (f) = 1,387/2,000

= 0.6935

Appendix D Raw Data of Effect of COD Loading Rate

D 1. COD loading rate = 30 kg/ m^3d pH = 5.5 Temperature = 55°C

Days	Amount of each component (mL)			Total amount (mL)	Produced gas composition (%)		
	H_2	CO_2	CH_4		H_2	CO_2	CH_4
1	0.0202	0.3199	0.0184	0.3585	5.63	89.23	5.13
2	0.0448	0.277	0.0184	0.3402	13.17	81.42	5.41
3	0.0783	0.3182	0.0184	0.4149	18.87	76.69	4.43
4	0.0772	0.2661	0.0186	0.3619	21.33	73.53	5.14
5	0.0725	0.3011	0.0184	0.392	18.49	76.81	4.69
6	0.086	0.3181	0.0184	0.4225	20.36	75.29	4.36
7	0.0558	0.1967	0.0183	0.2708	20.61	72.64	6.76
8	0.0751	0.2489	0.0184	0.3424	21.93	72.69	5.37
9	0.0906	0.2977	0.0184	0.4067	22.28	73.2	4.52
10	0.0768	0.2638	0.0187	0.3593	21.37	73.42	5.2
11	0.0691	0.2592	0.0225	0.3508	19.7	73.89	6.41
12	0.0573	0.2899	0.0184	0.3656	15.67	79.29	5.03
13	0.0465	0.265	0.0188	0.3303	14.08	80.23	5.69
Avg.	0.0654	0.2786	0.01876	0.3628	17.96	76.8	5.24

Gas production rate	=	0.42	l/h
Hydrogen production rate	=	0.08	l/h
Specific hydrogen production rate	=	62.32	ml H_2/g MLVSS d
VFA Concentration	=	4,354.7	mg/l as acetic acid
Hydrogen yield	=	82.09	ml H_2/g COD removed
COD removal efficiency	=	17.42	%
MLVSS	=	7,262	mg/l
TSS	=	1,616	mg/l

Distillated sample 100 µl + Internal standard (n-propanol 3,000 ppm) 100 µl

VFA	Concentration (ppm)
Ethanol	251.73
Acetic acid	1,222.52
Propionic acid	1,553.41
Butyric acid	797
Valeric acid	856.8

D 2. COD loading rate = 45 kg/ m^3d pH = 5.5 Temperature = 55°C

Days	Amount of each component (mL)			Total amount (mL)	Produced gas composition (%)		
	H_2	CO_2	CH_4		H_2	CO_2	CH_4
1	0.0632	0.347824	0.0197	0.4307	14.67	80.75	4.57
2	0.0528	0.255108	0.0184	0.3263	16.18	78.18	5.64
3	0.0664	0.23436	0.0183	0.319	20.81	73.45	5.74
4	0.0426	0.211991	0.0209	0.2755	15.46	76.95	7.59
5	0.0486	0.20484	0.0193	0.2727	17.82	75.1	7.08
6	0.0494	0.221128	0.0186	0.2891	17.09	76.48	6.43
7	0.0478	0.163662	0.0183	0.2298	20.8	71.23	7.96
8	0.071	0.227719	0.0184	0.3171	22.39	71.81	5.8
9	0.0662	0.197982	0.0183	0.2825	23.44	70.07	6.48
10	0.0237	0.058898	0	0.0826	28.69	71.31	0
11	0.0437	0.135814	0.0183	0.1978	22.09	68.66	9.25
12	0.0505	0.157969	0	0.2085	24.22	75.78	0
13	0.123	0.3274	0.0184	0.4688	26.24	69.84	3.92
Avg.	0.0576	0.2111	0.0159	0.2847	19.72	73.87	6.41

Gas production rate	=	0.48	l/h
Hydrogen production rate	=	0.09	l/h
Specific hydrogen production rate	=	65.33	ml H_2/g MLVSS d
VFA concentration	=	3,677	mg/l as acetic acid
Hydrogen yield	=	56.08	ml H_2/g COD removed
COD removal efficiency	=	21.11	%
MLVSS	=	8,602	mg/l
TSS	=	916.67	mg/l

Distillated sample 100 µl + Internal standard (n-propanol 3,000 ppm) 100 µl

VFA	Concentration (ppm)
Ethanol	225.29
Acetic acid	1,183.56
Propionic acid	540.63
Butyric acid	1,333.56
Valeric acid	792.79

D 3. COD loading rate = 60 kg/ m^3d pH = 5.5 Temperature = 55°C

Days	Amount of each component (mL)			Total amount (mL)	Produced gas composition (%)		
	H_2	CO_2	CH_4		H_2	CO_2	CH_4
1	0.0474	0.2351	0.0183	0.3008	15.76	78.16	6.08
2	0.0283	0.2004	0.0000	0.2287	12.37	87.63	0.00
3	0.0217	0.1904	0.0184	0.2305	9.41	82.60	7.98
4	0.0170	0.1776	0.0205	0.2151	7.90	82.56	9.54
5	0.0126	0.1793	0.0183	0.2102	5.99	85.29	8.72
6	0.0095	0.1540	0.0000	0.1635	5.81	94.19	0.00
7	0.0097	0.1665	0.0000	0.1762	5.51	94.49	0.00
8	0.0090	0.1515	0.0000	0.1605	5.61	94.39	0.00
9	0.0083	0.1436	0.0000	0.1519	5.47	94.53	0.00
10	0.0136	0.1770	0.0000	0.1906	7.13	92.87	0.00
11	0.0113	0.1123	0.0000	0.1236	9.14	90.86	0.00
12	0.0133	0.1731	0.0184	0.2047	6.50	84.53	8.97
13	0.0171	0.2189	0.0183	0.2543	6.73	86.06	7.21
14	0.0280	0.3189	0.0201	0.3670	7.63	86.89	5.48
15	0.0247	0.3098	0.0204	0.3549	6.96	87.28	5.76
16	0.0340	0.3510	0.0201	0.4051	8.39	86.66	4.95
17	0.0270	0.2667	0.0211	0.3148	8.58	84.71	6.71
18	0.0211	0.2972	0.0202	0.3385	6.23	87.79	5.97
19	0.0377	0.3200	0.0189	0.3766	10.01	84.96	5.03
Avg.	0.0206	0.2181	0.0123	0.2509	7.96	87.71	4.34

Gas production rate	=	0.96	l/h
Hydrogen production rate	=	0.08	l/h
Specific hydrogen production rate	=	33.69	ml H_2/g MLVSS d
VFA concentration	=	4,297	mg/l as acetic acid
Hydrogen yield	=	31	ml H_2/g COD removed
COD removal efficiency	=	23.26	%
MLVSS	=	13,611	mg/l
TSS	=	1,359	mg/l

Distillated sample 100 µl + Internal standard (n-propanol 3,000 ppm) 100 µl

VFA	Concentration (ppm)
Ethanol	546.82
Acetic acid	827.66
Propionic acid	462.8
Butyric acid	1,372.25
Valeric acid	732.81

D4. COD loading rate = 75 kg/ m^3d pH = 5.5 Temperature = 55°C

Days	Amount of each component (mL)			Total amount (mL)	Produced gas composition (%)		
	H_2	CO_2	CH_4		H_2	CO_2	CH_4
1	0.0471	0.2898	0.0184	0.3554	13.25	81.56	5.19
2	0.0564	0.3001	0.0184	0.3749	15.04	80.05	4.91
3	0.0623	0.3123	0.0184	0.3929	15.85	79.47	4.68
4	0.0141	0.1641	0.0184	0.1965	7.16	83.50	9.34
5	0.0149	0.2039	0.0183	0.2371	6.28	86.00	7.72
6	0.0200	0.2373	0.0183	0.2756	7.27	86.08	6.65
7	0.0260	0.2764	0.0183	0.3207	8.11	86.18	5.72
8	0.0254	0.2752	0.0183	0.3190	7.97	86.28	5.75
9	0.0342	0.2950	0.0184	0.3476	9.84	84.88	5.28
10	0.0384	0.2977	0.0184	0.3545	10.83	83.98	5.19
11	0.0403	0.3008	0.0184	0.3595	11.22	83.67	5.11
12	0.0519	0.2987	0.0183	0.3690	14.08	80.96	4.96
13	0.0729	0.2884	0.0184	0.3797	19.21	75.95	4.84
14	0.0563	0.2959	0.0186	0.3708	15.18	79.80	5.02
15	0.0377	0.3050	0.0185	0.3611	10.43	84.44	5.13
16	0.0433	0.2924	0.0184	0.3541	12.24	82.57	5.19
17	0.0539	0.2711	0.0183	0.3433	15.70	78.97	5.33
18	0.0511	0.2888	0.0183	0.3582	14.26	80.63	5.12
19	0.0768	0.3186	0.0185	0.4139	18.56	76.98	4.46
Avg.	0.0433	0.2795	0.0184	0.3413	12.24	82.21	5.56

Gas production rate	=	0.95	l/h
Hydrogen production rate	=	0.12	l/h
Specific hydrogen production rate	=	68.56	ml H_2/g MLVSS d
VFA concentration	=	4,527.7	mg/l as acetic acid
Hydrogen yield	=	34.36	ml H_2/g COD removed
COD removal efficiency	=	25.6	%
MLVSS	=	10,198	mg/l
TSS	=	1,870	mg/l

Distillated sample 100 µl + Internal standard (n-propanol 3,000 ppm) 100 µl

VFA	Concentration (ppm)
Ethanol	1,231.91
Acetic acid	558.47
Propionic acid	579.69
Butyric acid	1,729.64
Valeric acid	686.49

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