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APPENDICES

Appendix A Gas Chromatograph's Calibration Curves

Table A1 Gas chromatograph's calibration curves for hydrogen (H_2)

Volume of Hydrogen (mL)	Peak Area
0.02	16,313
0.04	58,770
0.06	131,648
0.08	180,674
0.1	226,743
0.2	427,198
0.3	610,005
0.4	778,509

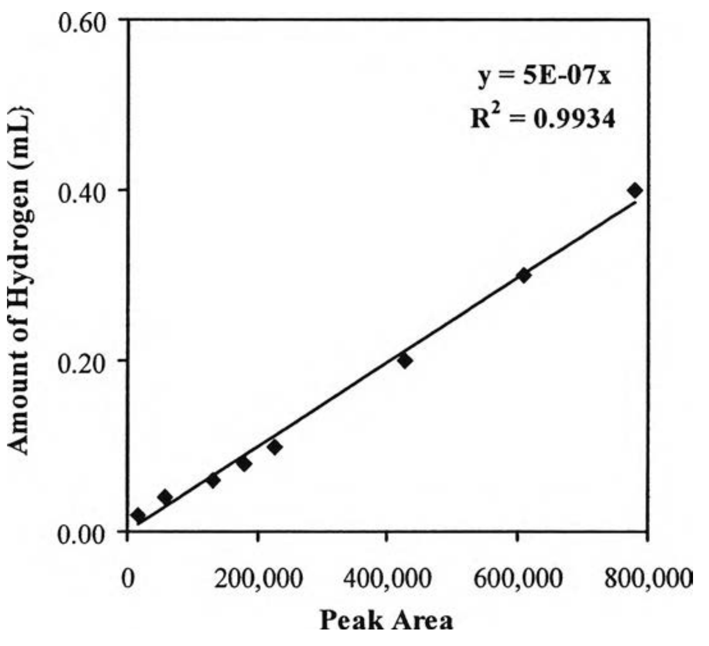

Figure A1 The relationship between amount of hydrogen (H_2) and peak area.

Equation

Amount of hydrogen = $5x10^{-7}$ x Peak area

Table A2 Gas chromatograph's calibration curves for air

Volume of Air (mL)	Peak Area
0.02	1,432
0.04	7,707
0.06	13,669
0.08	18,452
0.1	22,099
0.2	46,709
0.3	68,207
0.4	89,088

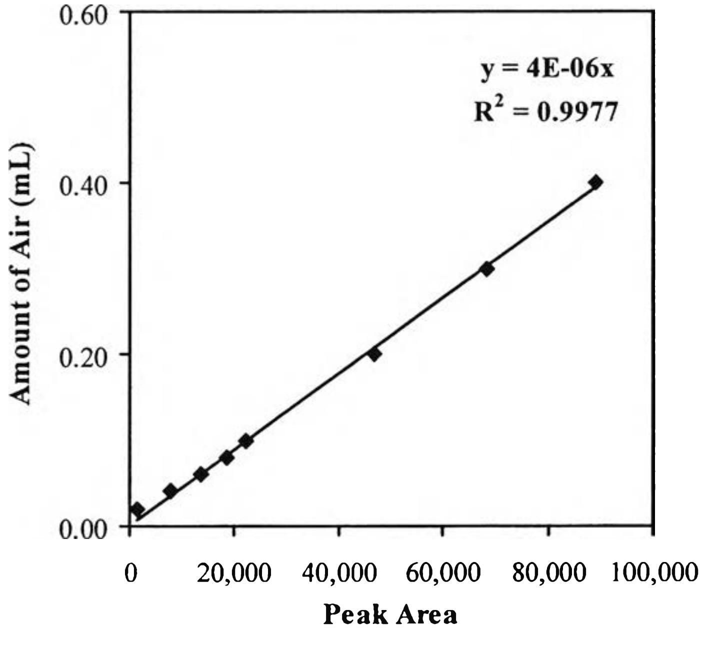

Figure A2 The relationship between amount of air and peak area.

Equation

$$\text{Amount of air} = 4\text{x}10^{-6} \text{ x Peak area}$$

Table A3 Gas chromatograph's calibration curves for methane (CH_4)

Volume of Methane (mL)	Peak Area
0.02	3,054
0.04	15,913
0.06	34,947
0.08	48,603
0.1	61,353
0.2	122,735
0.3	175,667
0.4	222,837

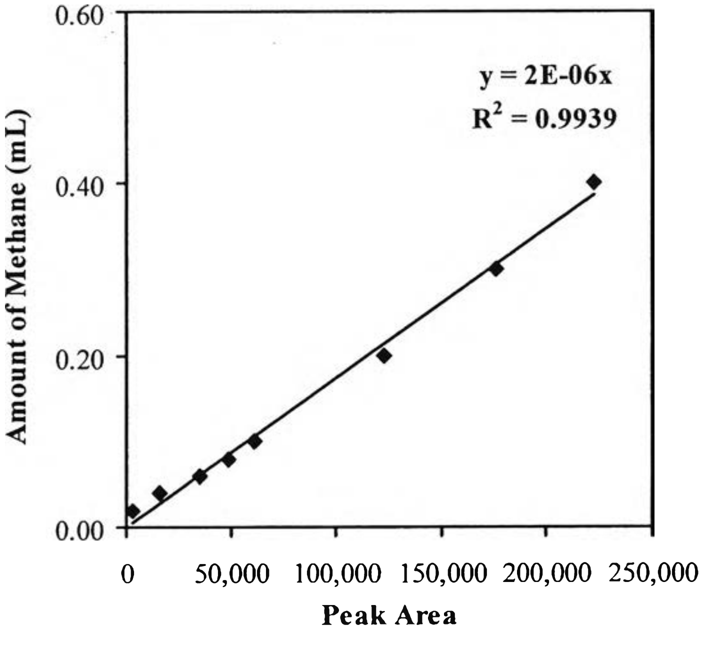

Figure A3 The relationship between amount of methane (CH_4) and peak area.

Equation

$$\text{Amount of methane} = 2\times10^{-6} \times \text{Peak area}$$

Table A4 Gas chromatograph's calibration curves for carbon dioxide (CO_2)

Volume of Carbon Dioxide (mL)	Peak Area
0.02	1,184
0.04	5,078
0.06	9,486
0.08	13,382
0.1	17,500
0.2	37,803
0.3	55,725
0.4	72,322

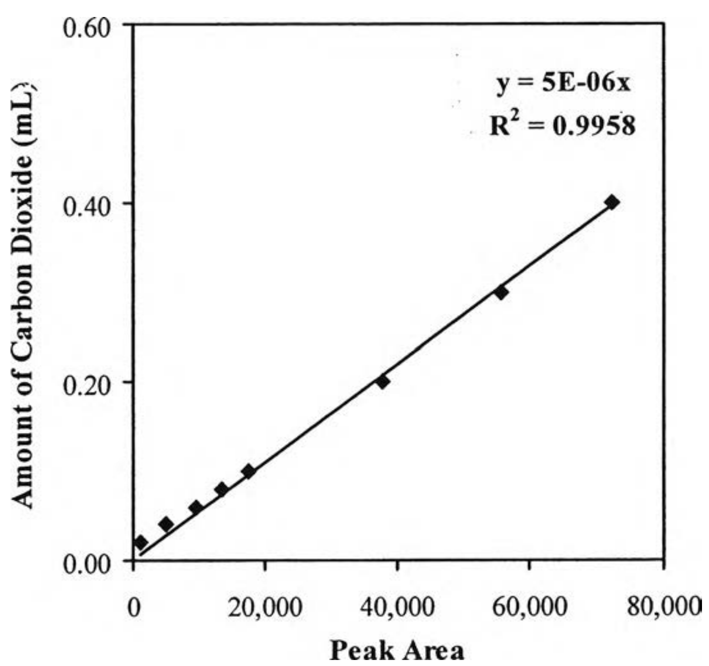

Figure A4 The relationship between amount of carbon dioxide (CO_2) and peak area.

Equation

Amount of carbon dioxide = 5×10^{-6} x Peak area

Table A5 Gas chromatograph's calibration curves for acetic acid

Acetic acid concentration (ppm)	Peak area of acetic acid / Peak area of n-propanol
0	0
1,000	0.4916
2,000	0.8158
3,000	1.2596
4,000	1.5860

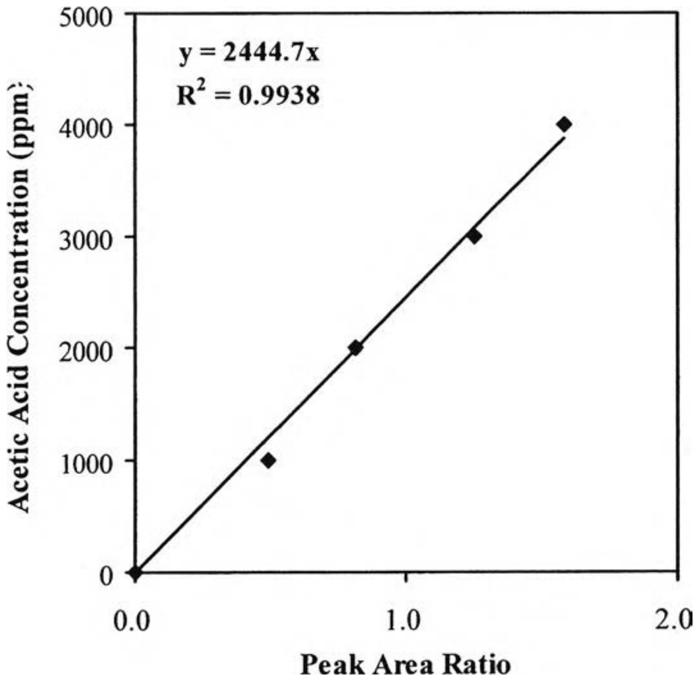

Figure A5 The relationship between acetic acid concentration and peak area ratio.

Equation

Acetic acid concentration (ppm) = 2444.7 x Peak area ratio

Table A6 Gas chromatograph's calibration curves for valeric acid

Valeric acid concentration (ppm)	$\frac{\text{Peak area of valeric acid}}{\text{Peak area of n-propanol}}$
0	0
1,000	0.9740
2,000	2.3376
3,000	3.3325
4,000	4.4053

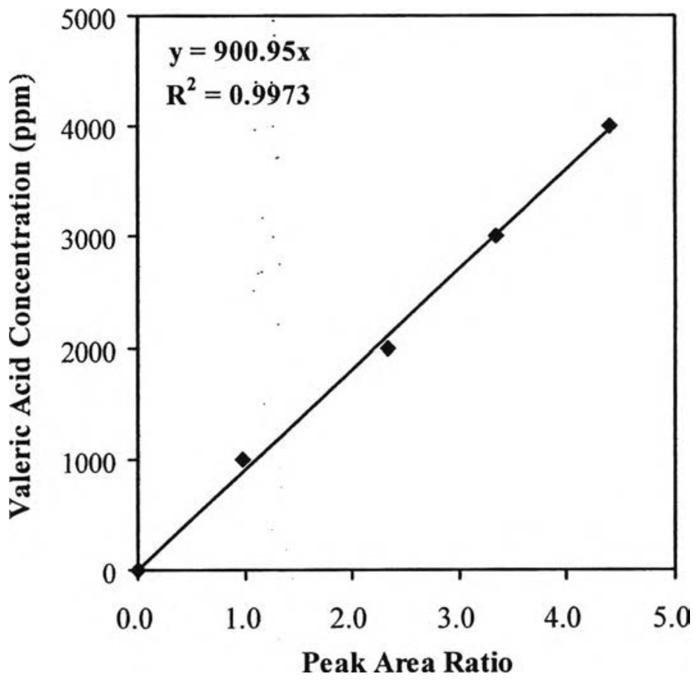

Figure A6 The relationship between valeric acid concentration and peak area ratio.

Equation

Valeric acid concentration (ppm) = 900.95 x Peak area ratio

Table A7 Gas chromatograph's calibration curves for propionic acid

Propionic acid concentration (ppm)	Peak area of propionic acid / Peak area of n-propanol
0	0
1,000	0.6819
2,000	1.4916
3,000	2.3378
4,000	3.2784

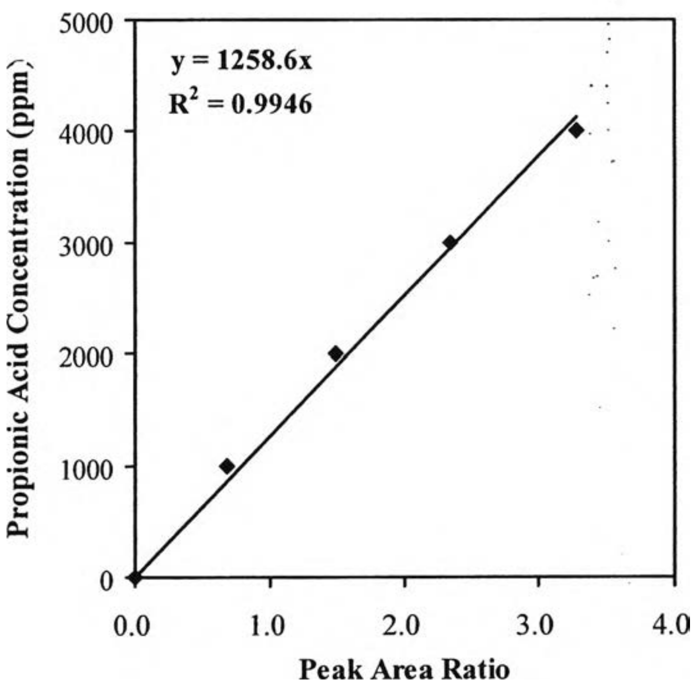

Figure A7 The relationship between propionic acid concentration and peak area ratio.

Equation

Propionic acid concentration (ppm) = 1258.6 x Peak area ratio

Table A8 Gas chromatograph's calibration curves for butyric acid

Butyric acid concentration (ppm)	Peak area of butyric acid / Peak area of n-propanol
0	0
1,000	0.5328
2,000	1.3043
3,000	1.8347
4,000	2.4220

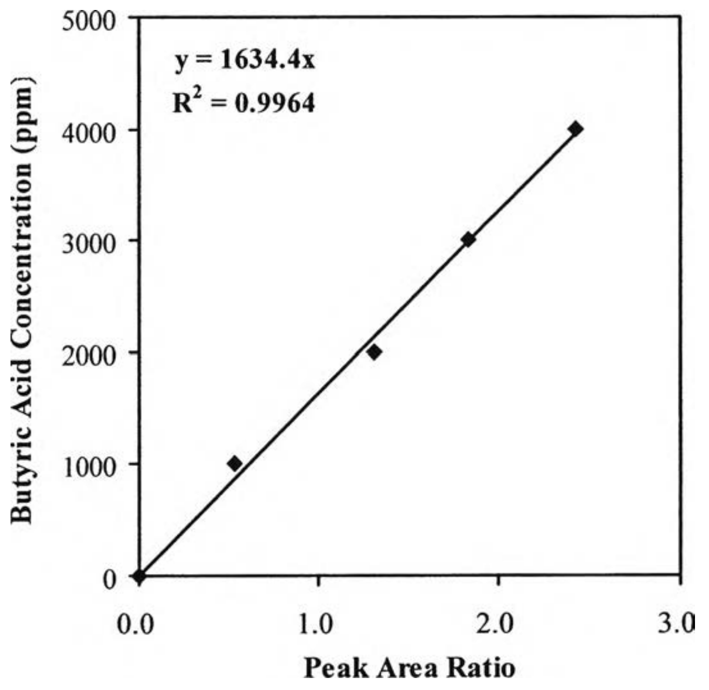

Figure A8 The relationship between butyric acid concentration and peak area ratio.

Equation

Butyric acid concentration (ppm) = 1634.4 x Peak area ratio

Table A9 Gas chromatograph's calibration curves for ethanol

Ethanol concentration (ppm)	Peak area of ethanol / Peak area of n-propanol
0	0
1,000	0.5682
2,000	1.1800
3,000	1.8570
4,000	2.4495

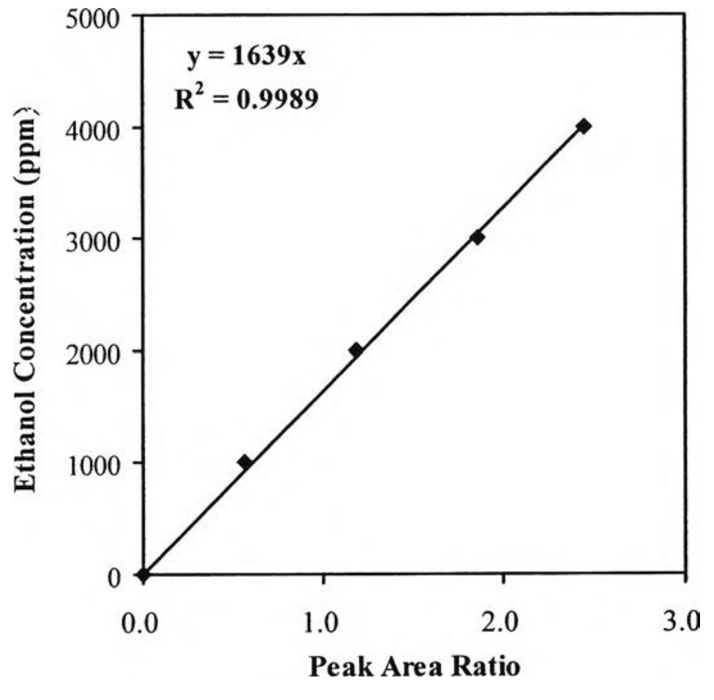

Figure A9 The relationship between ethanol concentration and peak area ratio.

Equation

Ethanol concentration (ppm) = 1639 x Peak area ratio

Appendix B Preparation of 1 M NaOH solution for pH Control System

Concentration of NaOH (solid)	=	99%
Molecular weight of NaOH	=	40

Preparation of NaOH at concentration of 1 M

$$= \frac{1\ \text{mol}}{1\ \text{L}} \times \frac{40\ \text{g}}{1\ \text{mol}} \times \frac{100}{99} = 40.40\ \text{g}$$

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

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

= 17.78 M

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

$$= 2{,}000\ \frac{\text{mg of acetic acid}}{\text{L of solution}} \times \frac{1\ \text{mole of acetic acid}}{60\ \text{g of acetic acid}}$$

= 0.0333 M

Dilution of acetic acid

N_1V_1	=	N_2V_2	
V_1	=	N_2V_2/N_1	
	=	(0.0333x1)/17.78	
	=	$1.873\text{x}10^{-3}$	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 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	=	$11.7 \times 10^{-3} \times 0.1$	
	=	1.17×10^{-3}	mol
Acetic acid in distillate	=	1.17×10^{-3}	mol
	=	$1.17 \times 10^{-3} \times 60.5$	
	=	0.07	g

Concentration of acetic acid in distillate

	=	0.07/50	
	=	1.405×10^{-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	
			=	$1.368x10^{-3}$	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 on hydrogen production

D 1 COD loading rate = 10 kg/ m^3d pH = 5.5 Temperature = 37°C

Day	Amount of each component (mL)			Total amount (mL)	Produced gas composition (%)		
	H_2	CH_4	CO_2		H_2	CH_4	CO_2
1	0.0304	0.0481	0.0000	0.0786	38.74	61.26	0.00
2	0.0319	0.0518	0.0000	0.0836	38.11	61.89	0.00
3	0.0283	0.0475	0.0000	0.0758	37.34	62.66	0.00
4	0.0327	0.0526	0.0004	0.0858	38.18	61.36	0.46
5	0.0212	0.0546	0.0144	0.0902	23.50	60.59	15.92
6	0.0161	0.0533	0.0106	0.0799	20.17	66.61	13.22
7	0.0152	0.0471	0.0206	0.0829	18.32	56.83	24.85
8	0.0195	0.0432	0.0201	0.0828	23.55	52.14	24.32
9	0.0137	0.0437	0.0292	0.0867	15.86	50.43	33.71
10	0.0153	0.0433	0.0284	0.0870	17.62	49.75	32.63
11	0.0132	0.0602	0.0131	0.0865	15.30	69.58	15.12
12	0.0122	0.0577	0.0148	0.0847	14.45	68.08	17.47
13	0.0098	0.0575	0.0157	0.0830	11.81	69.23	18.96
14	0.0114	0.0568	0.0163	0.0845	13.49	67.21	19.30
15	0.0112	0.0566	0.0158	0.0836	13.43	67.71	18.86
Avg.	0.0116	0.0577	0.0151	0.0845	13.70	68.36	17.94

Gas production rate	=	5.935	L/d
Hydrogen production rate	=	0.81	L/d
Volumetric hydrogen production rate	=	0.03	L H_2/L reactor d
Specific hydrogen production rate	=	1.96	L H_2/kg MLVSS d

VFA concentration	=	11,939	mg/L as acetic acid
Hydrogen yield	=	15.82	L H_2/kg COD removed
COD removal efficiency	=	23	%
MLVSS	=	17,300	mg/L
VSS	=	1,076	mg/L

Distillated sample 2 mL + Internal standard (n-propanol 3,000 ppm) 0.5 mL

VFA	concentration (ppm)	%
Acetic acid	697.47	8.12
Propionic acid	786.25	9.16
Butyric acid	4,674.06	54.44
Valeric acid	2,427.61	28.28

D 2 COD loading rate = 20 kg/ m^3d pH = 5.5 Temperature = 37°C

Day	Amount of each component (mL)			Total amount (mL)	Produced gas composition (%)		
	H_2	CH_4	CO_2		H_2	CH_4	CO_2
1	0.0350	0.0520	0.0004	0.0874	40.08	59.50	0.42
2	0.0314	0.0529	0.0017	0.0860	36.51	61.53	1.96
3	0.0389	0.0514	0.0007	0.0910	42.72	56.52	0.76
4	0.0426	0.0474	0.0006	0.0906	47.02	52.27	0.71
5	0.0374	0.0452	0.0007	0.0833	44.85	54.27	0.88
6	0.0349	0.0509	0.0007	0.0865	40.35	58.83	0.83
7	0.0387	0.0526	0.0003	0.0916	42.24	57.39	0.37
8	0.0325	0.0538	0.0002	0.0865	37.61	62.14	0.25
9	0.0403	0.0500	0.0004	0.0907	44.40	55.18	0.42
10	0.0364	0.0521	0.0006	0.0891	40.87	58.49	0.65
11	0.0325	0.0537	0.0014	0.0876	37.06	61.32	1.62
12	0.0298	0.0535	0.0056	0.0889	33.51	60.24	6.25
13	0.0264	0.0541	0.0077	0.0882	29.93	61.38	8.69
14	0.0278	0.0516	0.0093	0.0887	31.31	58.18	10.51
15	0.0276	0.0534	0.0078	0.0888	31.06	60.13	8.81
Avg.	0.0279	0.0532	0.0076	0.0887	31.47	59.96	8.57

Gas production rate	=	13.08	L/d
Hydrogen production rate	=	4.11	L/d
Specific hydrogen production rate	=	5.02	L H_2/kg MLVSS d
VFA Concentration	=	8,652	mg/L as acetic acid
Hydrogen yield	=	22.09	L H_2/kg COD removed
COD removal efficiency	=	38.5	%

MLVSS	=	34,180	mg/L
VSS	=	380	mg/L

Distillated sample 2 mL + Internal standard (n-propanol 3,000 ppm) 0.5 mL

VFA	concentration (ppm)	%
Acetic acid	478.31	7.80
Propionic acid	458.13	7.47
Butyric acid	3,214.37	52.42
Valeric acid	1,981.19	32.31

D 3 COD loading rate = 25 kg/ m^{3}d pH = 5.5 Temperature = 37°C

Day	Amount of each component (mL)			Total amount (mL)	Produced gas composition (%)		
	H_2	CH_4	CO_2		H_2	CH_4	CO_2
1	0.0335	0.0458	0.0030	0.0823	40.66	55.71	3.63
2	0.0303	0.0531	0.0043	0.0877	34.52	60.57	4.91
3	0.0329	0.0522	0.0043	0.0894	36.81	58.42	4.78
4	0.0389	0.0514	0.0007	0.0906	42.75	56.48	0.77
5	0.0426	0.0474	0.0006	0.0833	47.02	52.32	0.66
6	0.0374	0.0452	0.0007	0.0823	44.90	54.26	0.84
7	0.0298	0.0530	0.0007	0.0877	35.67	63.44	0.89
8	0.0264	0.0556	0.0004	0.0894	32.03	67.46	0.51
9	0.0271	0.0563	0.0000	0.0834	32.48	67.52	0.00
10	0.0321	0.0565	0.0000	0.0886	36.20	63.80	0.00
11	0.0310	0.0531	0.0000	0.0840	36.86	63.14	0.00
12	0.0302	0.0542	0.0000	0.0844	35.78	64.22	0.00
13	0.0312	0.0535	0.0000	0.0847	36.84	63.16	0.00
14	0.0309	0.0534	0.0000	0.0843	36.65	63.35	0.00
15	0.0311	0.0541	0.0000	0.0852	36.50	63.50	0.00
Avg.	0.0309	0.0538	0.0000	0.0847	36.44	63.56	0.00

Gas production rate	=	25.71	L/d
Hydrogen production rate	=	9.36	L/d
Specific hydrogen production rate	=	10.92	L H_2/kg MLVSS d
VFA concentration	=	8,219	mg/L as acetic acid
Hydrogen yield	=	39.83	L H_2/kg COD removed
COD removal efficiency	=	43.8	%

MLVSS	=	35,740	mg/L
VSS	=	39	mg/L

Distillated sample 2 mL + Internal standard (n-propanol 3,000 ppm) 0.5 mL

VFA	concentration (ppm)	%
Acetic acid	759.81	17.95
Propionic acid	392.05	9.26
Butyric acid	1,996.42	47.17
Valeric acid	1,083.93	25.61

D 4 COD loading rate = 30 kg/ m^3d pH = 5.5 Temperature = 37°C

Day	Amount of each component (mL)			Total amount (mL)	Produced gas composition (%)		
	H_2	CH_4	CO_2		H_2	CH_4	CO_2
1	0.0302	0.0585	0.0000	0.0887	34.03	65.97	0.00
2	0.0340	0.0552	0.0000	0.0892	38.09	61.91	0.00
3	0.0249	0.0588	0.0000	0.0838	29.74	70.26	0.00
4	0.0203	0.0648	0.0000	0.0851	23.81	76.19	0.00
5	0.0158	0.0672	0.0000	0.0830	19.02	80.98	0.00
6	0.0142	0.0666	0.0000	0.0809	17.62	82.38	0.00
7	0.0099	0.0624	0.0000	0.0724	13.73	86.27	0.00
8	0.0117	0.0641	0.0000	0.0758	15.46	84.54	0.00
9	0.0152	0.0640	0.0000	0.0792	19.17	80.83	0.00
10	0.0213	0.0574	0.0000	0.0787	27.02	72.98	0.00
11	0.0168	0.0590	0.0000	0.0758	22.17	77.83	0.00
12	0.0152	0.0578	0.0000	0.0730	20.84	79.16	0.00
13	0.0156	0.0573	0.0000	0.0729	21.39	78.61	0.00
14	0.0165	0.0596	0.0000	0.0760	21.68	78.32	0.00
15	0.0167	0.0569	0.0000	0.0736	22.67	77.33	0.00
Avg.	0.0162	0.0581	0.0000	0.0743	21.75	78.25	0.00

Gas production rate	=	29.47	L/d
Hydrogen production rate	=	6.40	L/d
Specific hydrogen production rate	=	8.67	L H_2/kg MLVSS d
VFA concentration	=	10,382	mg/L as acetic acid
Hydrogen yield	=	36.38	L H_2/kg COD removed
COD removal efficiency	=	30.6	%

MLVSS	=	30,760	mg/L
VSS	=	94	mg/L

Distillated sample 2 mL + Internal standard (n-propanol 3,000 ppm) 0.5 mL

VFA	concentration (ppm)	%
Acetic acid	1,181.03	9.05
Propionic acid	1,356.90	10.40
Butyric acid	6,454.08	49.48
Valeric acid	4,051.03	31.06

Appendix E Example of Calculation

E 1. Mixed Liquor Volatile Suspended Solids (MLVSS) Determination

COD loading rate = 10 kg/ m^3d   pH = 5.5   Temperature = 37°C

Volume of sample	=	5	mL
Weight of residue + filter paper (105°C)	=	0.2459	g
Weight of residue + filter paper (500°C)	=	0.2112	g

$$\text{MLVSS} = \frac{(0.2459 - 0.2112\ g) \times 10^6}{5\ mL} = 17{,}300\ \text{mg/L}$$

COD loading rate (kg/m^3d)	Volume of solution (mL)	Weight (105°C) (g)	Weight (500°C) (g)	MLVSS (mg/L)
10	5	0.2459	0.2112	17,300
20	5	0.3598	0.2975	34,180
25	5	0.4115	0.3025	34,542
30	5	0.3583	0.2783	30,760

E 2. Effluent Volatile Suspended Solids (VSS) Determination

COD loading rate = 10 kg/ m^3d   pH = 5.5   Temperature = 37°C

Volume of sample	=	50	mL
Weight of residue + filter paper (105°C)	=	0.1819	g
Weight of residue + filter paper (500°C)	=	0.1761	g

$$\text{VSS} = \frac{(0.1819 - 0.1761\ g) \times 10^6}{50\ mL} = 1{,}076\ \text{mg/L}$$

COD loading rate (kg/m^3d)	Volume of solution (mL)	Weight (105°C) (g)	Weight (500°C) (g)	VSS (mg/L)
10	50	0.1819	0.1761	1,076
20	30	0.1402	0.1357	380
25	50	0.1495	0.1265	39
30	50	0.1397	0.1307	97

E3. Volatile Fatty Acids as Acetic Acid Determination by Distillation

Formula

$$\frac{\text{mg volitile acids as acetic acid}}{\text{L}} = \frac{\text{mL NaOH x N x 60,000}}{\text{mL sample x f}}$$

where

N = Normality of NaOH solution

f = recovery factor

COD loading rate = 10 kg/m^3d pH = 5.5 Temperature = 37°C

Distillate = 10 mL

NaOH 0.1 M = 13.80 mL

$$\frac{\text{mg valitile acids as acetic acid}}{\text{L}} = \frac{13.80 \times 0.1 \times 60{,}000}{10 \times 0.6935}$$

$$= 11{,}939 \ \frac{\text{mg VFA as acetic acid}}{L}$$

COD loading rate (kg/m^3d)	Volume of distillate (mL)	Volume of 0.1 M NaOH (mL)	VFA (mg/L as acetic acid)
10	10	13.80	11,939
20	10	10.00	8,652
25	10	9.50	8,219
30	10	12.00	10,382

E 4. Hydrogen Yield Determination

COD loading rate = 10 kg/ m^3d pH = 5.5 Temperature = 37°C

Gas production rate = 5.935 L/d

Hydrogen fraction in produced gas = 0.137

Hydrogen production rate $= \frac{5.935\ L}{h} \times 0.137$

$= 0.813$ L/d

COD removed per day $= \left(18{,}625 - 14{,}341 \frac{mg}{L}\right) \times \frac{0.001 kg}{1{,}000\ mg} \times \frac{24\ L}{d}$

$= 0.051$ kg/d

Hydrogen yield $= \frac{\text{Hydrogen production rate}}{\text{COD removed per day}}$

$= \frac{0.813 L/d}{0.051 kg/d}$

$= 15.81$ L H_2/kg COD removed

COD loading rate (kg/m^3d)	Hydrogen production rate (L/d)	COD removed per day (kg/d)	Hydrogen yield (L H2/kg COD removed)
10	0.81	0.051	15.82
20	4.11	0.186	22.09
25	9.36	0.235	39.83
30	6.40	0.175	36.38

E-5. Specific Hydrogen Production Rate (SHPR)

COD loading rate = 10 kg/ m^3d pH = 5.5 Temperature = 37°C

Hydrogen production rate = 5.935 L/d

MLVSS $= 17{,}300\frac{mg}{L} \times 24\ L \times \frac{0.001\ kg}{1{,}000\ mg}$

$= 0.415$ kg VSS

SHPR (L H_2/kg VSS d) $= \frac{\text{Hydrogen production rate (mL / d)}}{\text{MLVSS (g VSS)}}$

$= \frac{0.81 L/d}{0.415\ kg\ VSS}$

$= 1.96$ L H_2/kg MLVSS d

SHPR (L H2/L reactor d) $= \frac{Hydrogen\ production\ rate\ (L/d)}{Working\ volume\ of\ reactor\ (L)}$

$= \frac{0.81\ L/d}{24\ L}$

$= 0.034$ L H_2/L-reactor d

COD loading rate (kg/m^3d)	Hydrogen production rate (L/d)	MLVSS (kg VSS)	SHPR (L H_2/ kg VSS d)	SHPR (L H_2/L d)
10	0.81	0.415	1.96	0.034
20	4.11	0.820	5.02	0.171
25	9.36	0.857	10.92	0.390
30	6.40	0.738	8.67	0.267

E 6. COD Removal Efficiency Determination

COD loading rate = 10 kg/ m^3d   pH = 5.5   Temperature = 37°C

Feed COD = 18,625 mg/L

Effluent COD = 14,341 mg/L

$$\text{COD removal efficiency} = \frac{18{,}625 - 14{,}341\ mg/L}{18{,}625\ mg/L}$$

= 23.0%

COD loading rate (kg/m^3d)	Feed COD (mg/L)	Effluent COD (mg/L)	COD removal efficiency (%)
10	18,625	14,341	23.0
20	20,180	12,419	38.5
25	22,350	12,553	43.8
30	23,982	16,649	30.6

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