Efficient biohydrogen production from POME by two-stage dark fermentation and electrohydrogenesis

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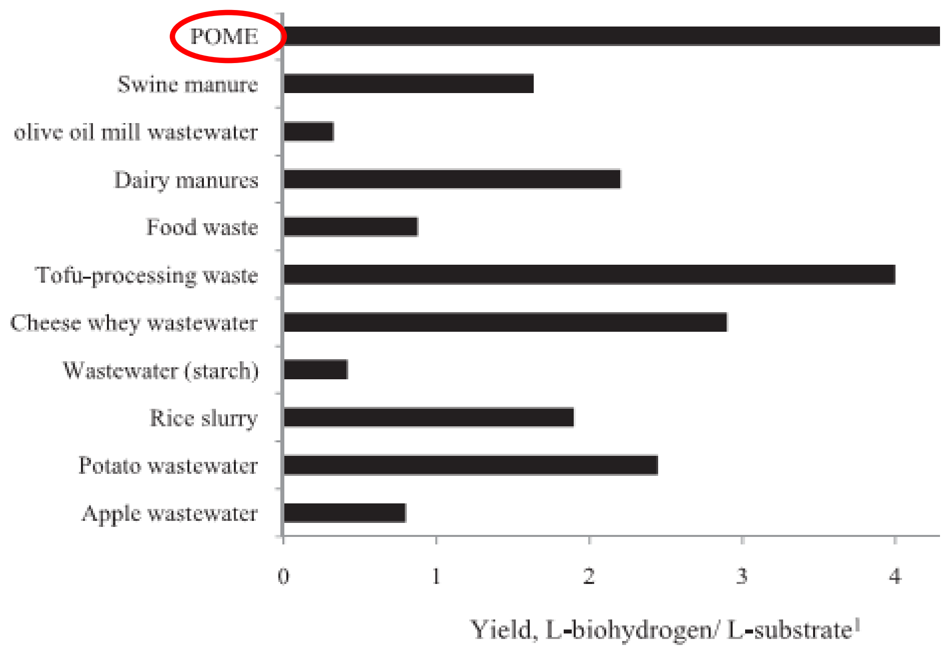
H_2 production from renewable feedstock



The yield of biohydrogen from POME is the highest in comparison with other wastes and wastewaters

Sugar

- glucose, sucrose, xylose etc.
- showing yields between 1.84 - 3.85 mol H_2/mol glucose
- **in practice it may not be feasible to use pure cultures for H_2 production in large scale production facilities**

Agricultural waste and energy crop

- highest yields of 3.8 mol H_2/mol glucose from wheat straw hydrolysates (Ivanova et al., 2009)
- **pretreat feedstock requirement**, In some studies the focus was on different pretreatment methods used

Starch and mix biomass

- H_2 yields varied from 1.84 to 2.82 mol H_2/mol glucose
- high H_2 yields on starch (3.3 mol H_2 / mol hexose)

Management of Palm Oil Industrial Effluent

Palm Oil Mill Effluent (POME) is suitable for biohydrogen production

- hydrogen at mesophilic = 1.5 L H_2/L-POME
- hydrogen at thermophilic = 3.5 L H_2/L-POME

65% of the energy contained still remains in the liquid

↓

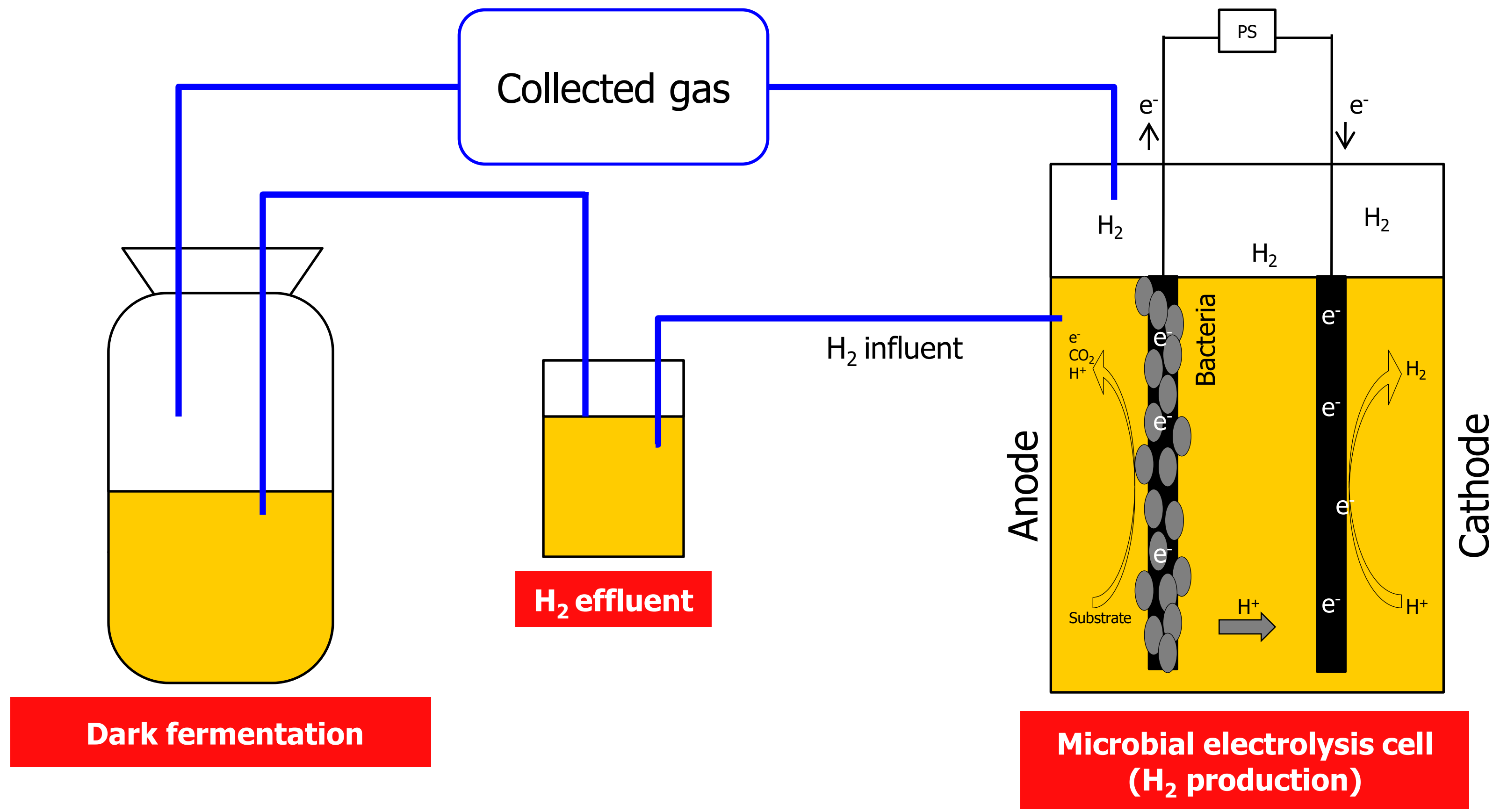
ethanol, formate, acetic acid,
propionic acid and butyric acid
0-300 mmol/L-H_2 production

↓

Not economic

Two-stage dark fermentation and electrohydrogenesis

Fermentation H_2 production



Dark fermentation

$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH^- + \mathbf{4H_2} + 2CO_2$

Microbial electrolysis cell

$C_2H_4O_2 + 2H_2O \longrightarrow \mathbf{4H_2} + 2CO_2$

$C_4H_8O_2 + 10H_2O \longrightarrow \mathbf{8H_2} + 4HCO_3^- + 3H^+$

Theoretical Biological Hydrogen Production

Dark fermentation

$C_6H_{12}O_6 + 2H_2O \quad 2CH_3COOH^- + 4H_2 + 2CO_2$

$C_6H_{12}O_6 + 2H_2O \quad 2CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$

Microbial electrolysis cell

$C_2H_4O_2 + 2H_2O \longrightarrow 4H_2 + 2CO_2$

$C_4H_8O_2 + 10H_2O \longrightarrow 8H_2 + 4HCO^-_3 + 3H^+$

Anode : $CH_3COOH + 2H_2O \quad 2CO_2 + 8e^- + 8H^+$

Cathode: $8H^+ + 8e^- \quad 4H_2$

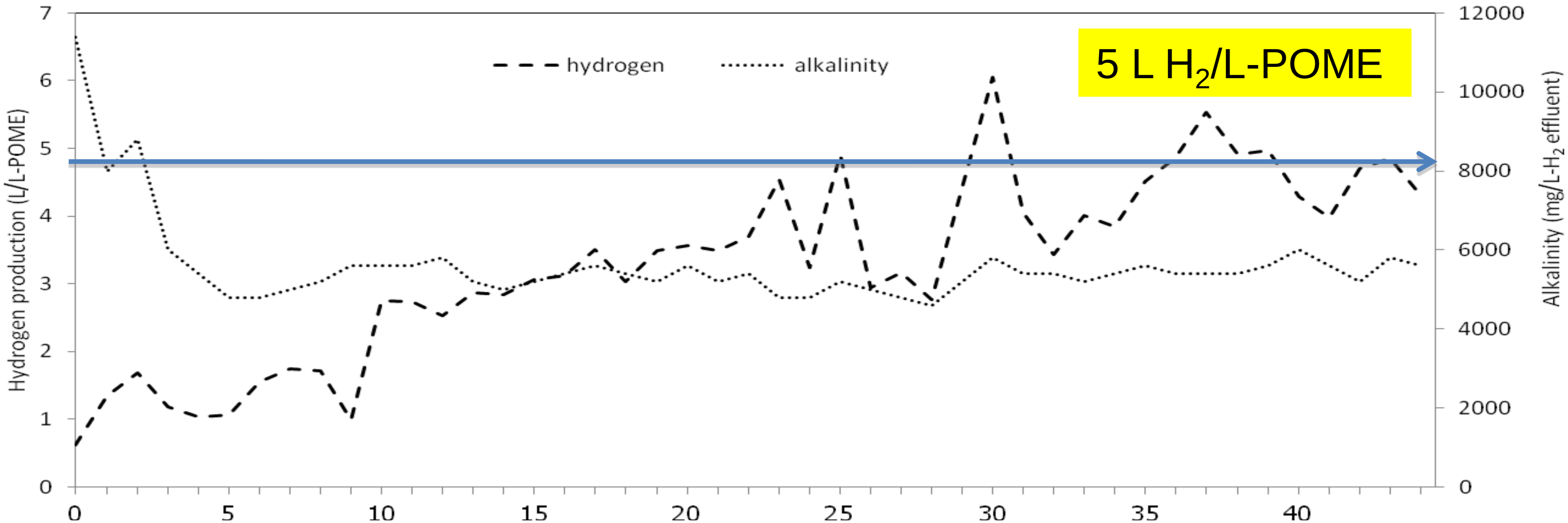
Dark fermentation + Microbial electrolysis cell

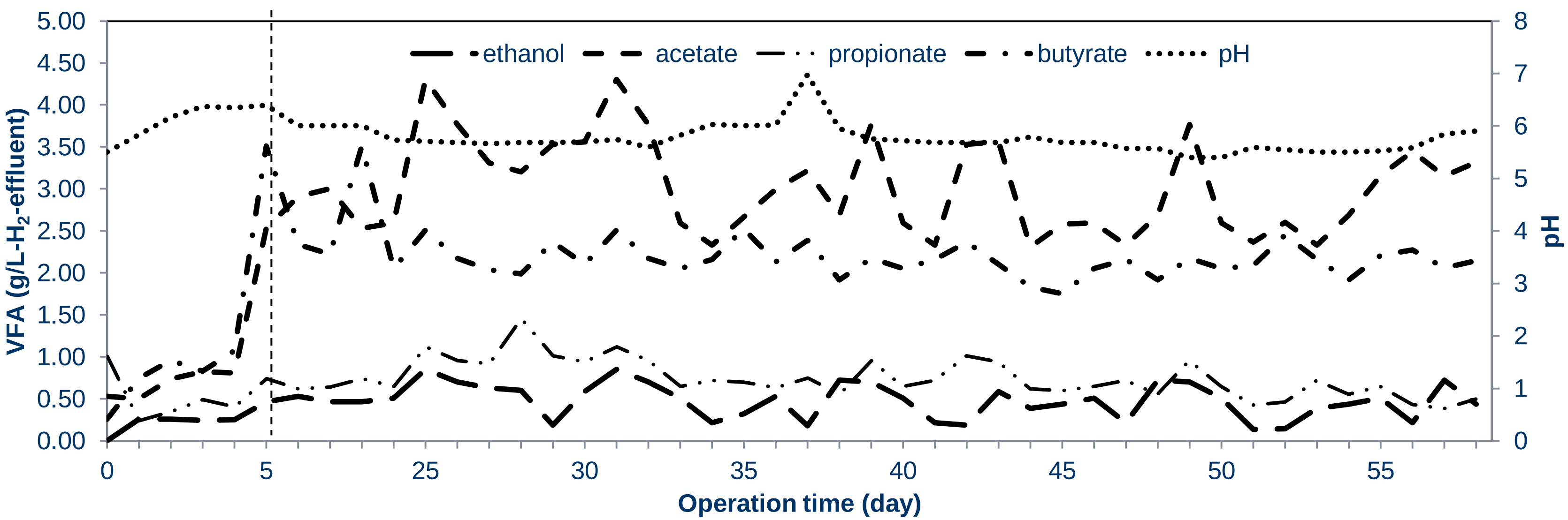
$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH^- + 4H_2 + 2CO_2$

$2CH_3COOH^- + 2H_2O \longrightarrow 8H_2 + 2CO_2$

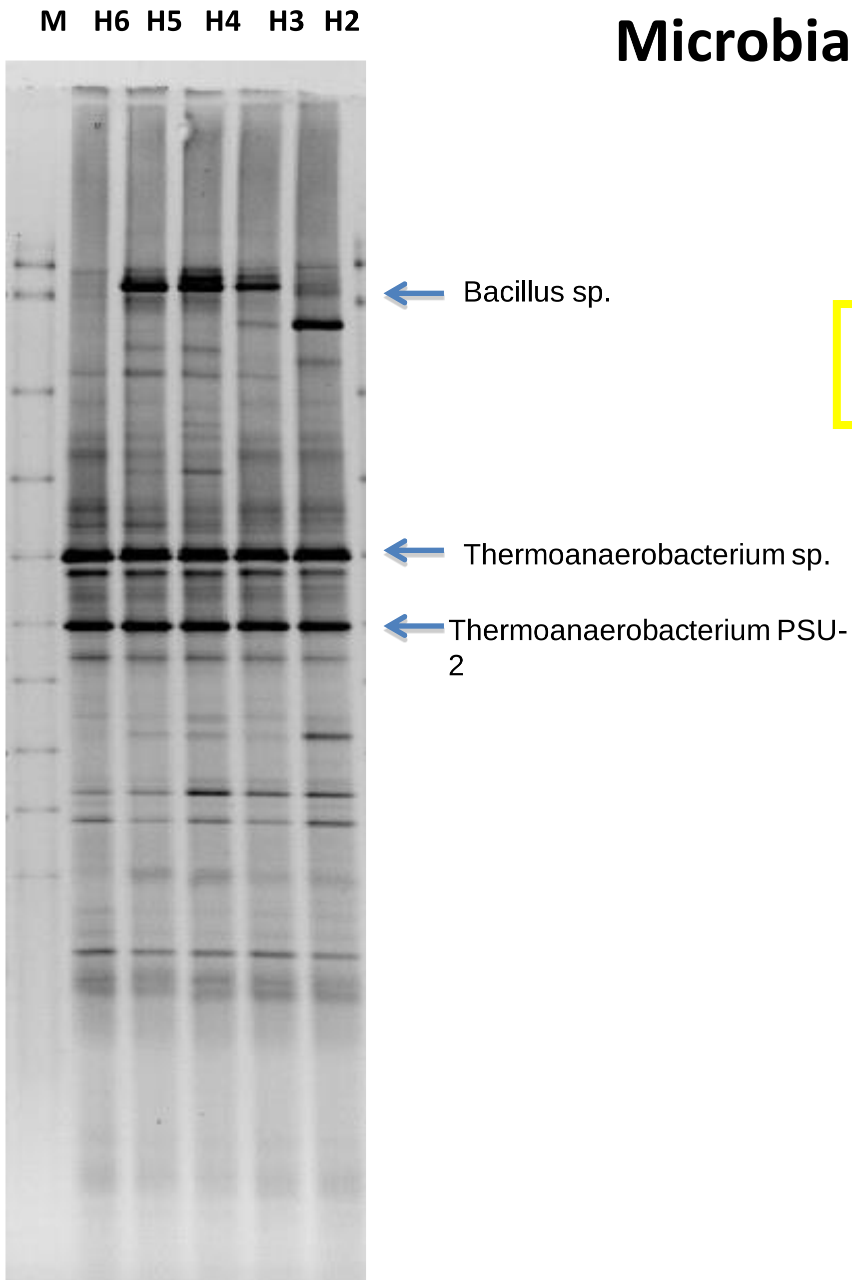
Continuous hydrogen production in 10 L CSTR by dark fermentation process

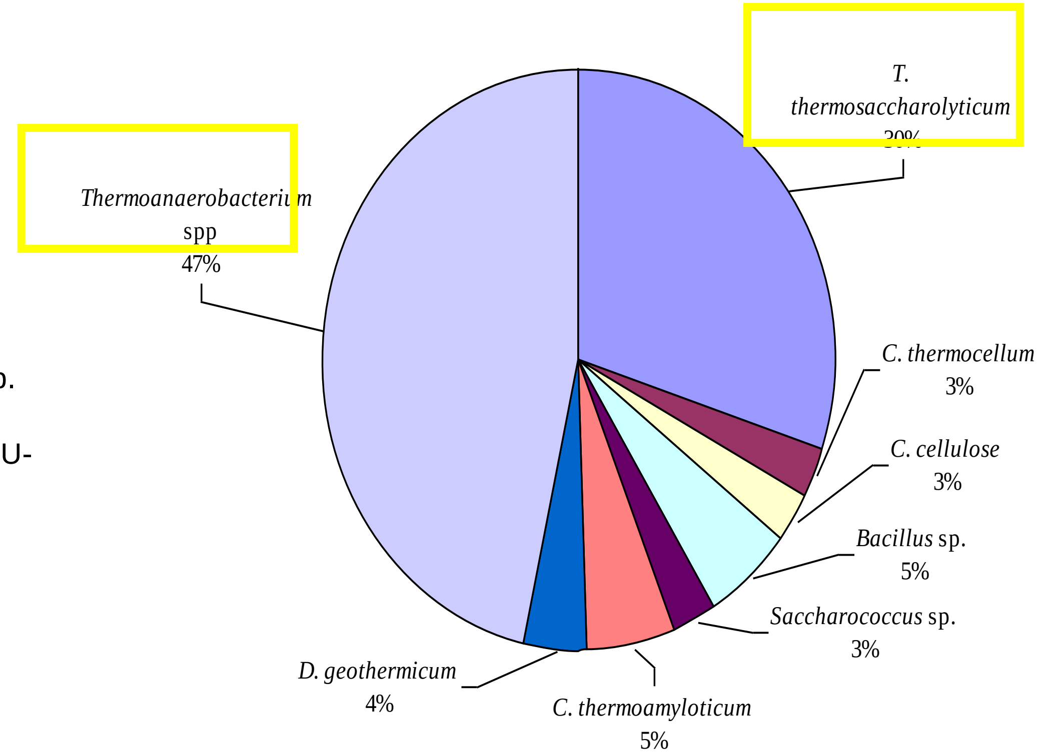
Hydrogen production from POME by fermentation process





Microbial community





Thermophilic H_2 production

Manage biohydrogen process

- **Biostimulization with adding nutrient species specific for *Thermoanaerobacterium* PSU-2.**

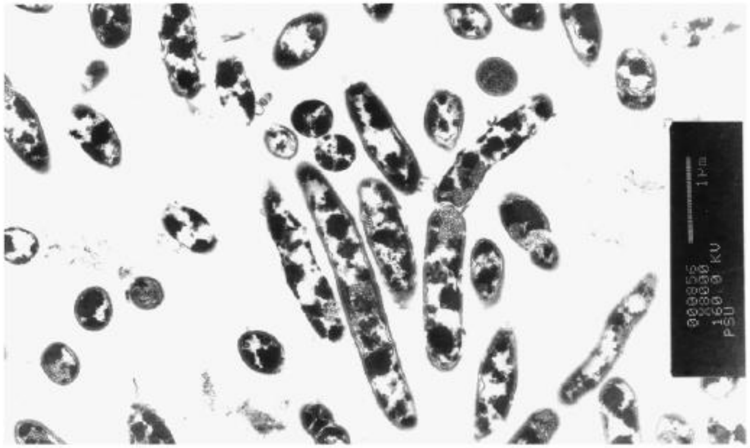
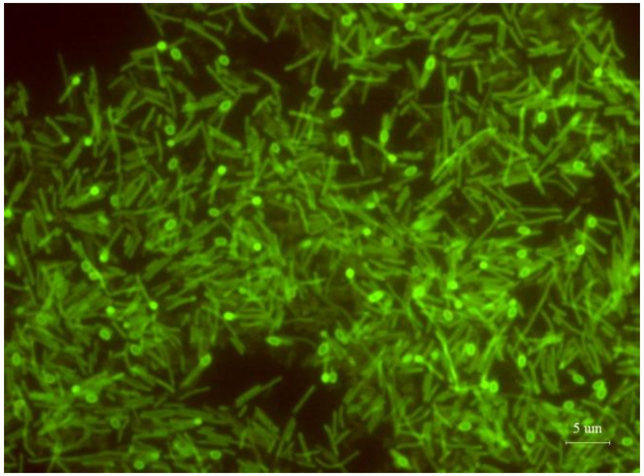
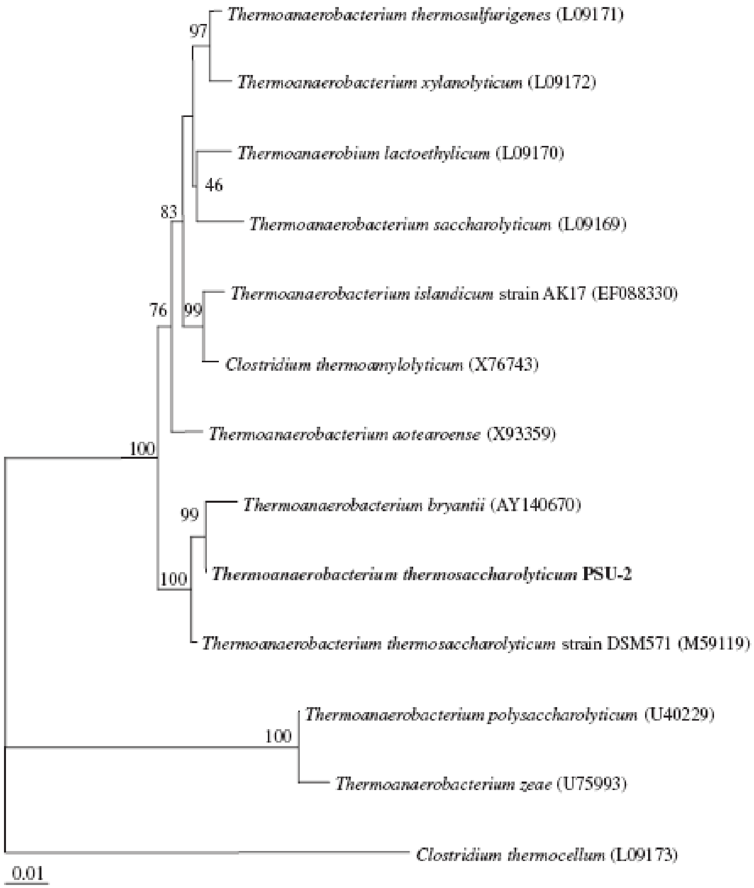


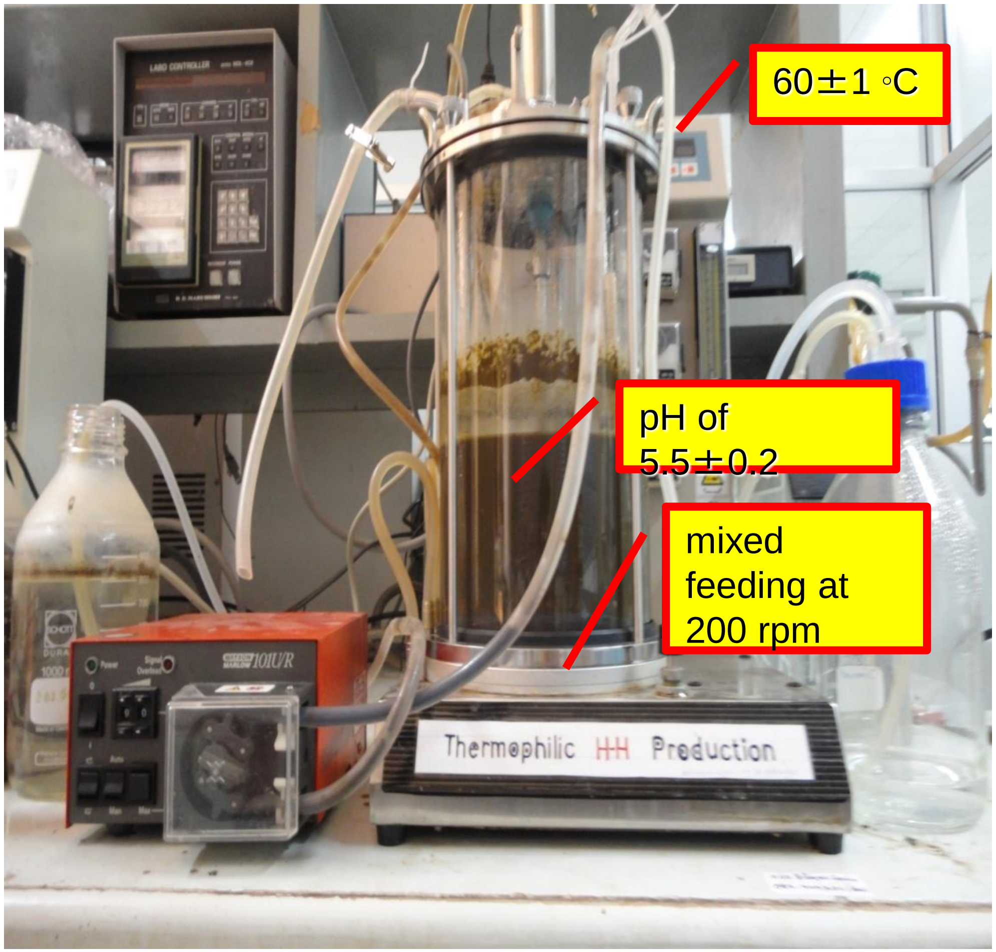
Fig. 1 – Transmission electron micrograph of *T. thermosaccharolyticum* PSU-2.





O-Thong et al., 2009

Start-up process for continuous biohydrogen production from POME



Anaerobic sequencing batch reactor for hydrogen production

- 10% v/v
- 20% v/v
- 30% v/v
- 0% (control)

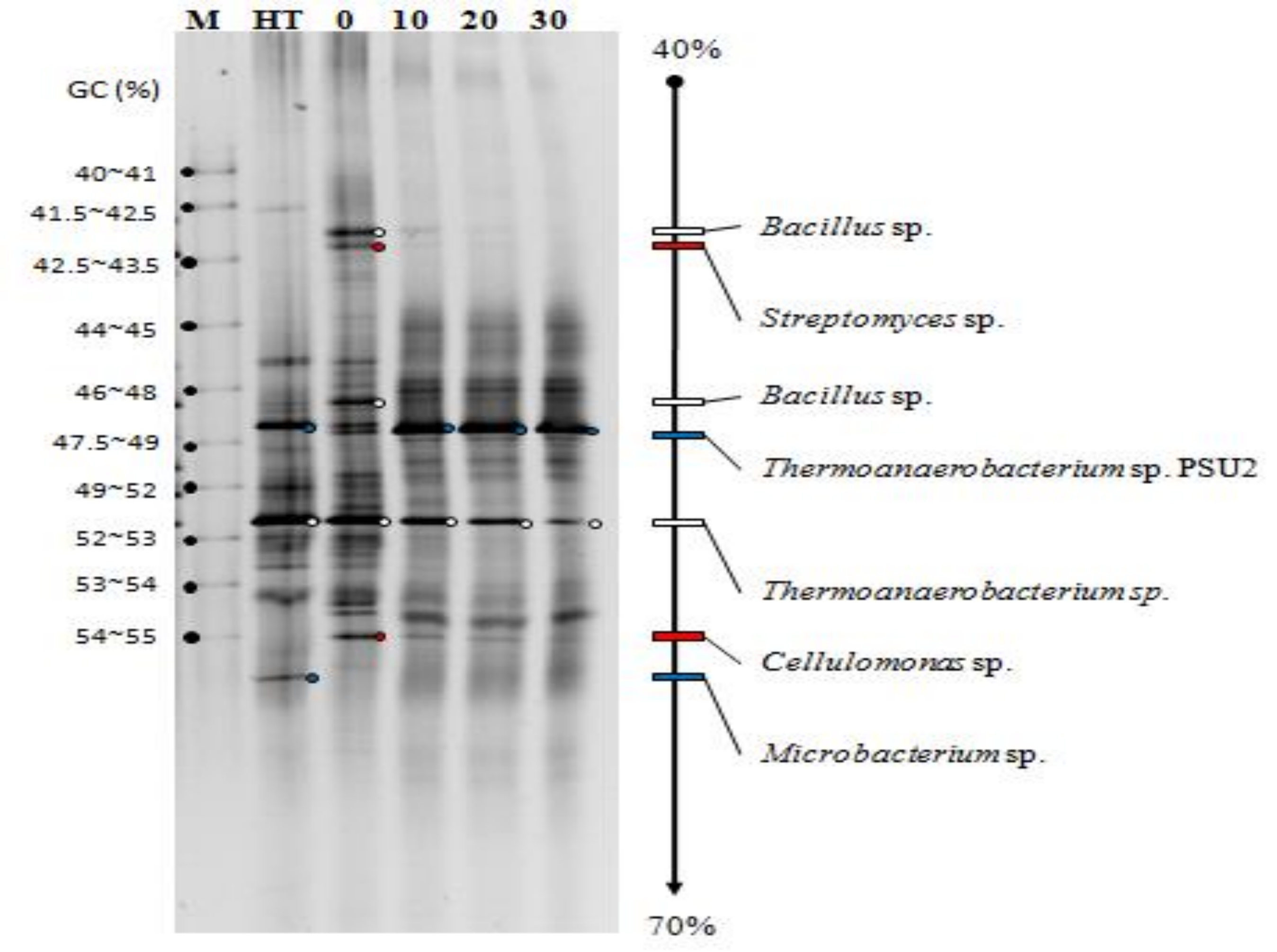
PSU-2

+ POME

The reactor tank was made from a glass bottle with a total volume of 1L. The operating volume was 800 mL. The reactor was run by intermittent mixed feeding at 200 rpm and with 24 h cycles. Each cycle consisted of 30 min fill, 22 h 40 min reaction, 30 min settlement, 10 min draw and 10 minidle.

Table 3. Comparative hydrogen production performance from various methods used for preparing thermophilic hydrogen producing seed

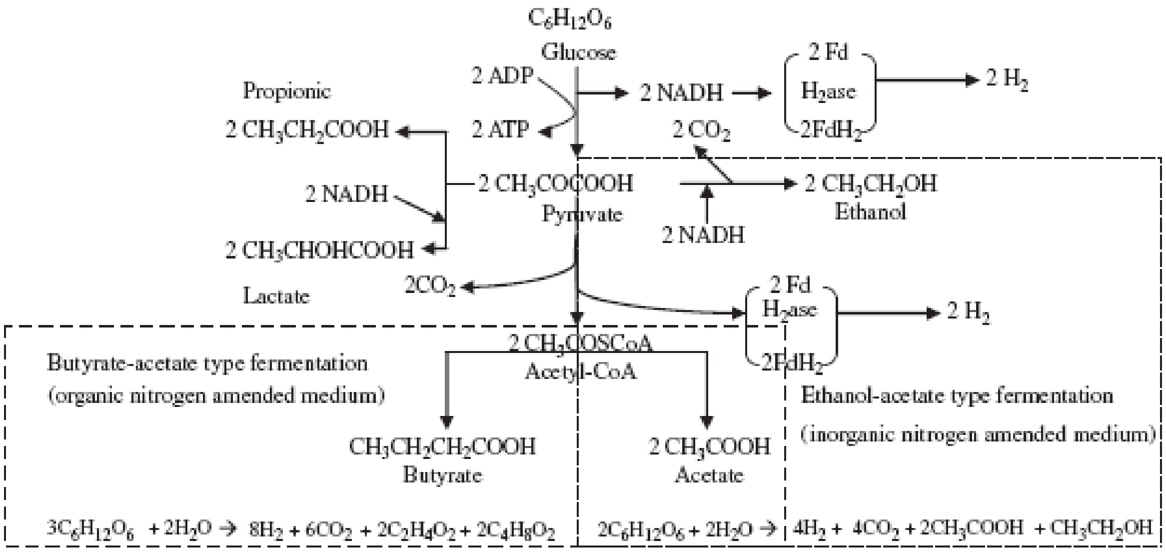
Parameters	HT	0%-PSU 2	10%-PSU 2	20%-PSU 2	30%-PSU 2
Initial pH	5.57	5.59	5.58	5.53	5.52
Final pH	5.37	5.29	5.34	5.37	5.37
H_2 (%)	40.87	44.06	42.15	39.51	41.32
Yield H_2 (L/L)	2.01	2.32	1.65	1.78	1.94
HY (mmol/gCOD)	12.01	11.55	9.00	11.02	13.22
Yield H_2 (mLH_2 /gCOD)	249.13	208.63	211.51	246.86	296.14
Acetic acid (g/L)	5.94	4.82	4.10	3.72	4.46
Butyric acid (g/L)	4.57	4.73	4.50	4.31	3.83
Lactic acid (g/L)	0.21	0.22	0.21	0.19	0.18
Formic acid (g/L)	0.23	0.24	0.20	0.18	0.17
Propionic acid (g/L)	0.69	0.69	0.65	0.60	0.55
Total sugar utilization (%)	53.10	53.40	51.30	57.50	60.70
Total carbohydrate utilization (%)	81.51	80.77	78.84	82.72	84.22
Total alkalinity (g/L)	2.80	3.20	2.30	2.70	2.10
COD reduction (%)	23.07	23.05	23.04	23.09	23.09
Total Solids (g/L)	52.01	35.12	47.18	59.04	33.88
Volatile Solids (g/L)	22.03	14.16	22.37	29.98	17.98
Volatile Organic Acids (g/L)	3.32	3.55	3.19	2.88	2.74



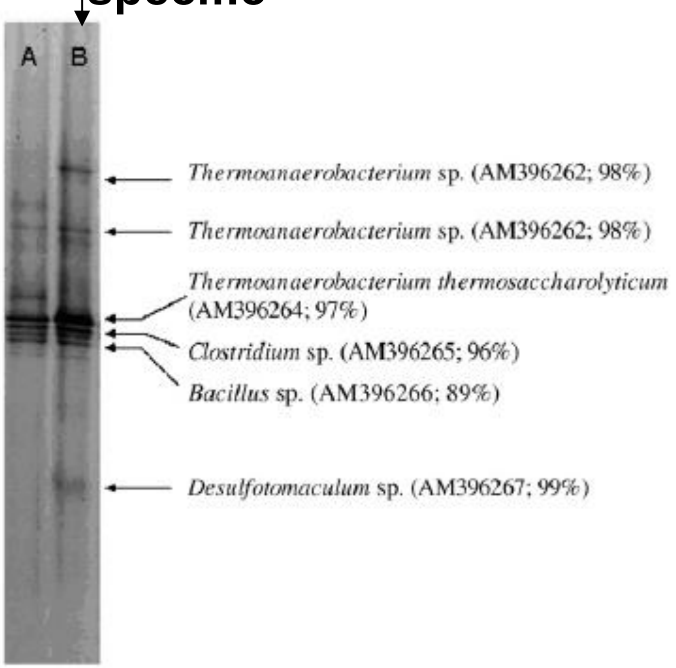
The microbial populations that result from various methods used for preparing thermophilic hydrogen production by (Denaturing Gradient Gel Electrophoresis) DGGE technique

Manage Biohydrogen Process

- **Biostimulization with adding nutrient species specific (organic nitrogen) for their community**

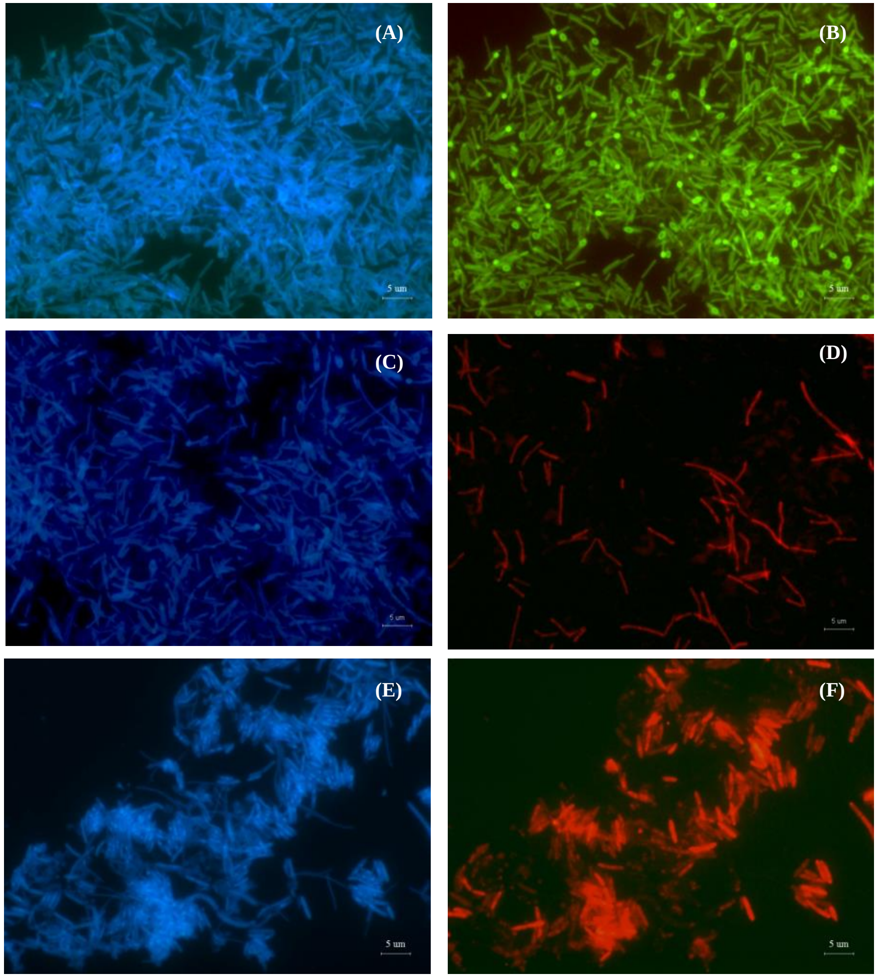


Add **nutrient species specific**



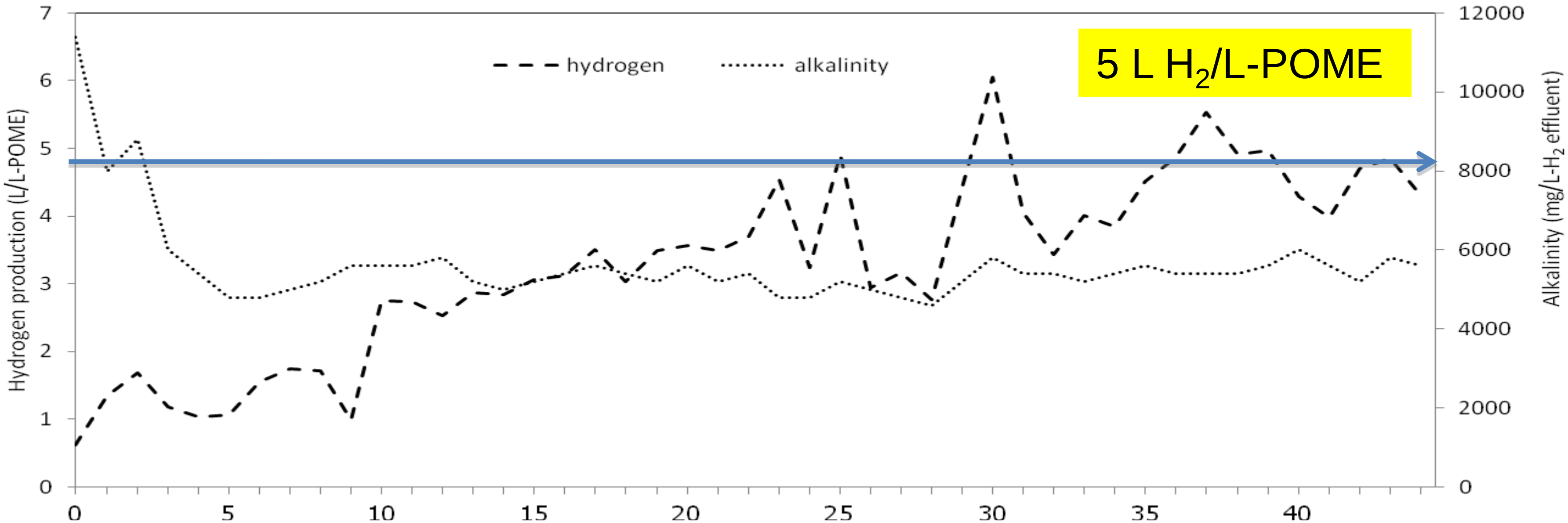
Manage Biohydrogen Process

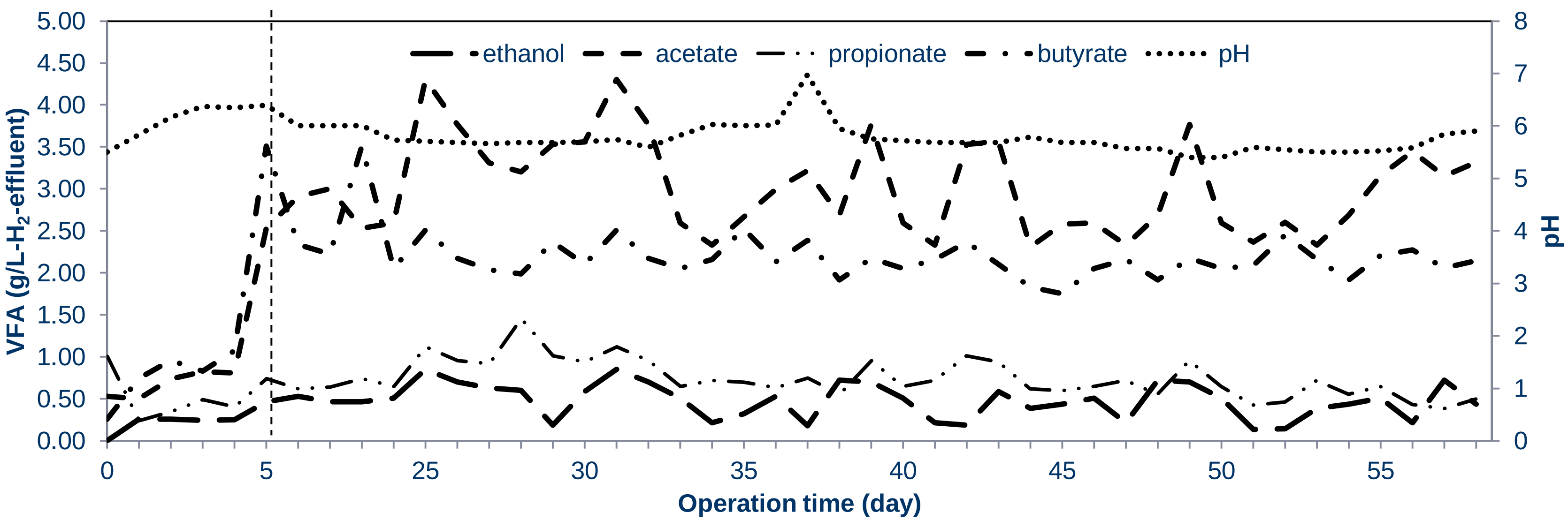
- **Process control for maintaining their community by monitor and quantify major hydrogen producing bacteria**



Fluorescence image of sludge samples from thermophilic biohydrogen producing systems stained with DAPI (A and C), green *Thermoanaerobacterium* spp. detected by Tbm1282 probe labeled with FITC (B) and red *T. thermosaccharolyticum* detected by Tbmthsacc184 probe with Cy3 (D). Fluorescence images of sludge samples from extreme-thermophilic system stained with DAPI (E) and red *Caldicellulosiruptor* spp. detected by Ccs432 probe labeled with Cy3.

Hydrogen production from POME by fermentation process





Biohydrogen production by electrohydrogenesis in batch experiment

Anode
- Graphite

Cathode
- carbon felt with 0.5 mg/cm^2 Pt

Hydrogen effluent from dark fermentation

Power supply
0.5 V

Substrate 120 mL (80% v/v)
Inoculum 30 mL (20% v/v)

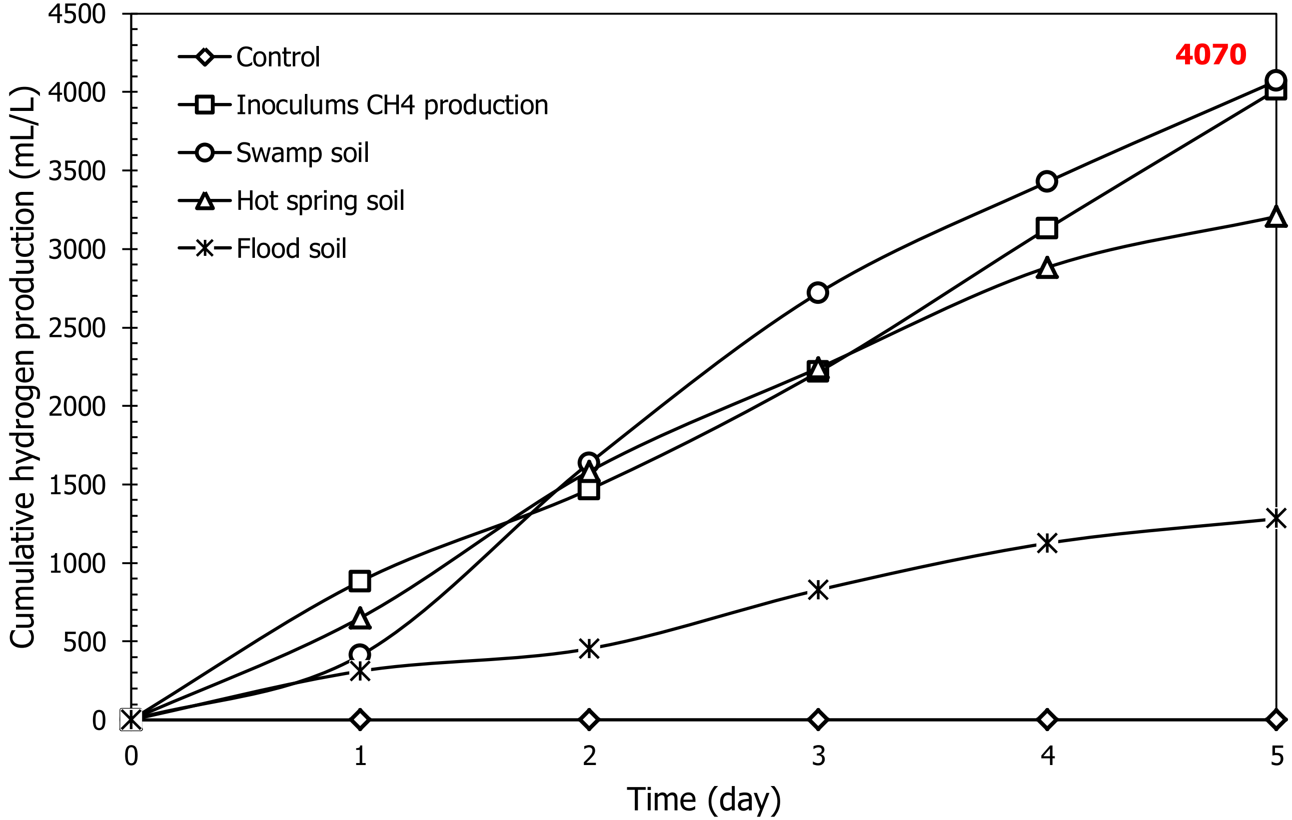
Source of inoculum different

Incubated at 55° c

- Inoculums methane production (pretreatment to boil 100° C 2 h)
- Swamp soil
- Hot springs soil
- Flood soil

Biogas production was determined through the use of the water replacement and $\%H_2$ by GC analysis

Results of batch hydrogen production from fermentation effluent by MEC



Accumulative hydrogen production from fermentation effluent by electrohydrogenesis

Results of batch hydrogen production from fermentation effluent by MEC

Table 3. Net energy productions of hydrogen production from fermentation effluent by MEC

Source of inoculums	Hydrogen yield (mL/g-COD)	Received power (V)	Energy used (V)	Net energy (V)	VFA removal (%)
Control	0.1	0	0.33	-0.33	0.1
Inoculums CH_4 production	321.9	9.49	3.4	6.09	88.33
Swamp soil	**326.5**	**9.63**	**3.5**	**6.13**	**80.25**
Hot spring soil	257.3	7.59	2.13	5.46	53.08
Flood soil	102.8	4.82	4.53	0.29	60.17

Results of batch hydrogen production from fermentation effluent by MEC

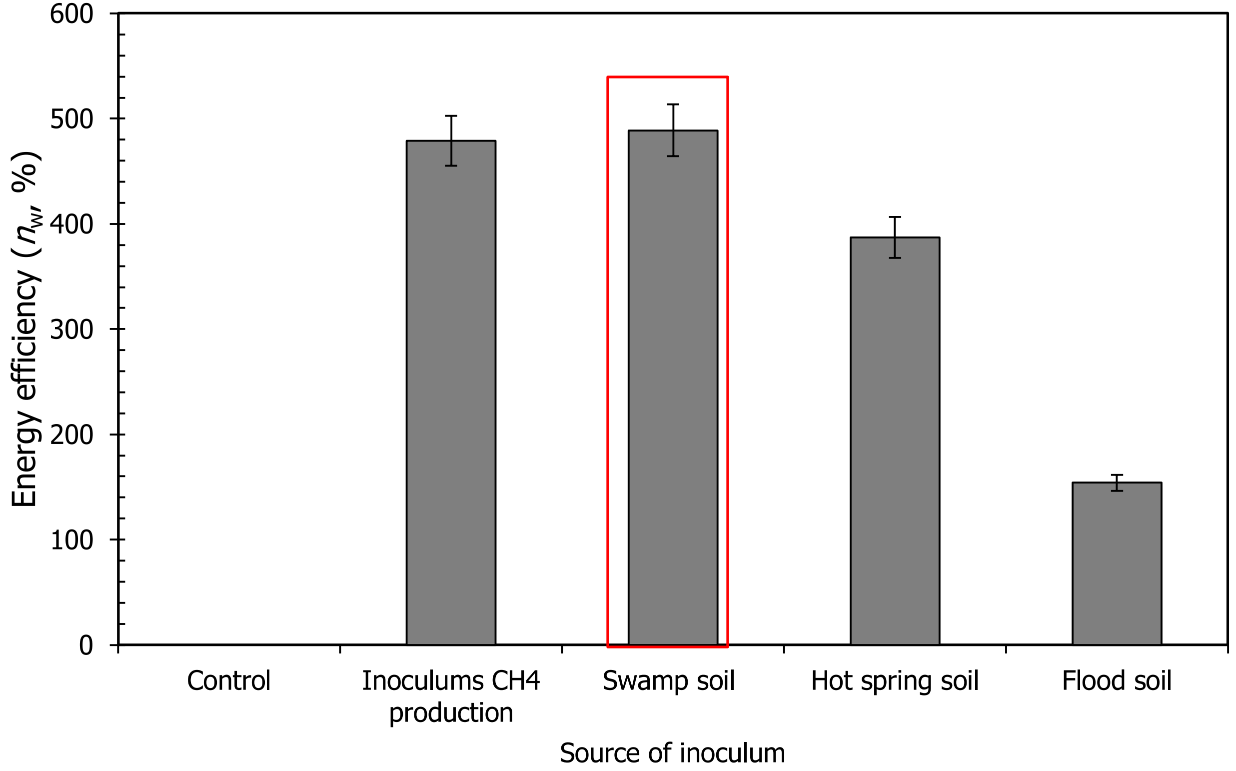


Figure 5. Energy efficiency from microbial electrolysis cell at difference source of inoculum

Continuous hydrogen production from fermentation effluent by MEC

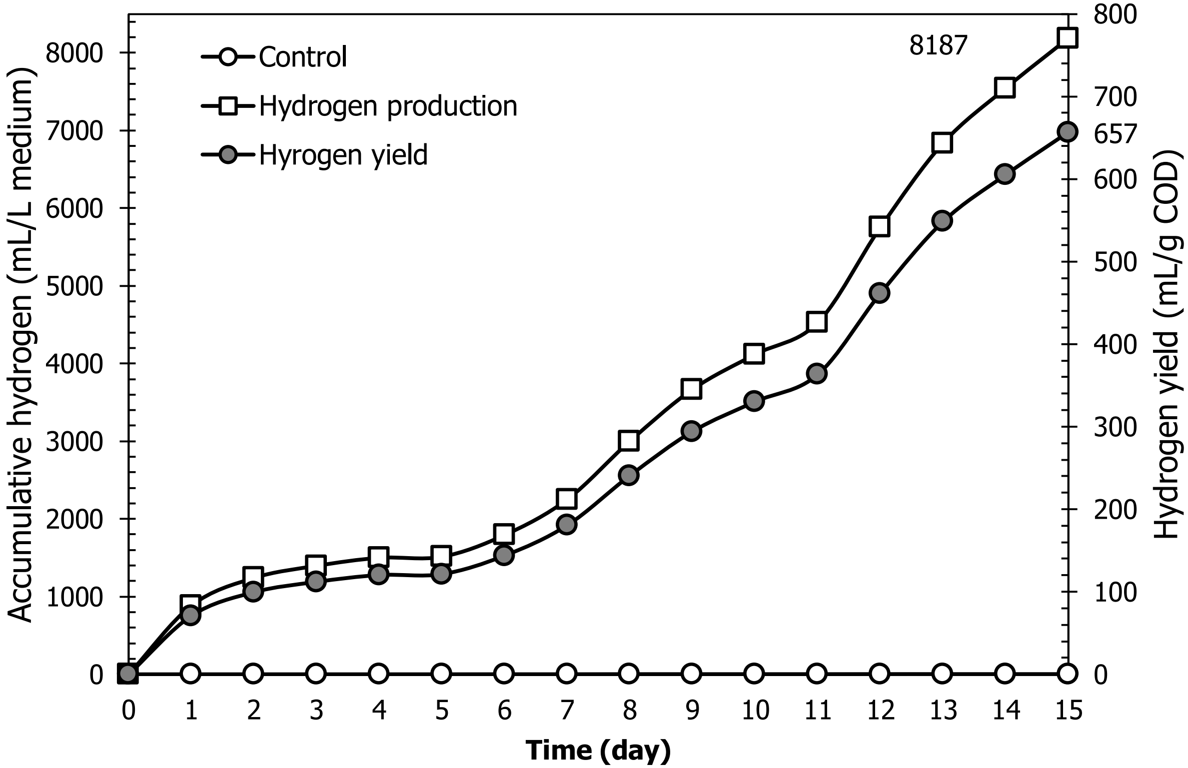


Figure 6. Accumulative hydrogen production from fermentation effluent by electrohydrogenesis

3. Results of Continuous hydrogen production by MEC

Parameter	Swamp soil	Control
Hydrogen production (mL/L)	8187	3
Hydrogen yield (mL/g COD)	657	0.2
Received power (V)	29.06	0.01
Energy used (V)	9.53	4.73
Net energy (V)	**19.53**	-4.72
Energy efficiency (%)	330	0
VFA removal (%)	95	0

Effect of applied voltage on biohydrogen production from dark fermentation effluent

Applied voltage

Power supply

Incubated at 55° c

Hydrogen effluent from dark fermentation

Substrate 120 mL (80% v/v)
Inoculum 30 mL (20% v/v)

0.3 V

0.4 V

0.5 V

0.6 V

0.8 V

0.9 V

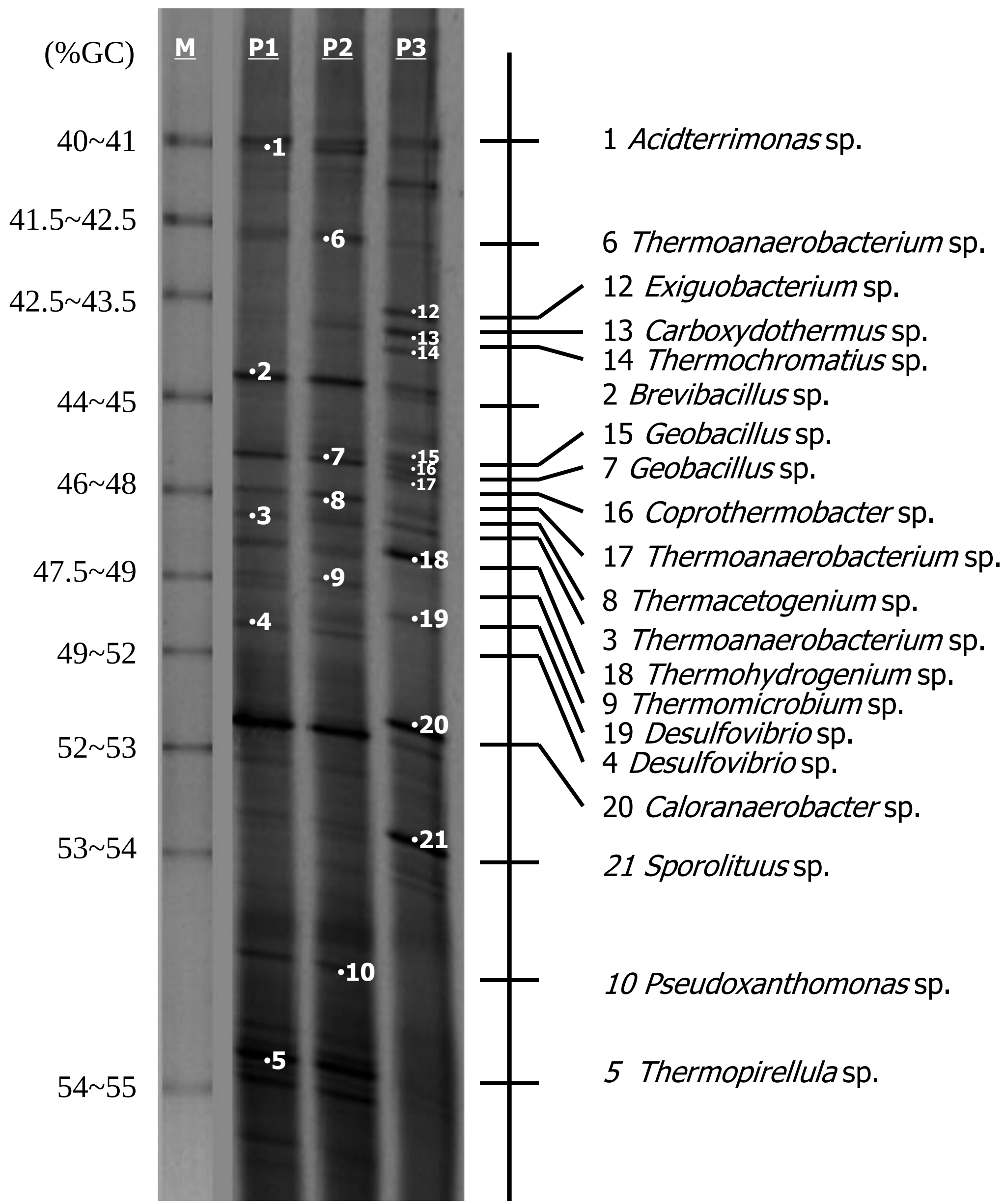
Anode
- Graphite

Cathode
- carbon felt with 0.5 mg/cm^2 Pt

Biogas production was determined through the use of the water replacement and $\%H_2$ by GC analysis

Applied voltage (V)	Hydrogen production (mL H_2/L)	Hydrogen yield (mL H_2/g COD)	Specific hydrogen yield (mL H_2/g COD/V)
0.3	0.22	0.01	0.02
0.4	1.56	0.29	0.29
0.5	30.75	5.67	3.78
0.6	3,004.70	554.37	**277.19**
0.7	3,460.32	**638.44**	255.38
0.8	2,241.48	413.56	137.85

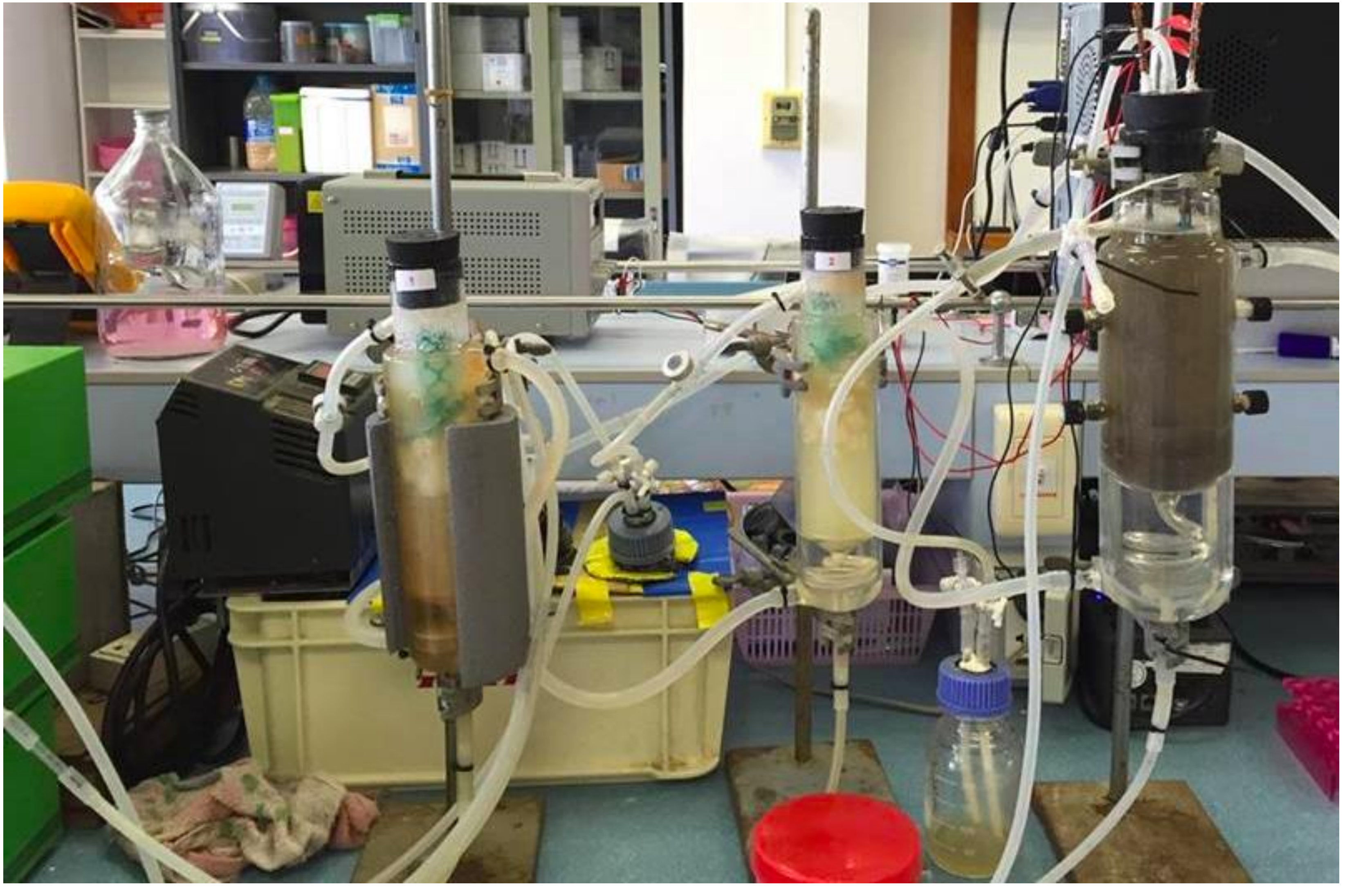
Microbial community

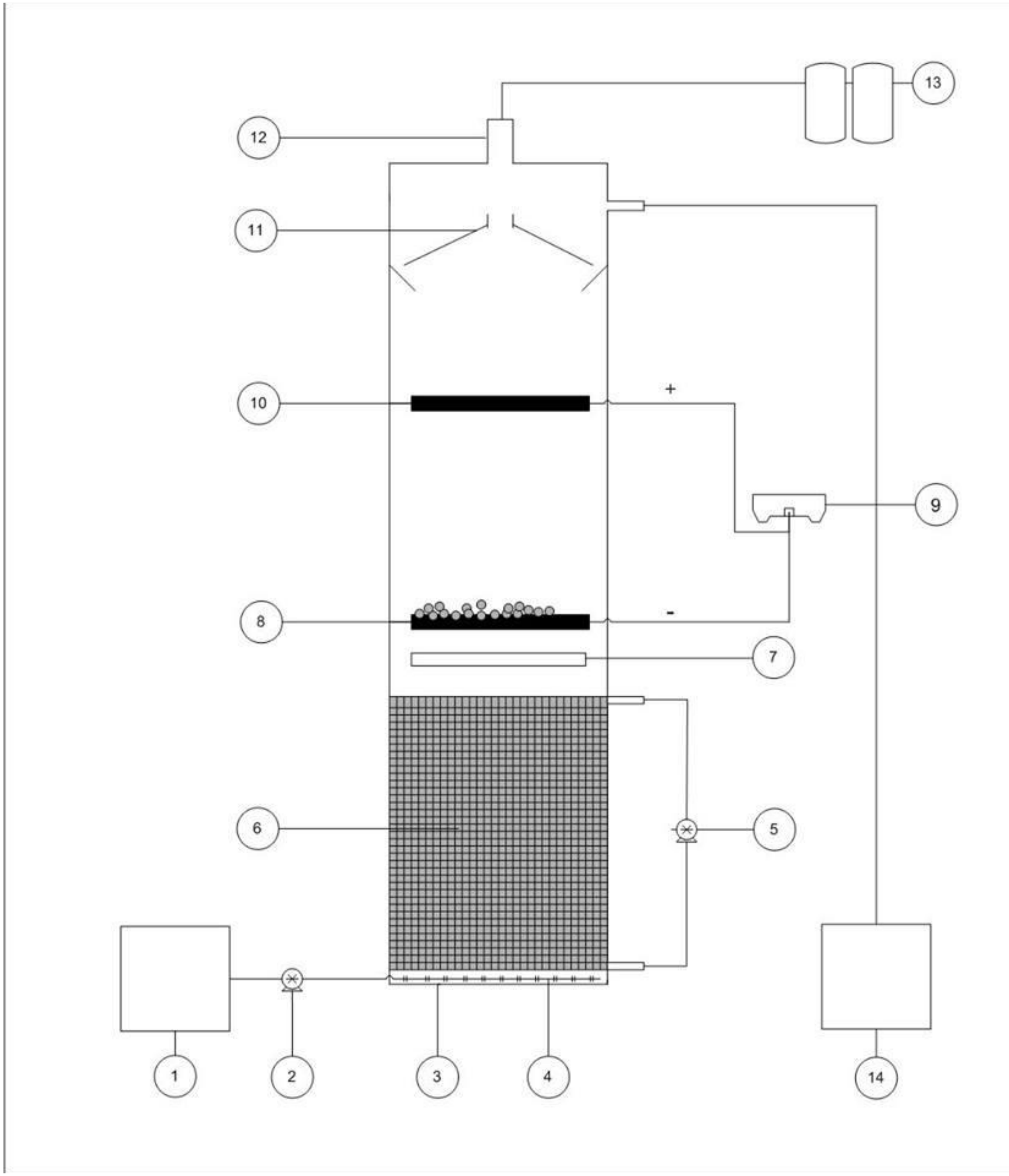


M, DGGE marker
P1, Before fermentation
P2, Sediment (after fermentation)
P3 Electrode (after fermentation)

Dominated species
***Aciditerrimonas* sp.**
***Geobacillus* sp.,**
***Thermohydrogenium* sp.**
***Brevibacillus* sp.,**
***Caloranaerobacter* sp.**

Continuous efficient biohydrogen production from POME by two-stage dark fermentation and electrohydrogenesis



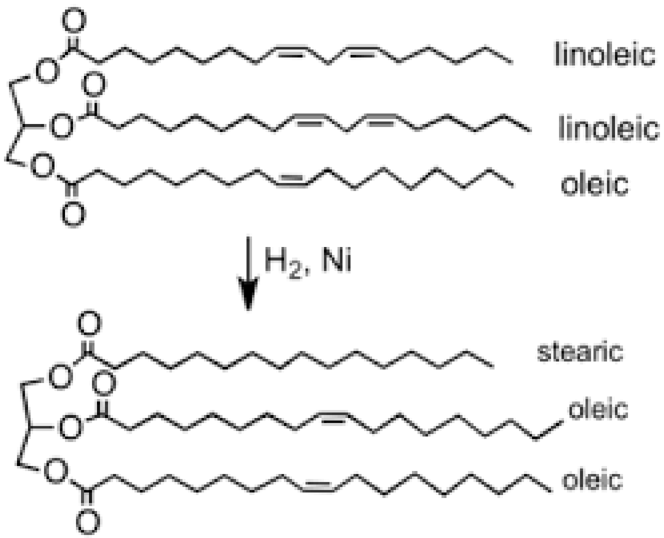


Current work:

- To design new reactor for integrated system of two stage dark fermentation and microbial electrohydrogenesis
- Scale up
- Control and monitoring microbial in the systems

Application of Biohydrogen

Partial hydrogenation of palm oil



Commercial hydrogen = 18 Thai bath/kg
Biohydrogen = 7 Thai bath/kg