Biogas Production from Biological Sludge

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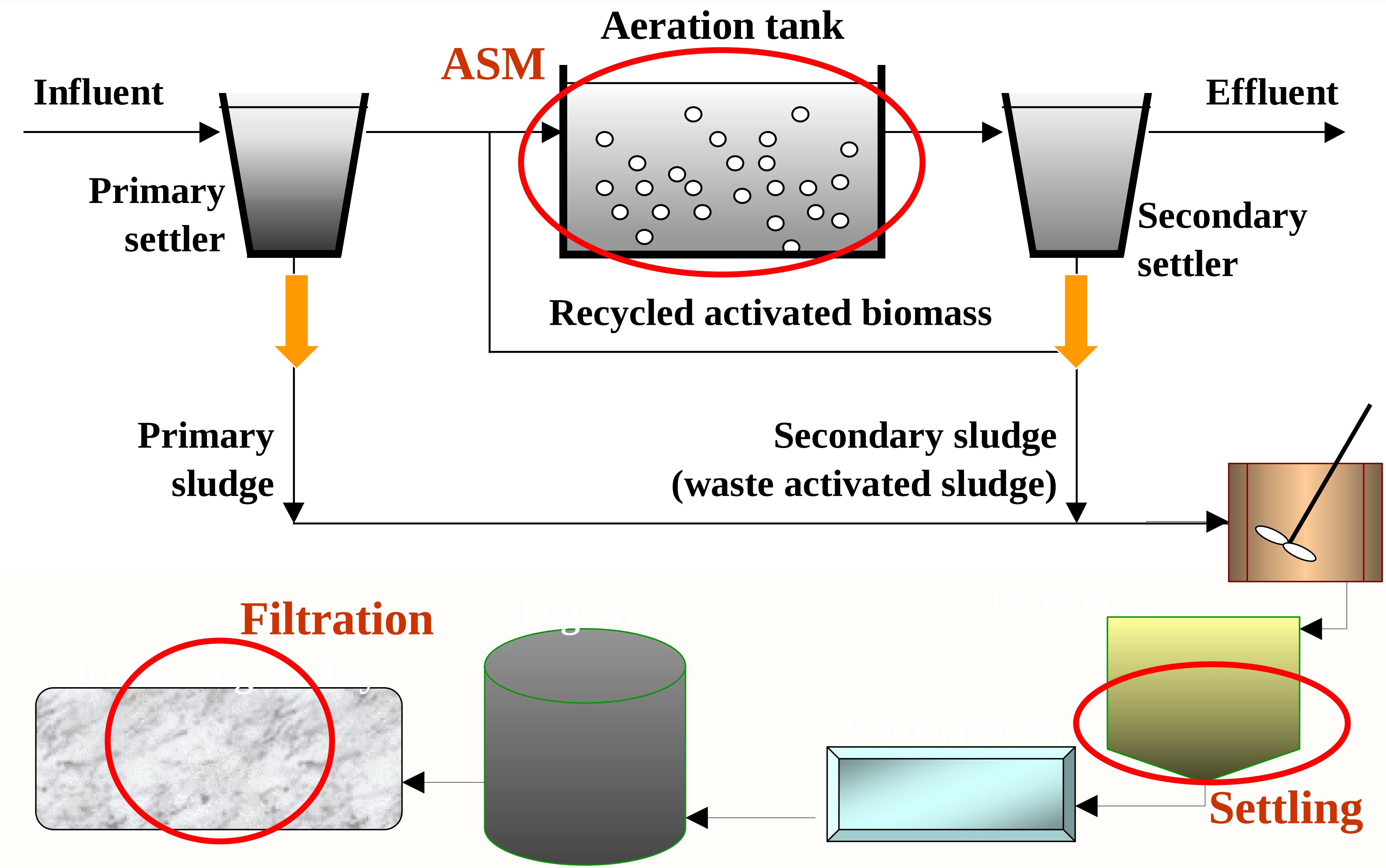
Sludge?



Aeration tank
ASM
Influent
Effluent
Primary
settler
Secondary
settler
Recycled activated biomass
Primary
sludge
Secondary sludge
(waste activated sludge)
Filtration
Settling

Biological Sludge Floc

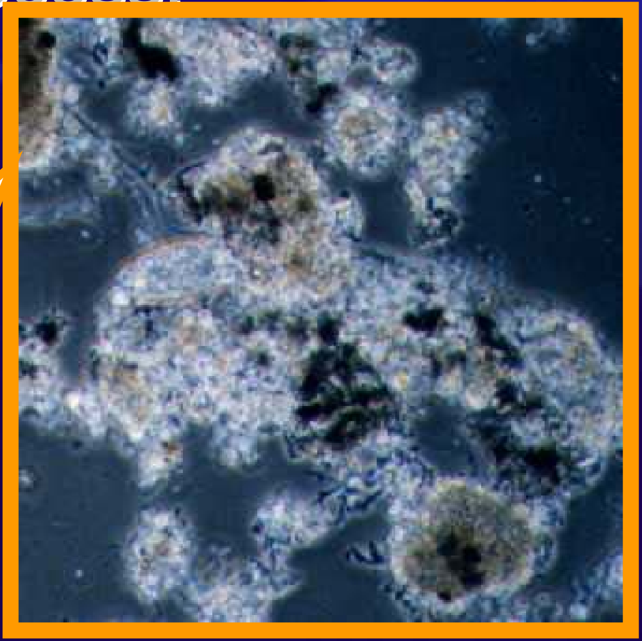
- Floc is a common form of bioaggregates appearing in the wastewater treatment process.

•*Irregular shape;*

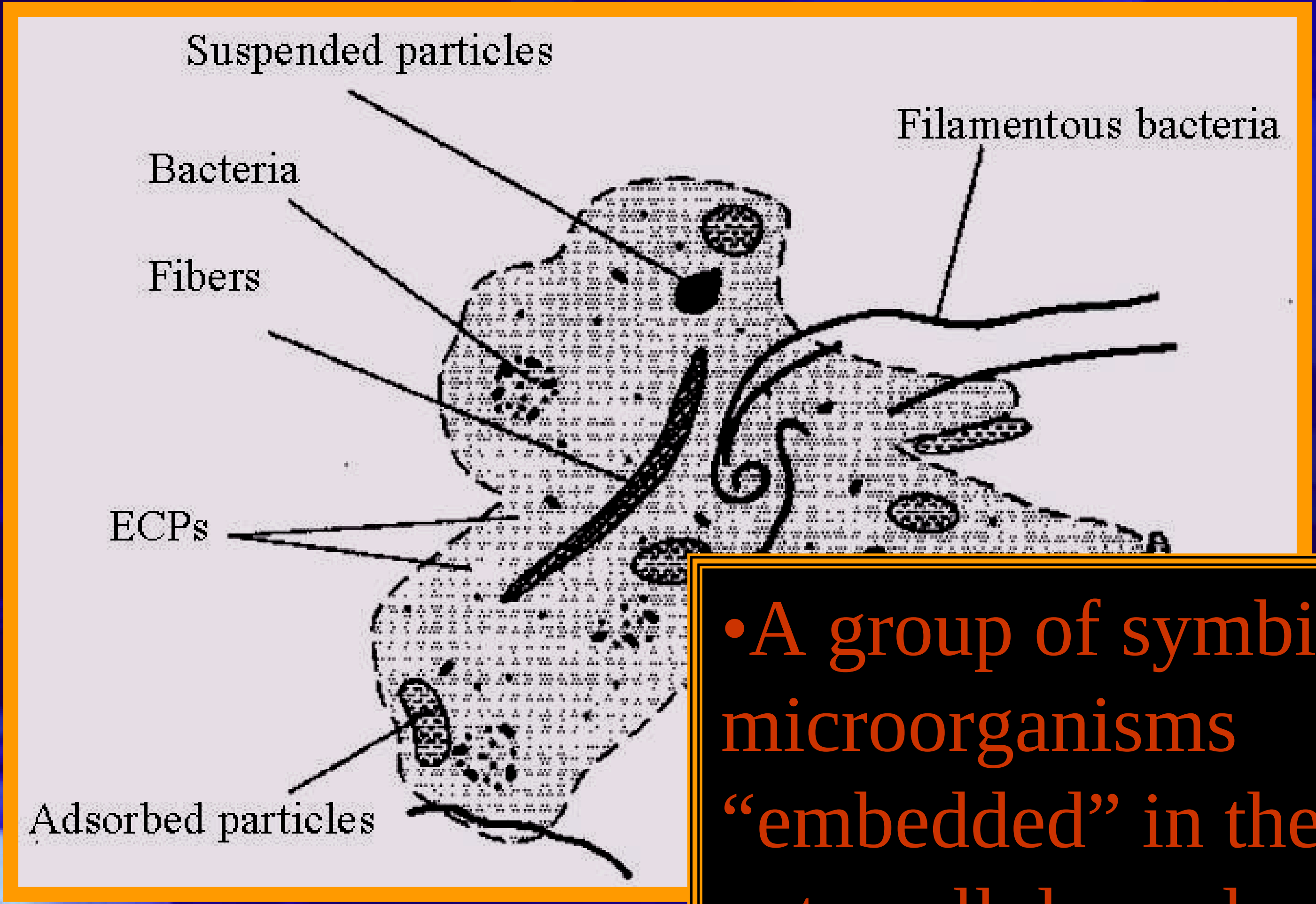
•*Highly porous;*

•*Compressible and fragile;*

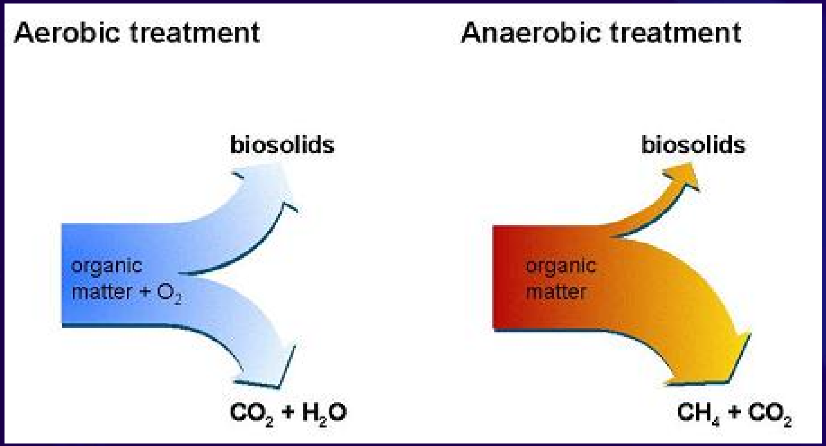
•*Inhomogeneous distribution of internal mass.*



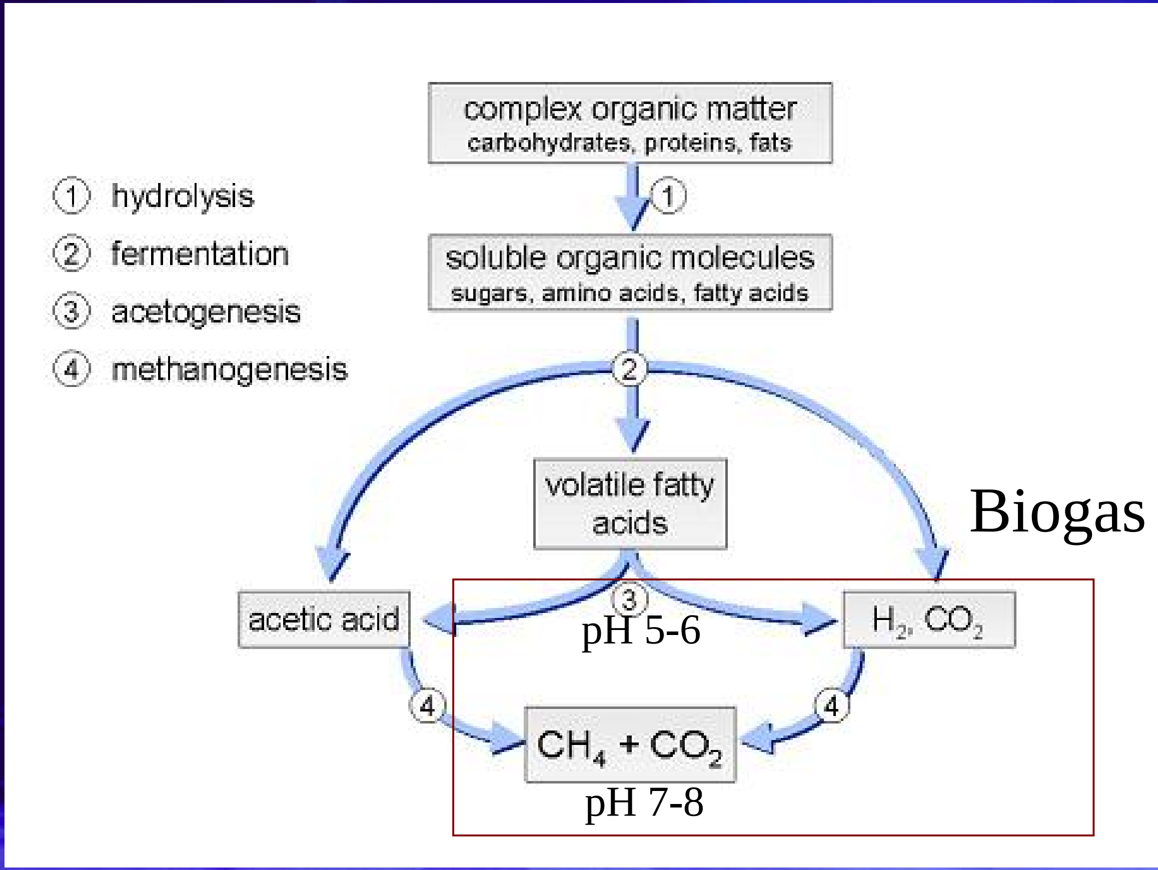
Sludge Floc



- A group of symbiotic microorganisms “embedded” in the extracellular polymers

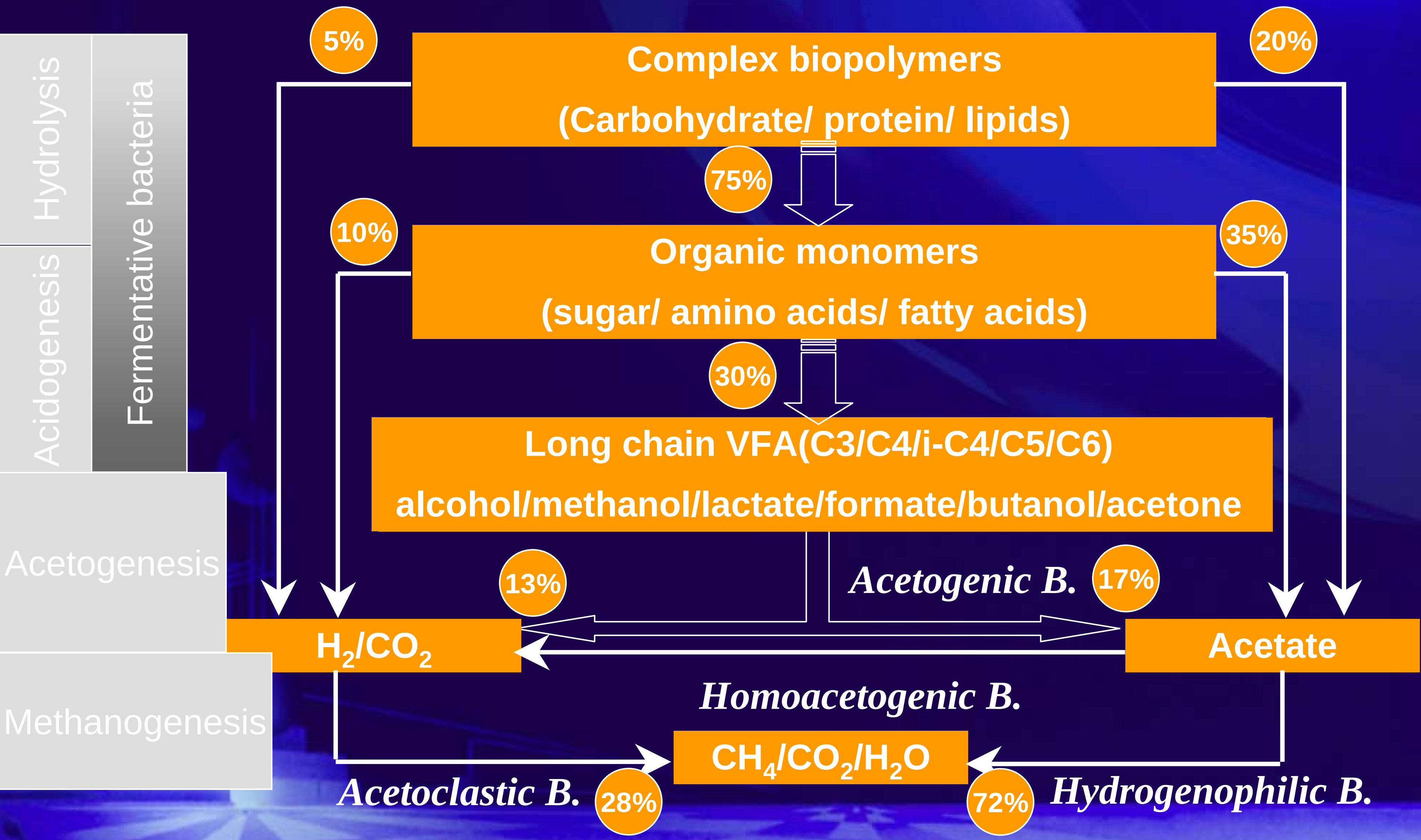


Aerobic treatment
Anaerobic treatment
biosolids
organic matter + O_2
$CO_2 + H_2O$
biosolids
organic matter
$CH_4 + CO_2$



complex organic matter
carbohydrates, proteins, fats
1 hydrolysis
2 fermentation
3 acetogenesis
4 methanogenesis
soluble organic molecules
sugars, amino acids, fatty acids
volatile fatty acids
acetic acid
H_2, CO_2
pH 5-6
$CH_4 + CO_2$
pH 7-8
Biogas

Anaerobic digestion



$\Delta G^{o\prime}$

Step	Reaction	$\Delta G^{o\prime}$
Fermentation	$C_6H_{12}O_6 + 4H_2O \longrightarrow 2CH_3COO^- + 2HCO_3^- + 4H^+ + 4H_2$	-207
	$C_6H_{12}O_6 + 2H_2O \longrightarrow CH_3(CH_2)_2COO^- + 2HCO_3^- + 3H^+ + 2H_2$	-135
	$3C_6H_{12}O_6 \longrightarrow 4CH_3CH_2COO^- + 2CH_3COO^- + 2CO_2 + 2H_2O + 2H^+ + H_2$	-922
Acetogenesis	$CH_3CH_2OH + H_2O \longrightarrow CH_3COO^- + H^+ + 2H_2$	+10
	$CH_3CH_2COO^- + 3H_2O \longrightarrow CH_3COO^- + H^+ + 3H_2 + HCO_3^-$	+76
	$CH_3(CH_2)_2COO^- + 2H_2O \longrightarrow 2CH_3COO^- + H^+ + 2H_2$	+48
	$2HCO_3^- + 4H_2 + H^+ \longrightarrow CH_3COO^- + 4H_2O$	-105
Methanogenesis	$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$	-130
	$4HCOO^- + 4H^+ \longrightarrow CH_4 + 3CO_2 + 2H_2O$	-120
	$4CO + 2H_2O \longrightarrow CH_4 + 3CO_2$	-186
	$CH_3COO^- + H^+ \longrightarrow CH_4 + CO_2$	-33
	$4CH_3OH \longrightarrow 3CH_4 + CO_2 + 2H_2O$	-309
	$4(CH_3)_3NH^+ + 6H_2O \longrightarrow 9CH_4 + 3CO_2 + 4NH_4^+$	-666

Step

Step		
Denitrification	$12NO_3^- + C_6H_{12}O_6 \longrightarrow 12NO_2^- + 6CO_2 + 6H_2O$	-1946
	$8NO_2^- + C_6H_{12}O_6 \longrightarrow 4N_2O + 6CO_2 + 6H_2O$	-632
	$12N_2O + C_6H_{12}O_6 \longrightarrow 12N_2 + 6CO_2 + 6H_2O$	-134
Sulphate reduction	$4H_2 + SO_4^{2-} + H^+ \longrightarrow 4H_2O + HS^-$	-152
	$CH_3COO^- + SO_4^{2-} \longrightarrow 2HCO_3^- + HS^-$	-48
	$4CH_3CH_2COO^- + 3SO_4^{2-} \longrightarrow 4CH_3COO^- + 4HCO_3^- + H^+$	-151

Phase

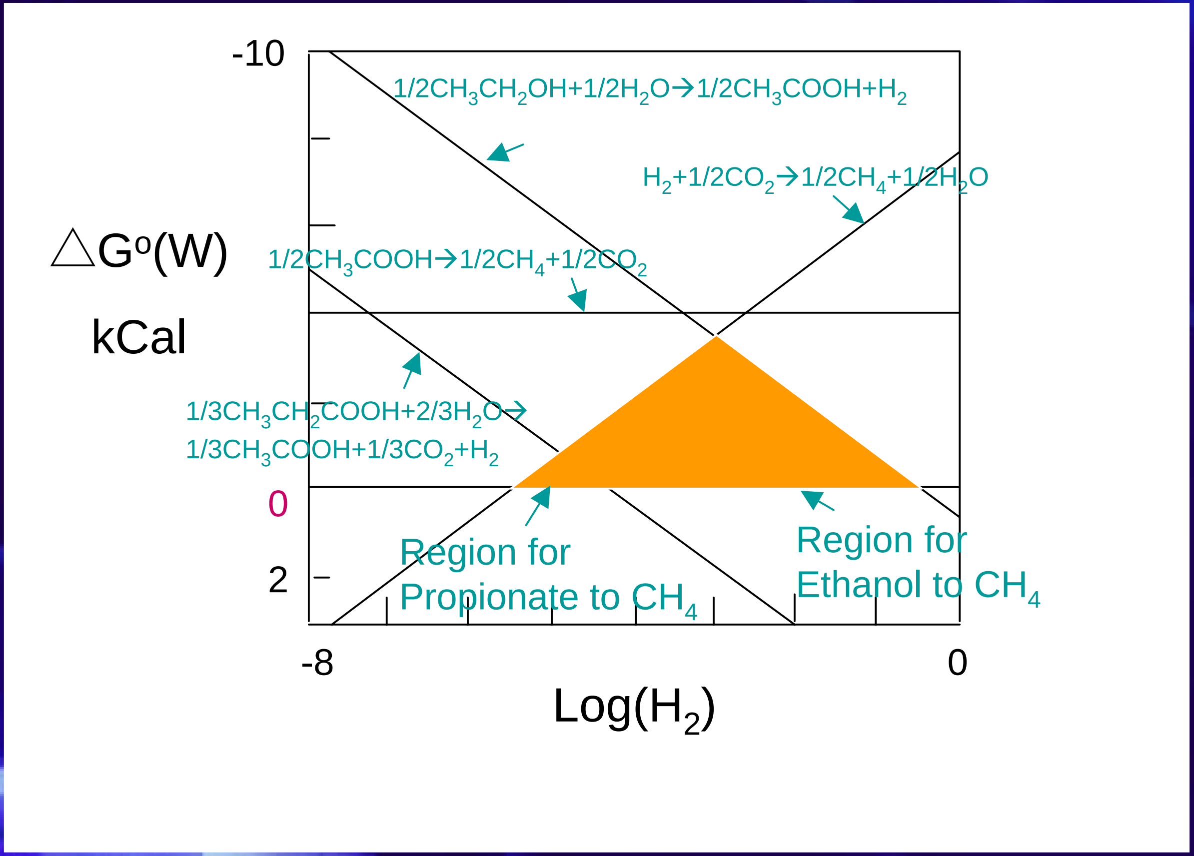
- Fermenting Bacteria
  - pH=5.2~6.3
  - Y_X=0.2g-VS g-COD^{-1}
  - Faculative anaerobic
- Acedogenesis and Methadogenesis
  - pH=6.8~7.2
  - Y_X=0.03~0.05 g-VS g-COD^{-1}
  - Obligate anaerobic
  - Syntrophic reaction
    - ↔ Interspecies hydrogen transfer

Propionate and H_2

Propionate: account for over 30% of the electron flow

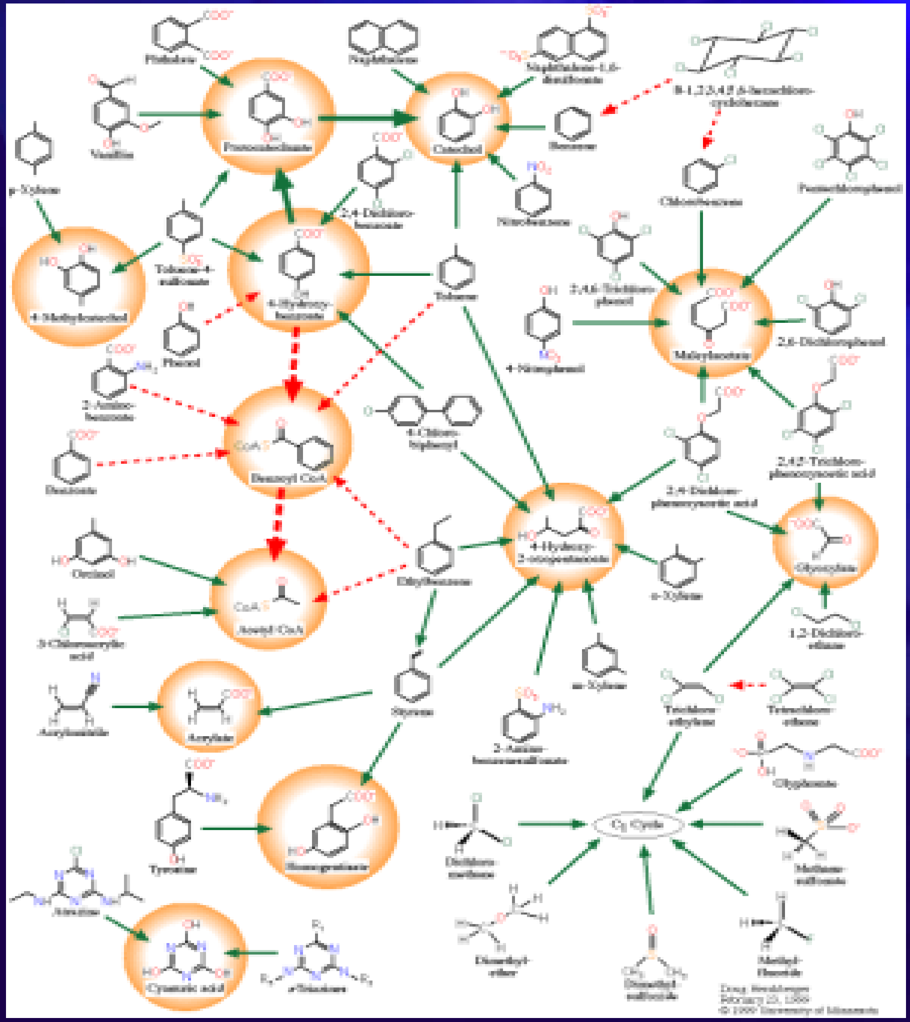
Deterioration of propionate degradation

→ Decrease in VFA removal efficiency

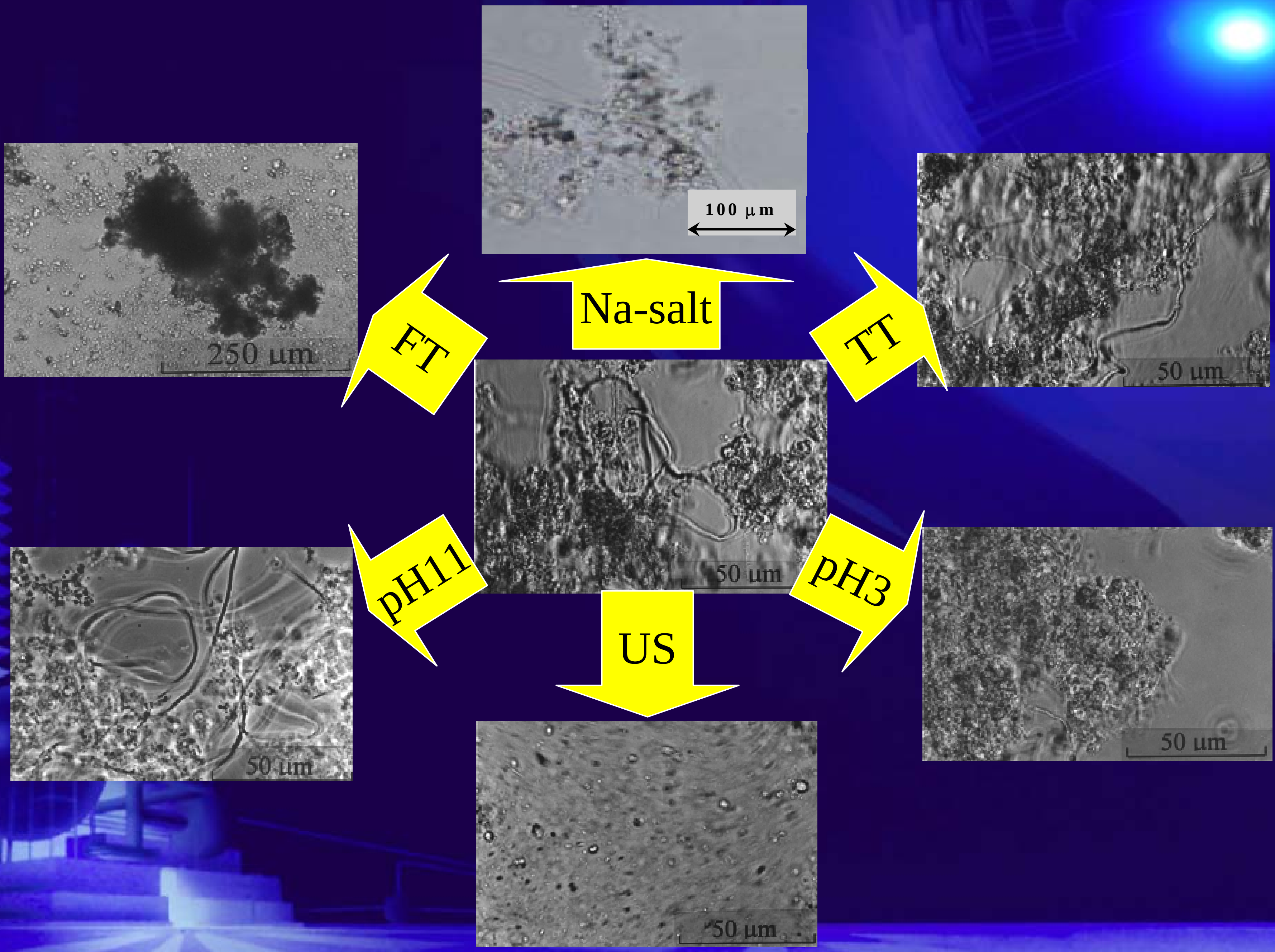


McCarty, P.L. and Smith, D.P. Anaerobic wastewater treatme[n]
[J]. Environ. Sci. Technol., 1986,20:1200-1206

Through enzymes



Enhanced Hydrolysis

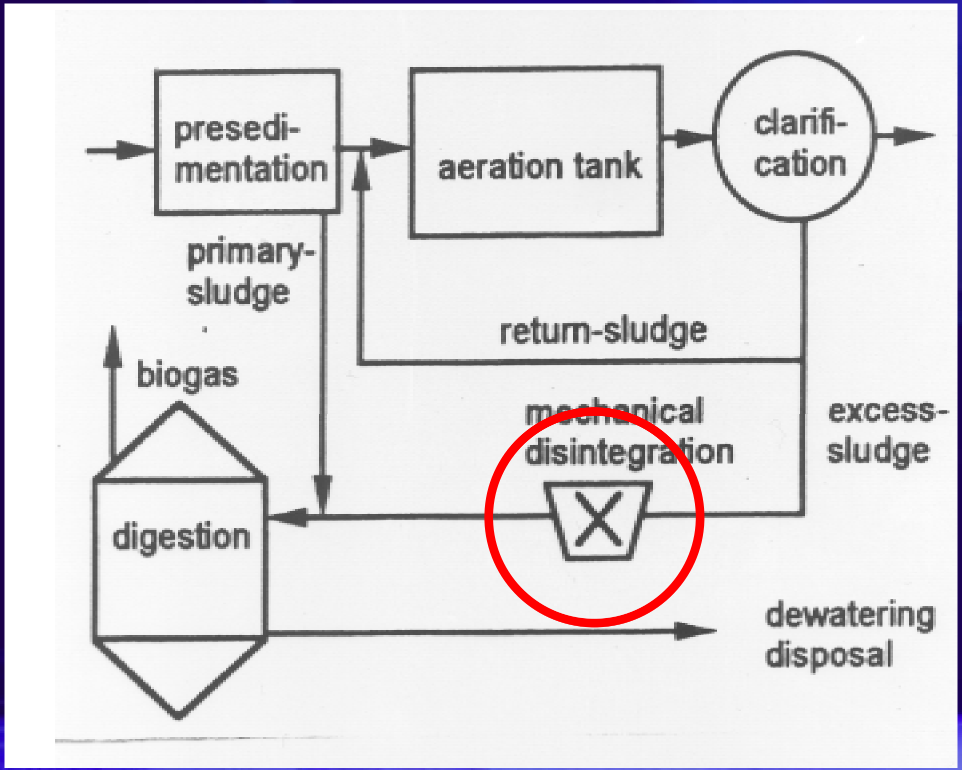


Na-salt
100 µm
FT
250 µm
TT
50 µm
50 µm
pH11
50 µm
pH3
50 µm
US
50 µm

Pre-hydrolysis

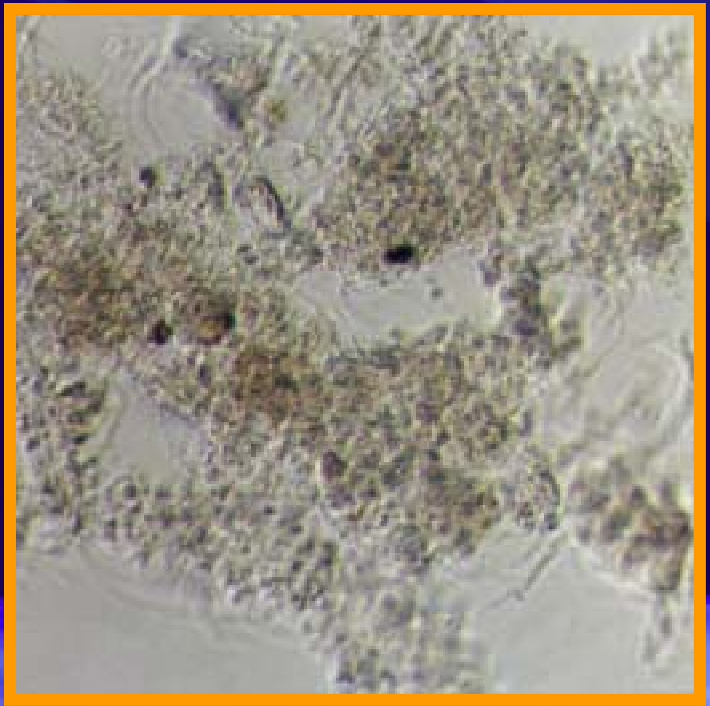
- Pre-hydrolysis of sludge is often applied in prior to the anaerobic digestion to:
  - *Disintegrate the suspended particles*
  - *Decompose the insoluble organic molecules*.
- Alkaline treatment and ultrasonication were reported as effective pre-hydrolytic treatments.

Enhancing Digestion

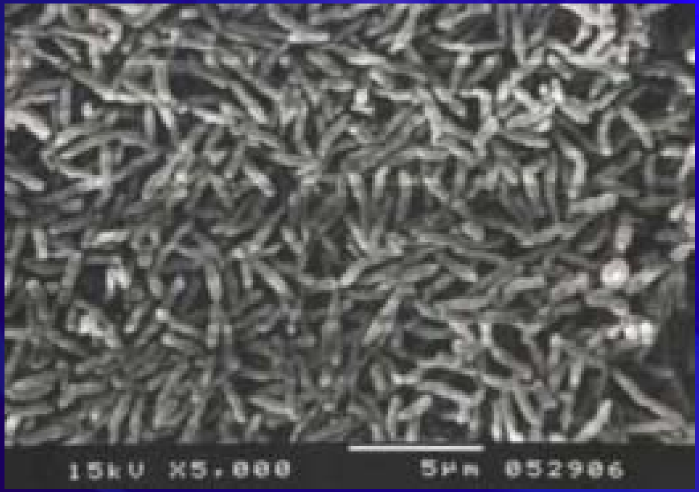


Waste Activated Sludge

- Sampling from the recycled stream in the secondary treatment stage in St. Marys sewage treatment plant in Sydney, Australia.
- pH = 7.50
- TSS = 10,700 mg/L.
- ρ_S = 1,612 kg/m^3.

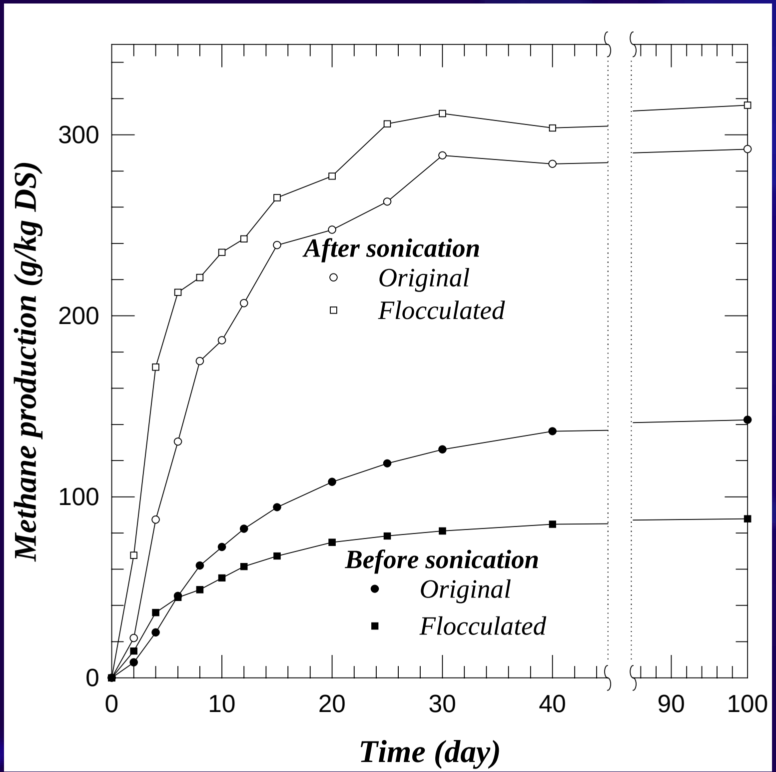


(a)

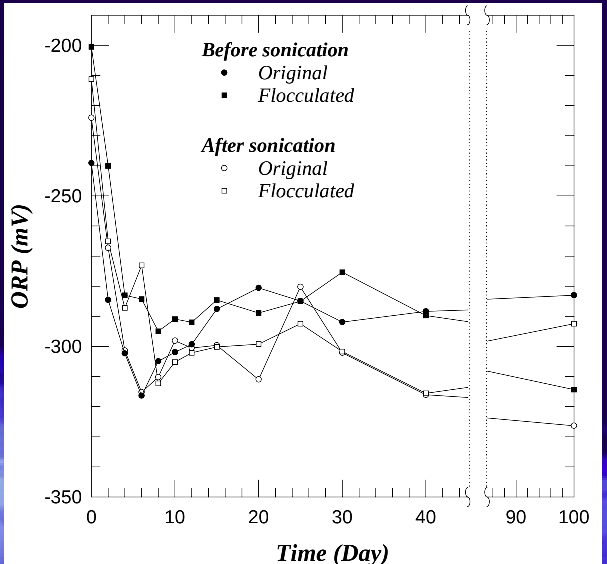


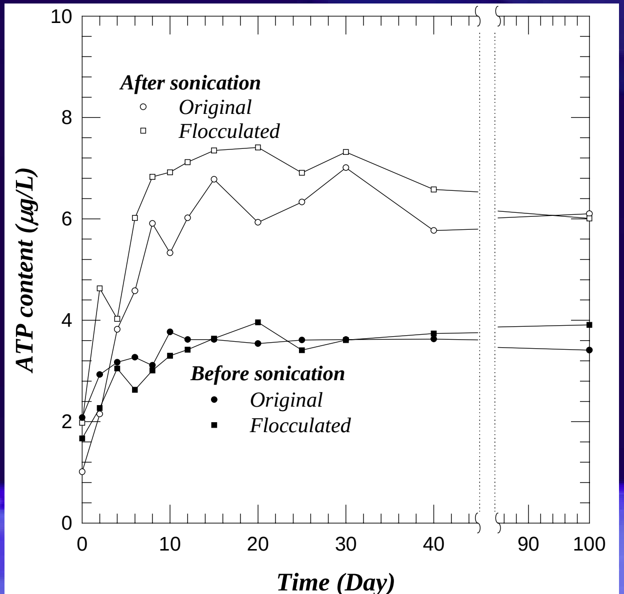
(b)

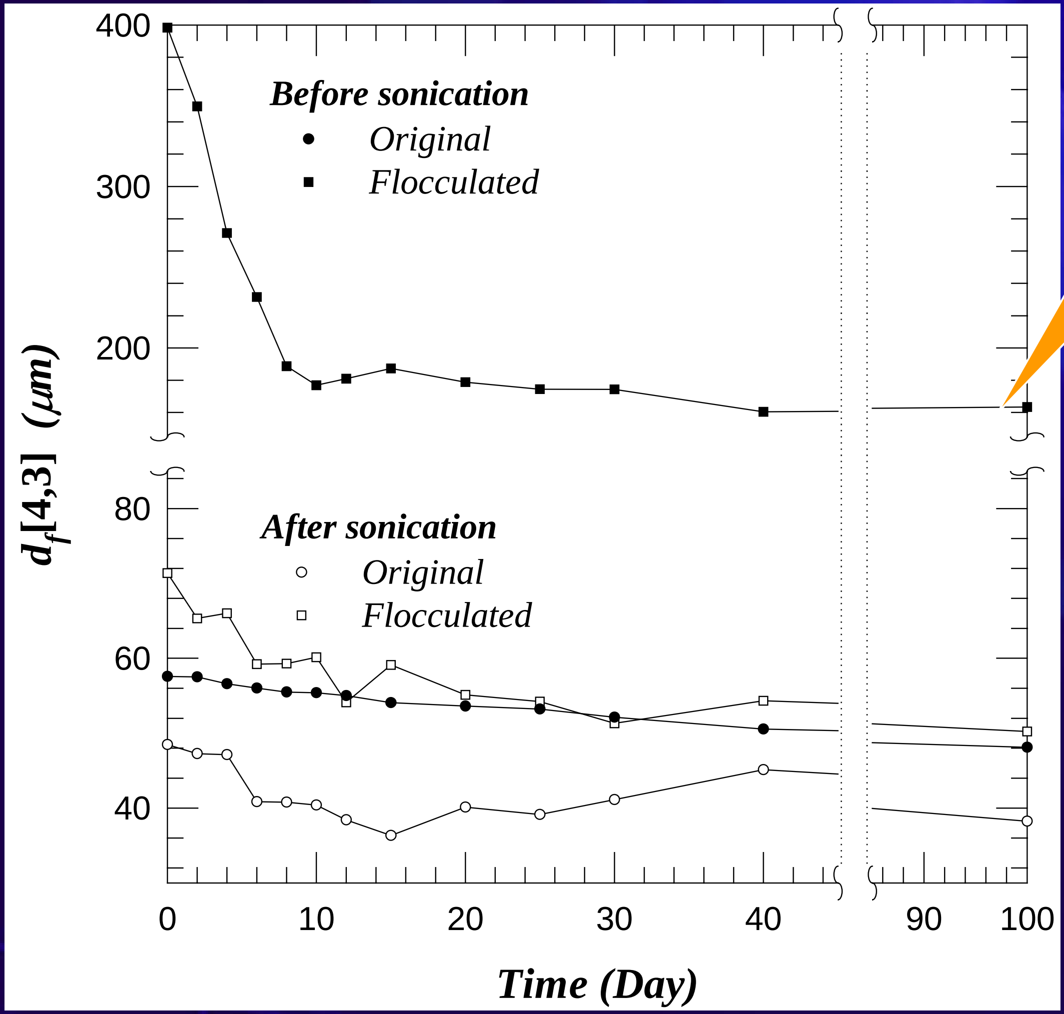
Strains in innoculum K8: (a) *bacillus*; (b) *cocci*.



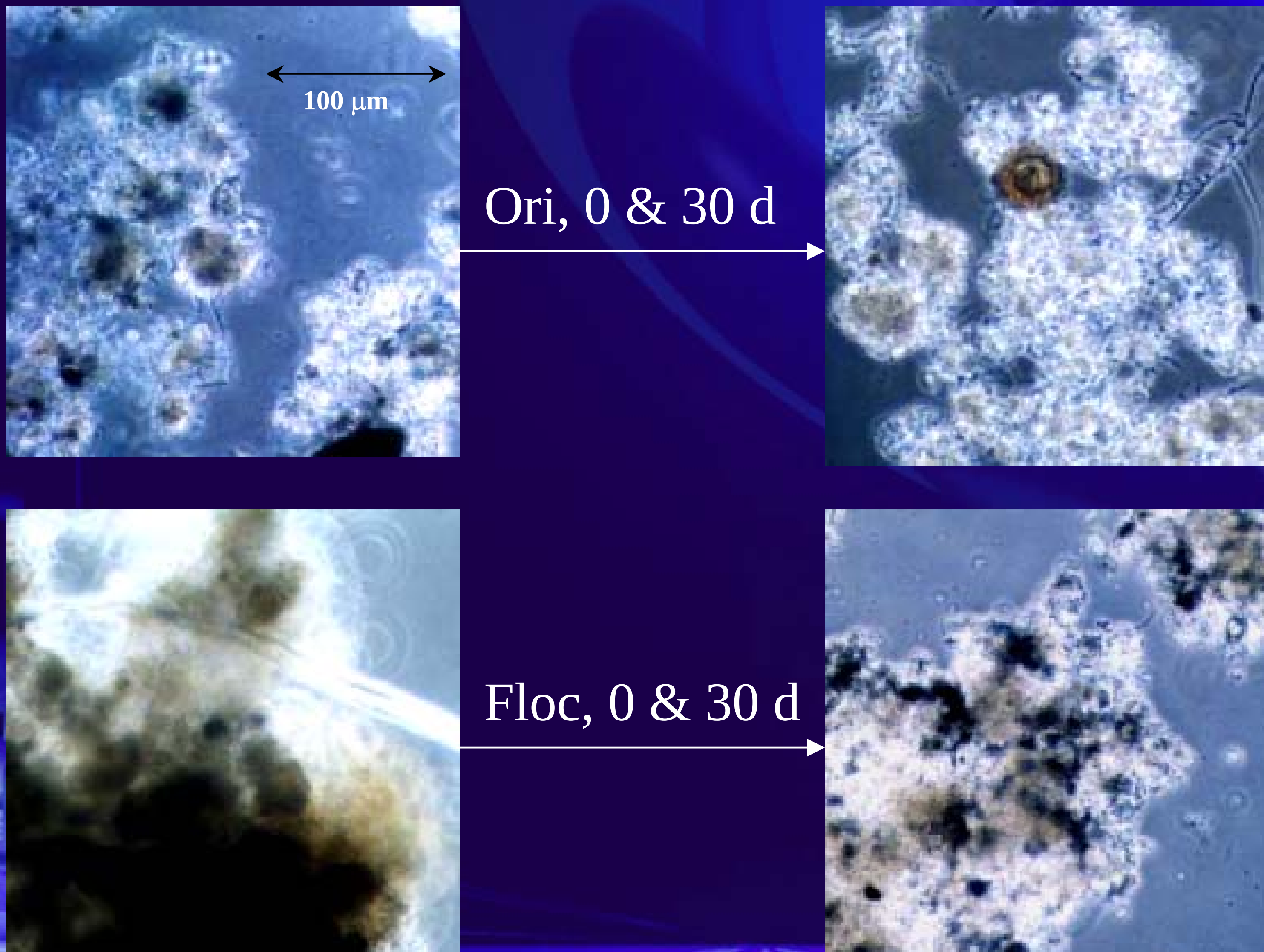
Flocculation retards Digestion; while Ultrasonication Enhances it.



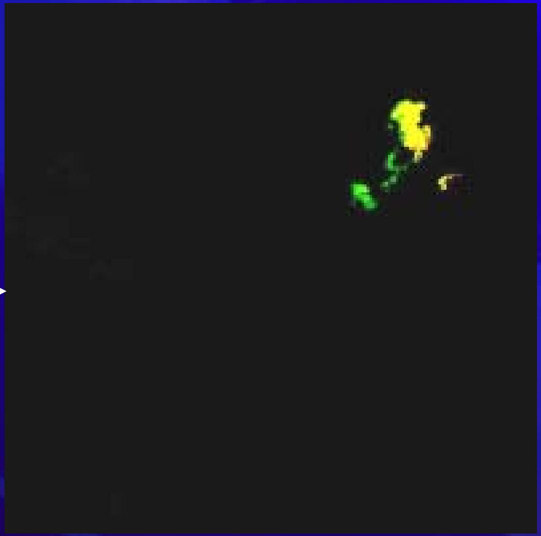


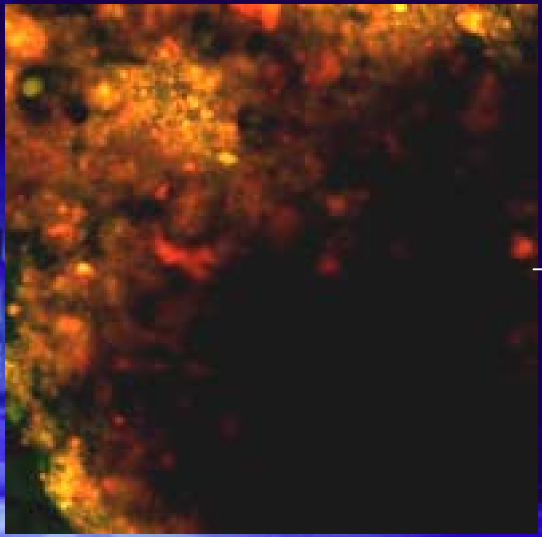


Poor digestion

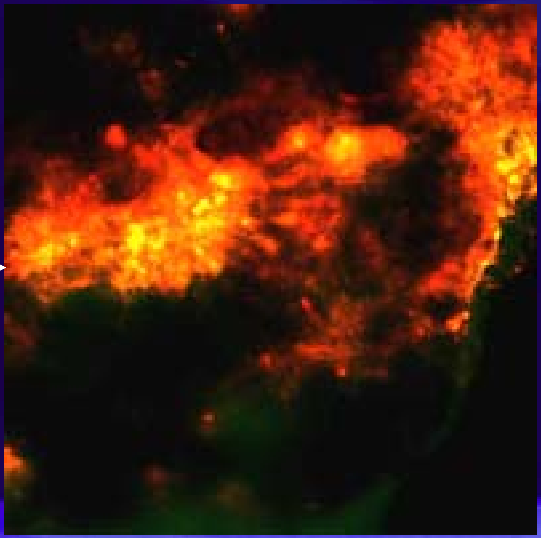

100 μm
Ori, 0 & 30 d
Floc, 0 & 30 d

Ori, 0 & 30 d

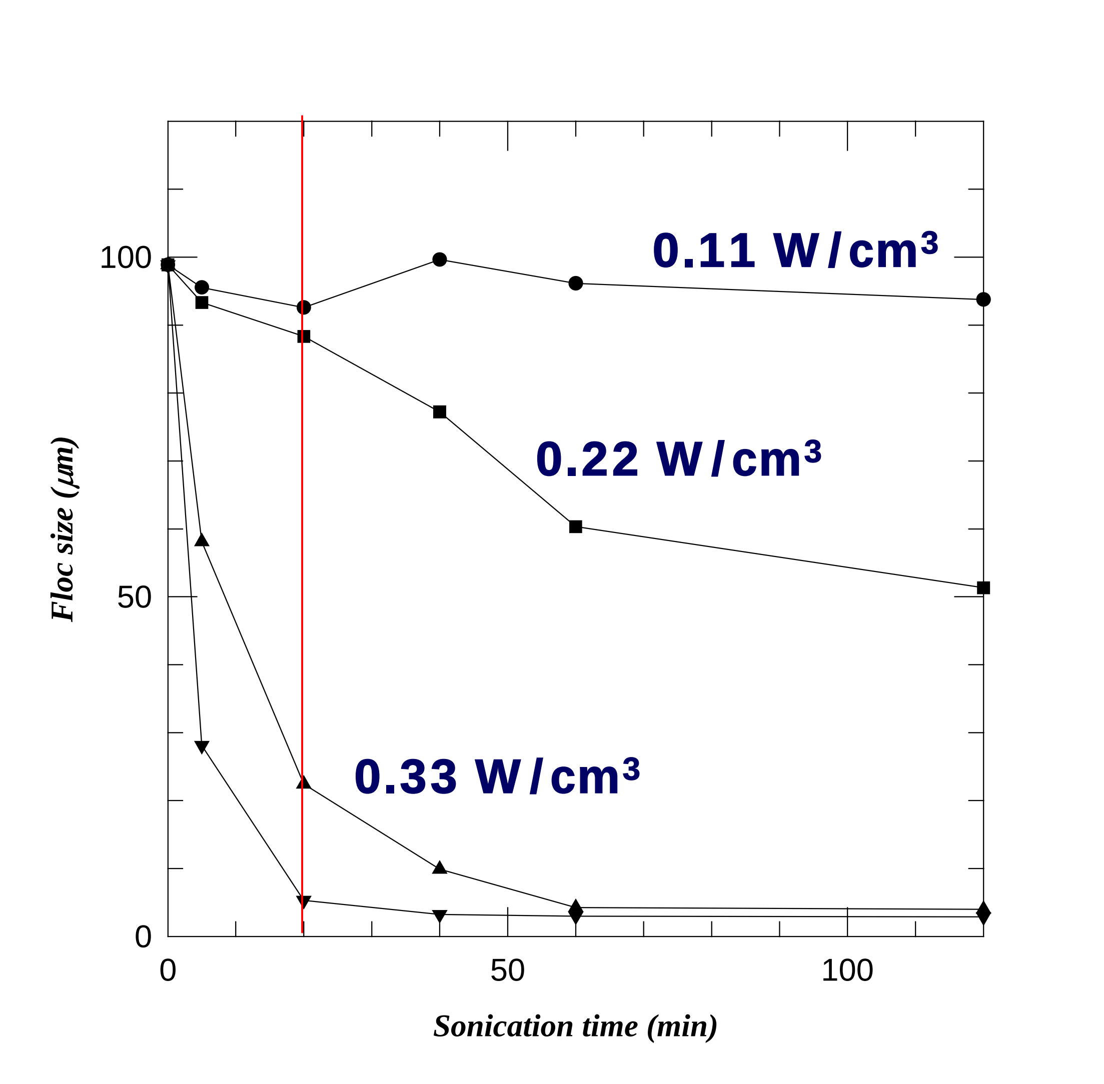


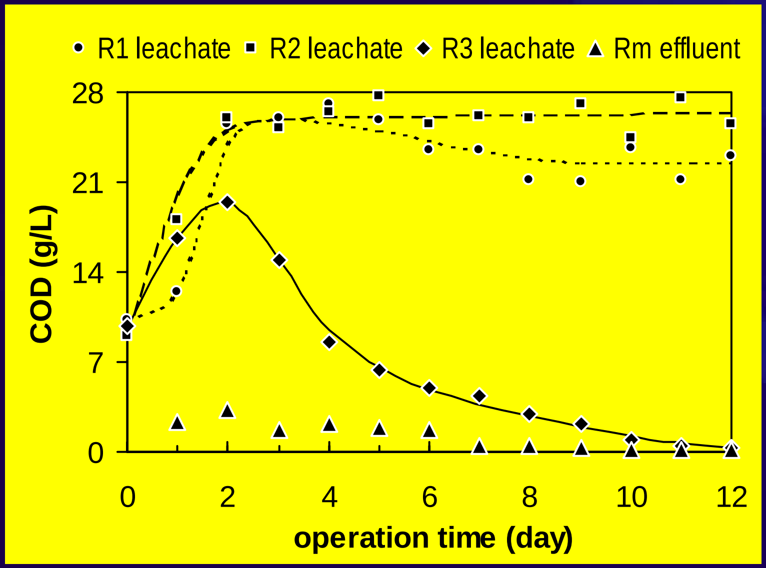


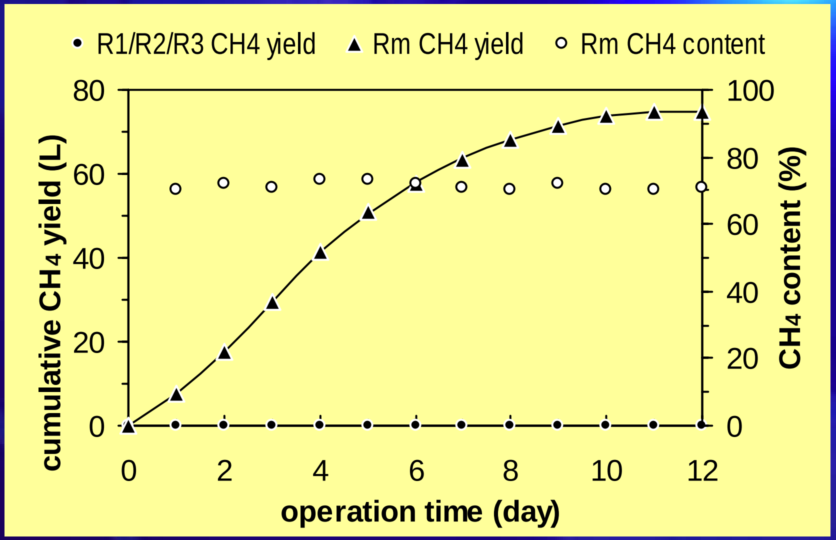
Floc, 0 & 30 d

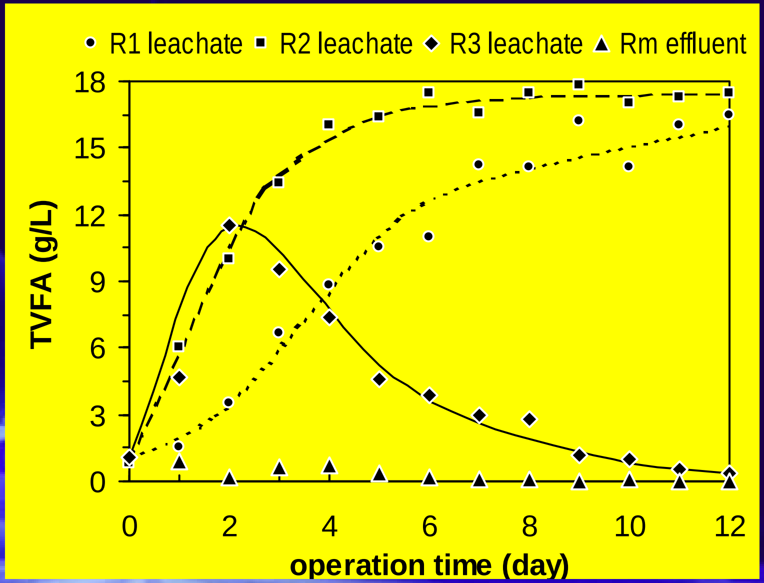


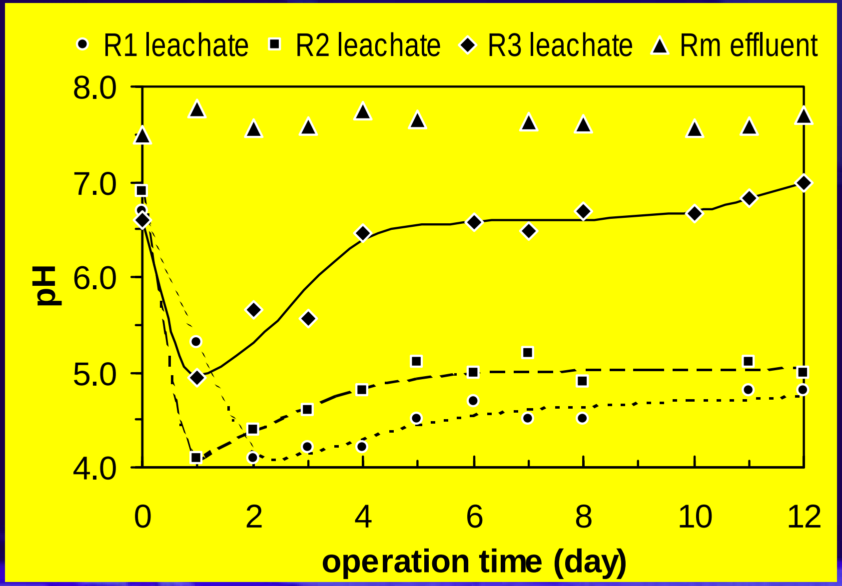
Insufficient Challenge




R1 leachate
R2 leachate
R3 leachate
Rm effluent
COD (g/L)
operation time (day)


R1/R2/R3 CH4 yield
Rm CH4 yield
Rm CH4 content
cumulative CH4 yield (L)
CH4 content (%)
operation time (day)

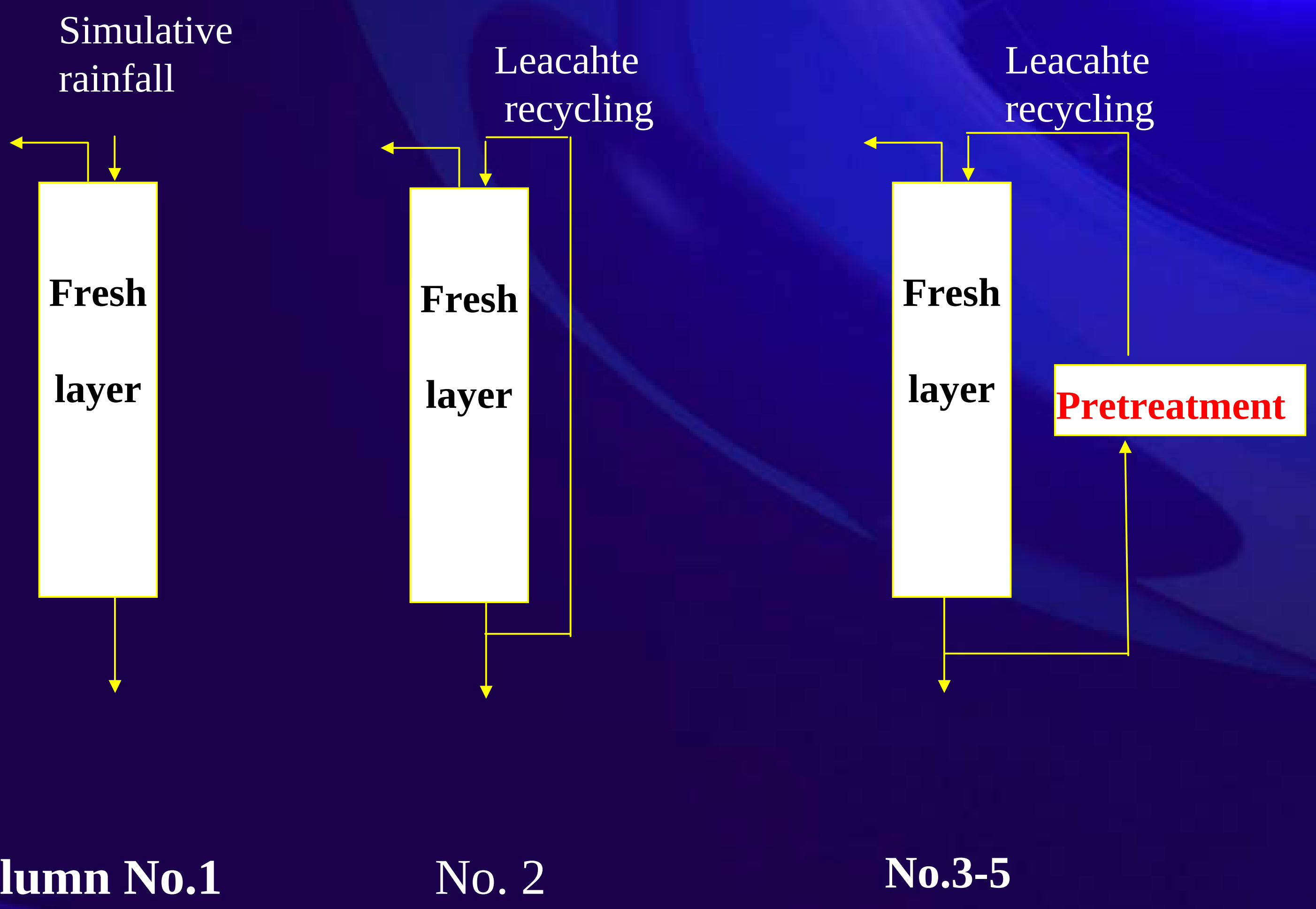

R1 leachate
R2 leachate
R3 leachate
Rm effluent
TVFA (g/L)
operation time (day)


R1 leachate
R2 leachate
R3 leachate
Rm effluent
pH
operation time (day)

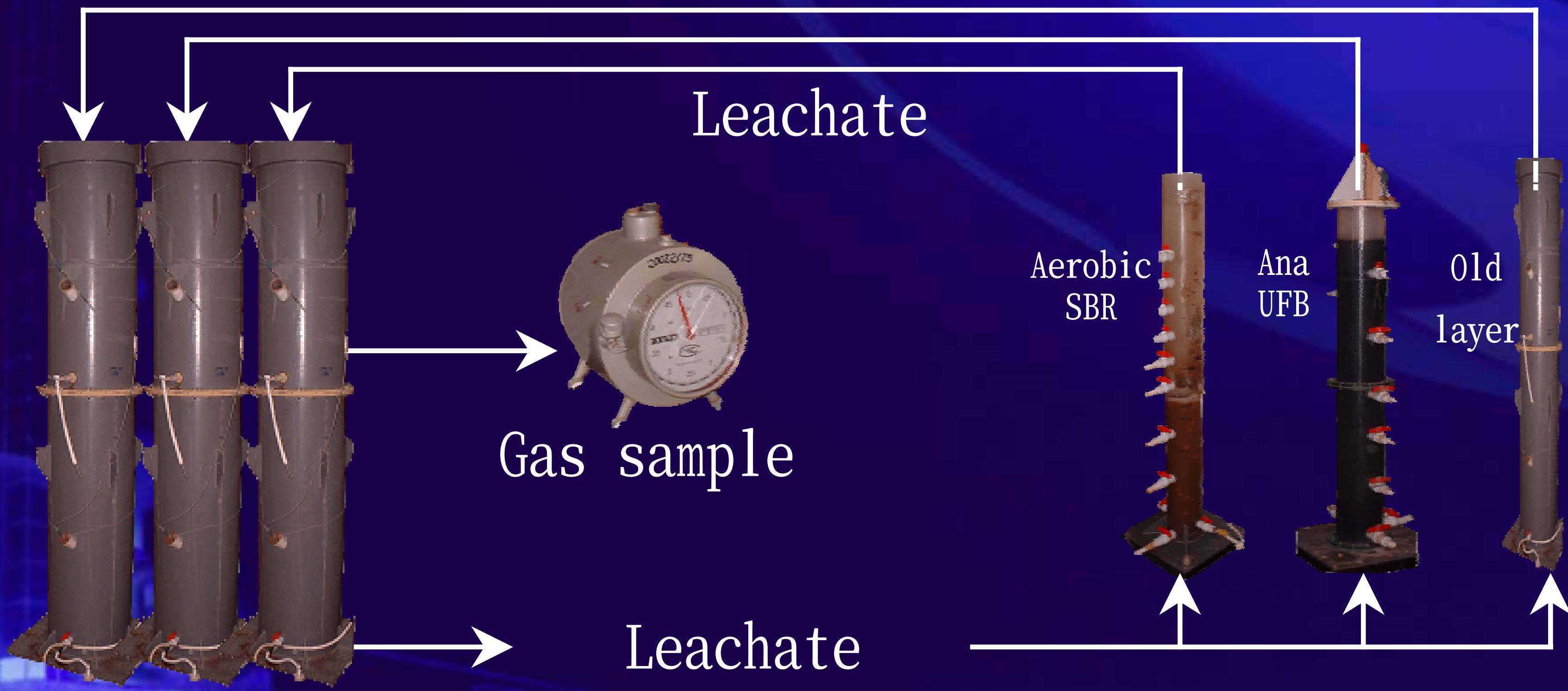
Full-Scale Landfill Site

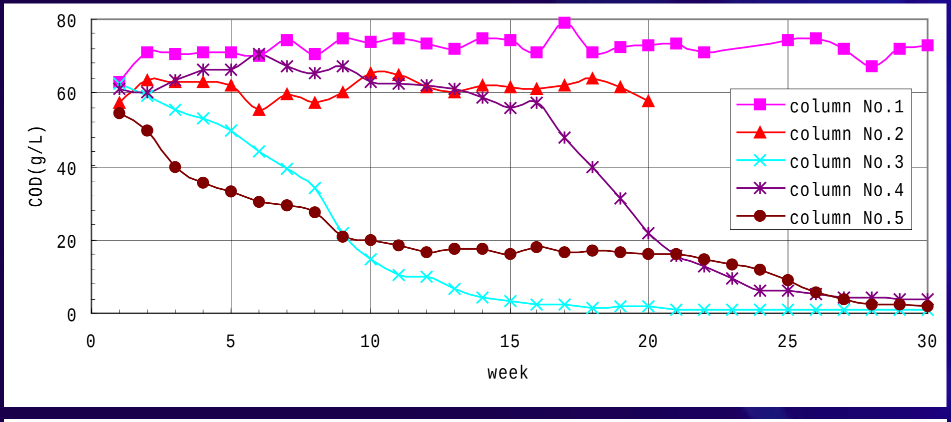
断面结构示意图

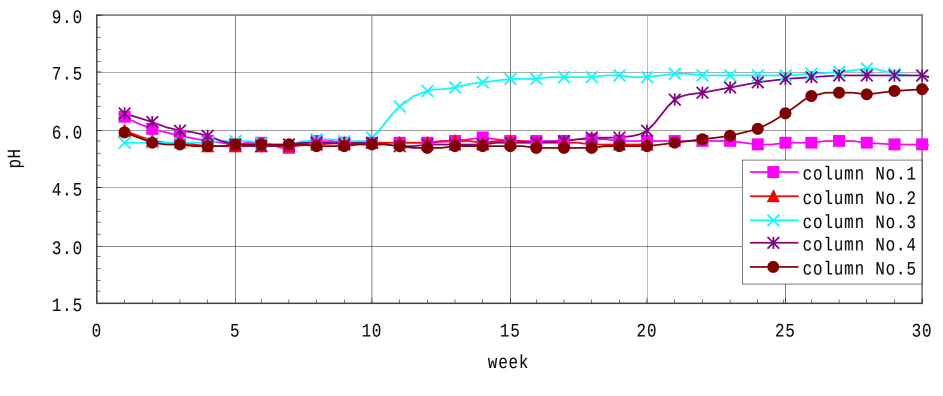
Sustainable Landfill

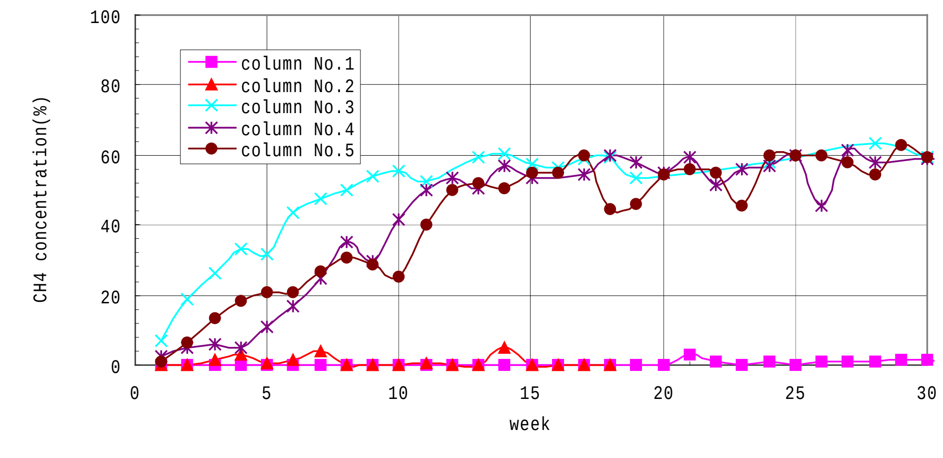


❑Internal Circulation



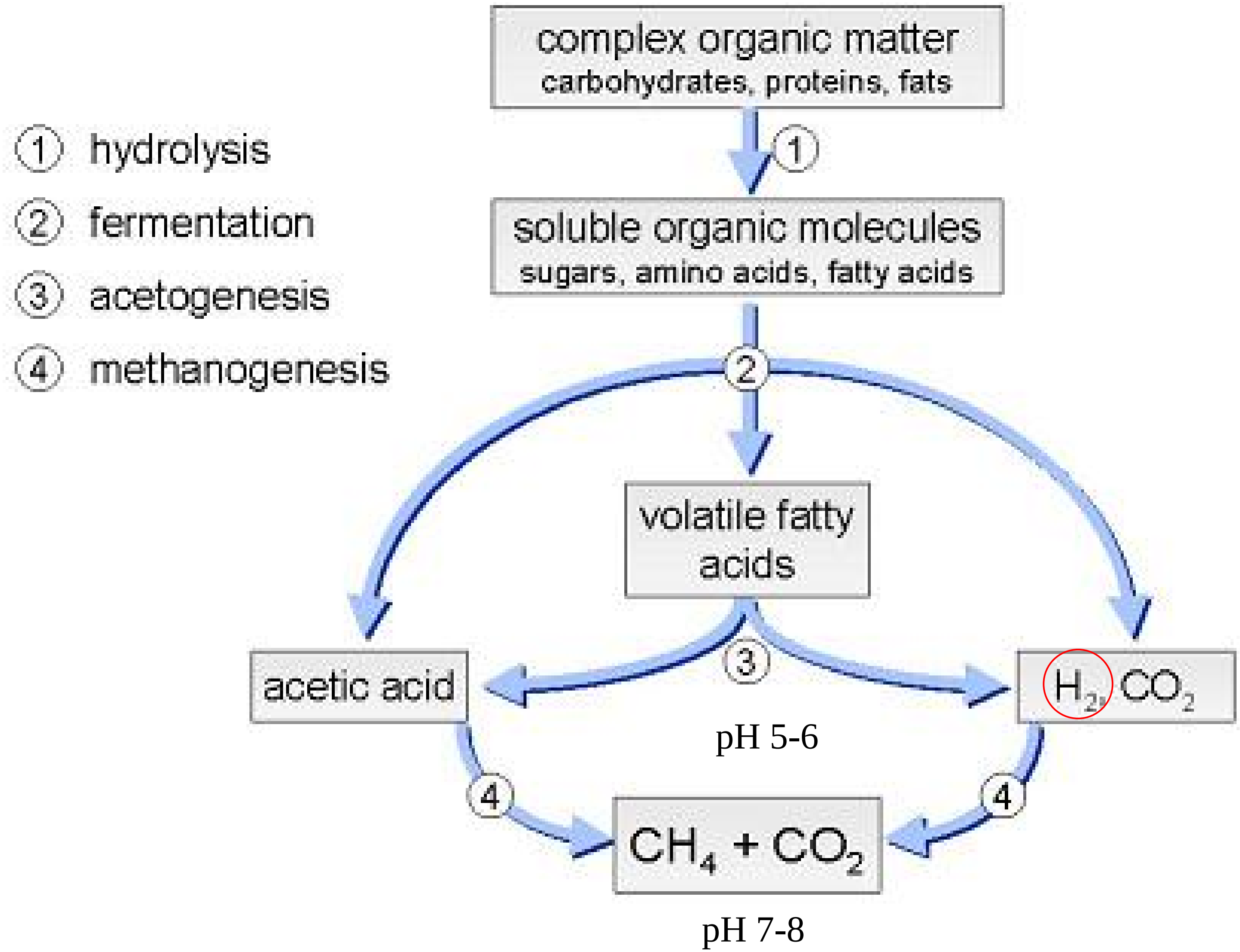






Biogas production

天子岭Site in HangZhu

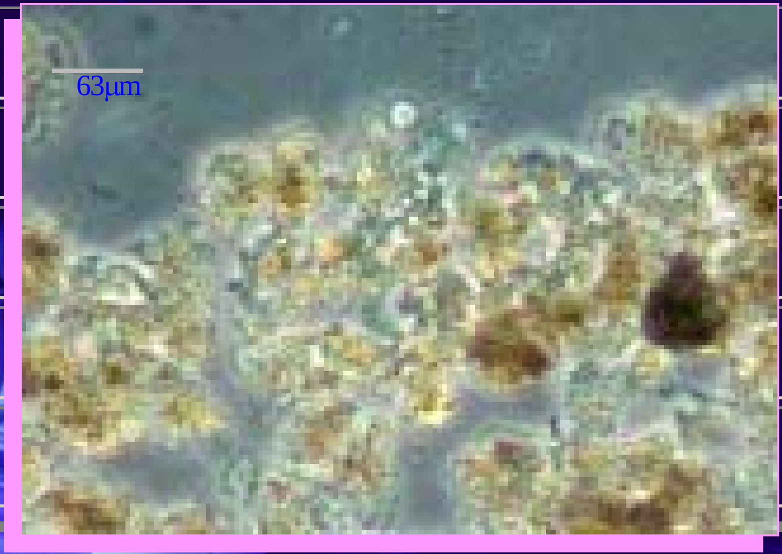

complex organic matter
carbohydrates, proteins, fats
1 hydrolysis
2 fermentation
3 acetogenesis
4 methanogenesis
soluble organic molecules
sugars, amino acids, fatty acids
volatile fatty acids
acetic acid
H_2, CO_2
pH 5-6
$CH_4 + CO_2$
pH 7-8

Hydrogen from waste

- **Hydrogen production by pure substance or mixture**
  - molasses (Tanisho and Ishiwata, 1994)
  - glucose (Kataoka *et al.*, 1997; Lin and Chang, 1999)
  - crystalline cellulose (Lay, 2001)
  - peptone (Bai *et al.*, 2001)
  - starch (Lay, 2001)
- **Hydrogen production by concentrated wastewater**
  - (Bolliger *et al.*, 1985 ; Liu *et al.*, 1995 ; Ueno *et al.*,1996 ; Zhu *et al.*, 1999)
- **Hydrogen production by solid waste**
  - municipal solid waste (Lay *et al.*, 1999)
  - bean curd manufacturing waste (Mizuno *et al.*, 2000)
- **Hydrogen production by biological sludge**
  - ???

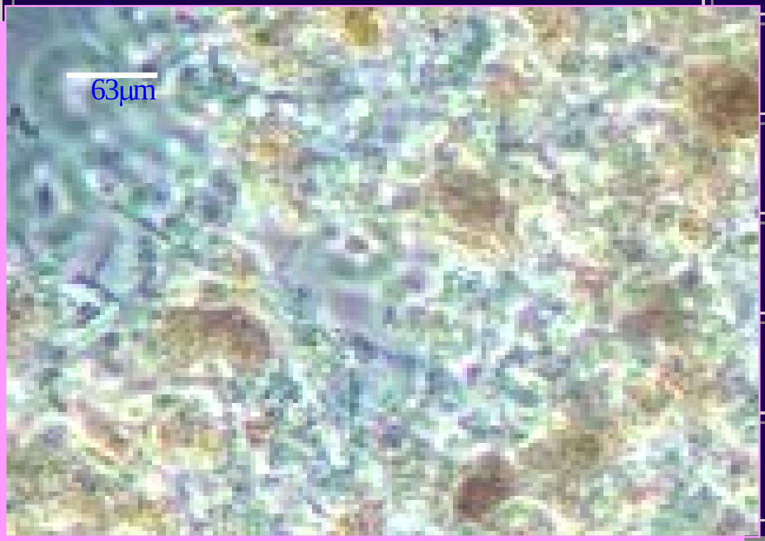
Min-sheng Sludge

Concentration of wet solids	
Concentration of dry solids	
pH value	
Neutron particle size	
	24,800 mg/L
	435 mg/L
	325 mg/L
	34.3%、H 5.3%、N 5.4%、 O 55 %



Tong-yi Sludge

Concentration of wet solids	
Concentration of dry solids	
pH value	
Neutron particle size	
	16,000mg/L
	86.7 mg/L
	410 mg/L
	41.3%、H 6.6%、N 5.4%、O 46.7%



Strains screening DNA sequencing

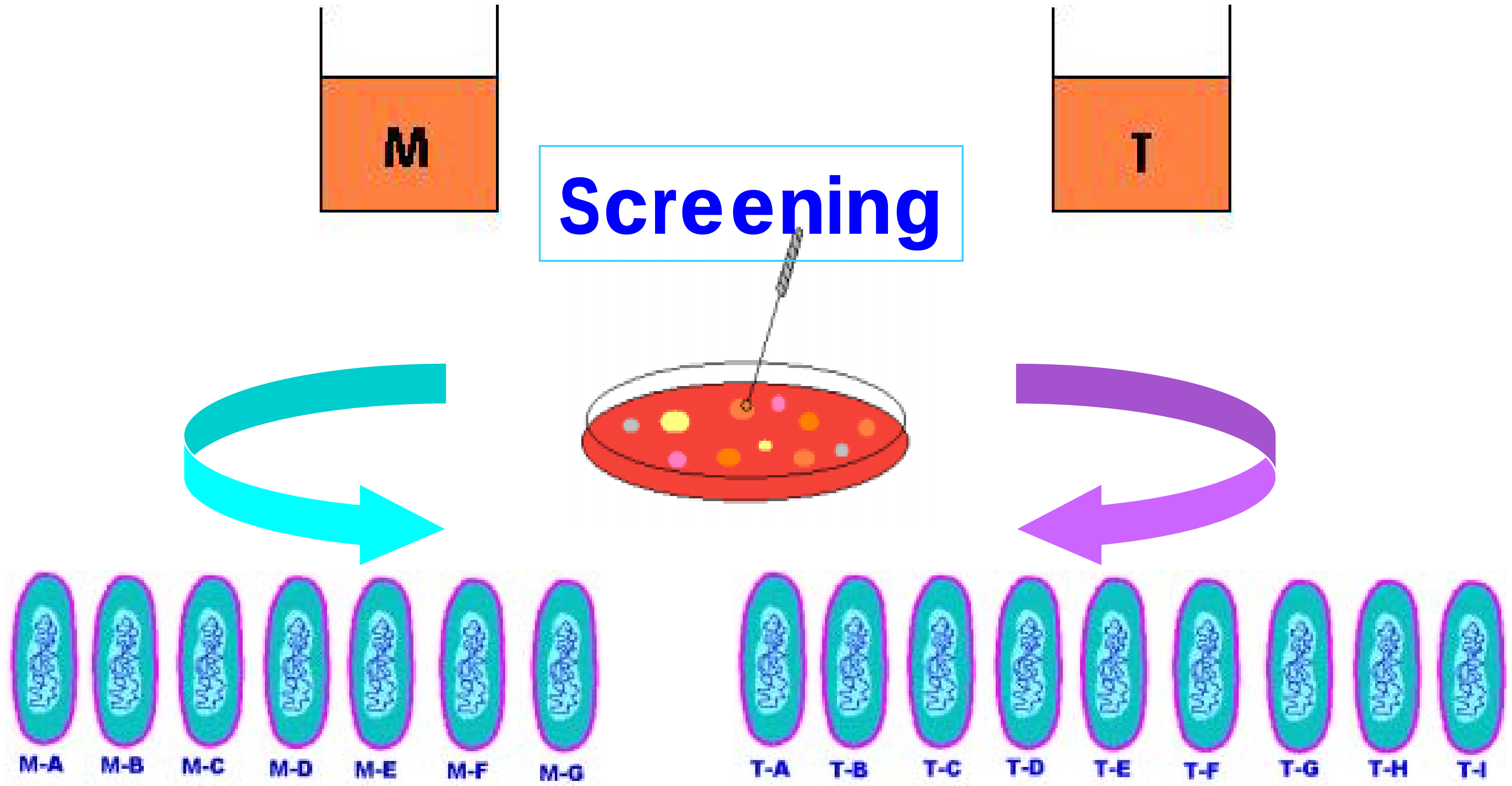
Finding optimal dealing parameters

- Concentration
- Pretreatment methods
- Inhibitors
- Measuring time points

Continuous anaerobic experiments

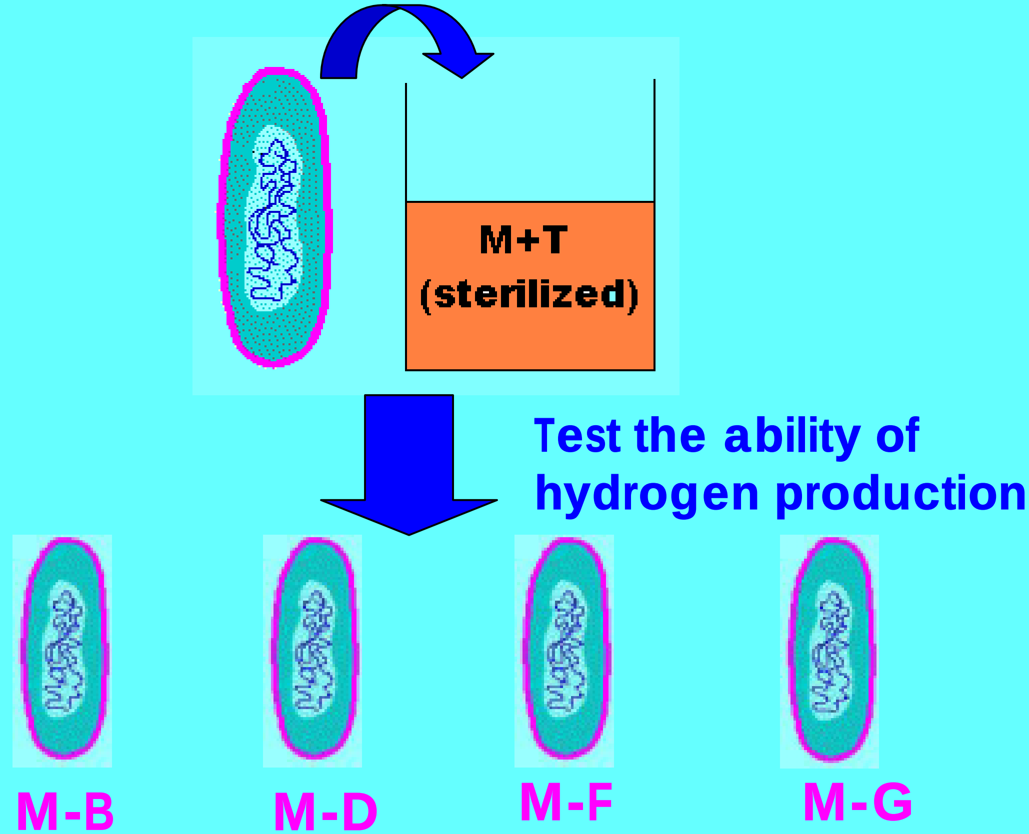
- Gas production
- Hydrogen productive substrates
- Composition analysis

Strains screening (1)



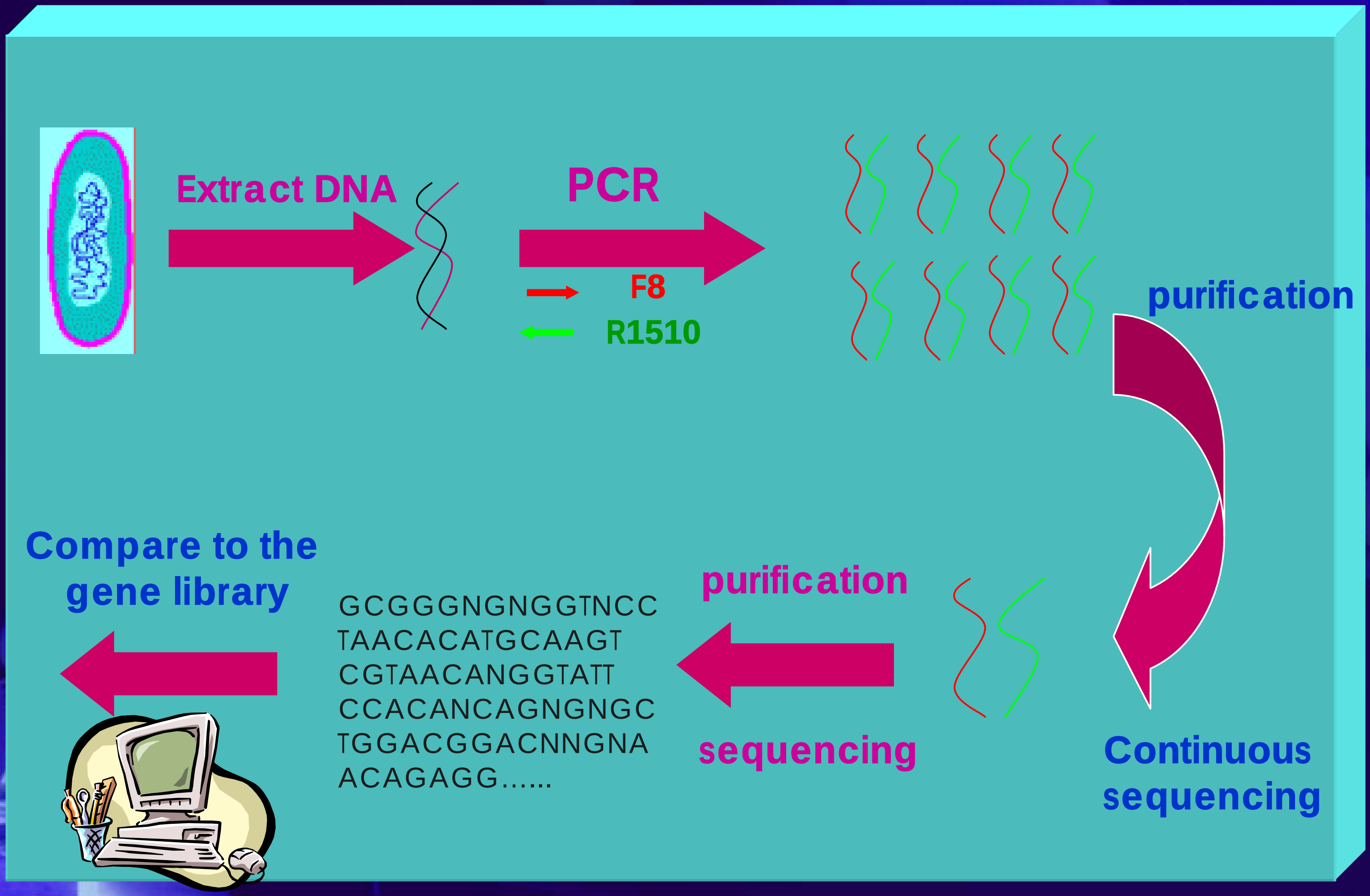
Strains screening (2)

Add them individually



The ability of hydrogen production is about 0.65-1.11 H_2/kg DS

Species identification



DNA Sequence

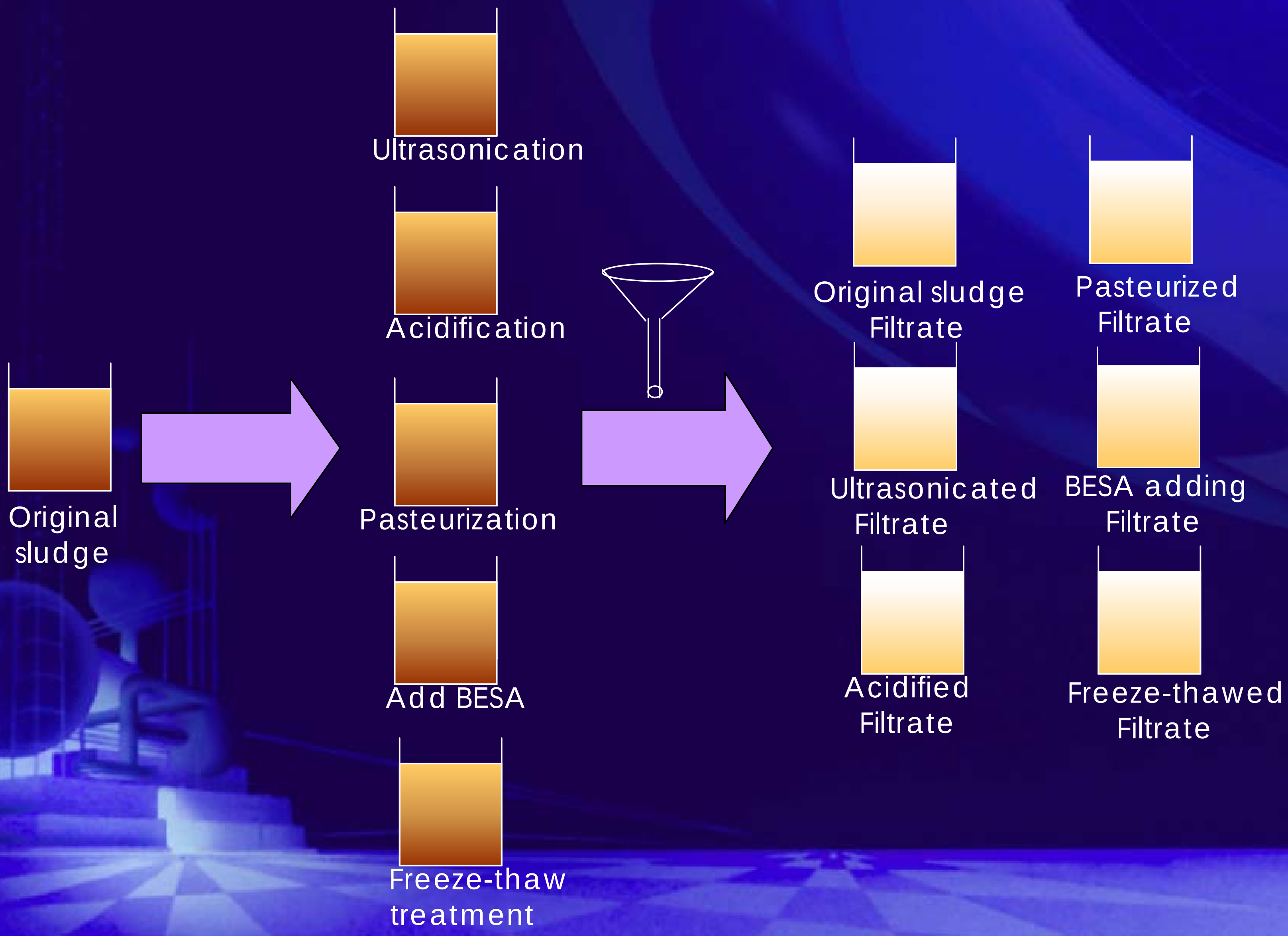
M-B M-D

M-F M-G

→ ***Clostridium bifermentans***

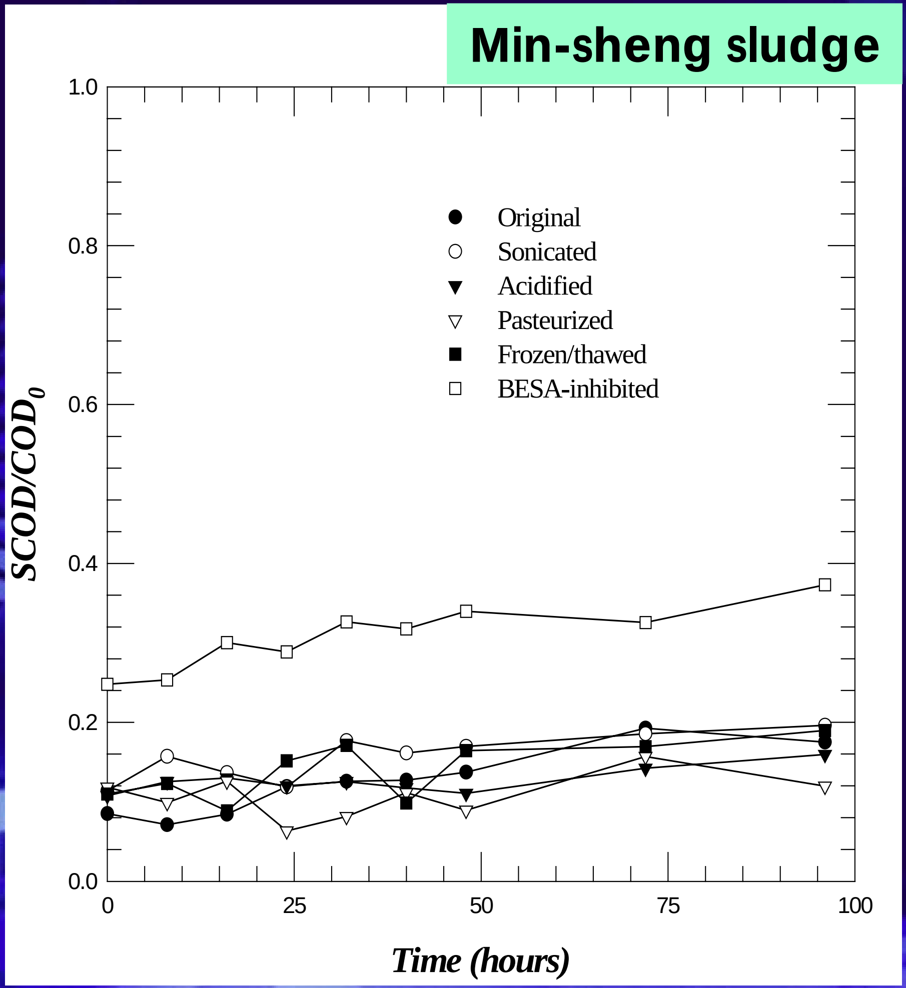
Clostridium bifermentans

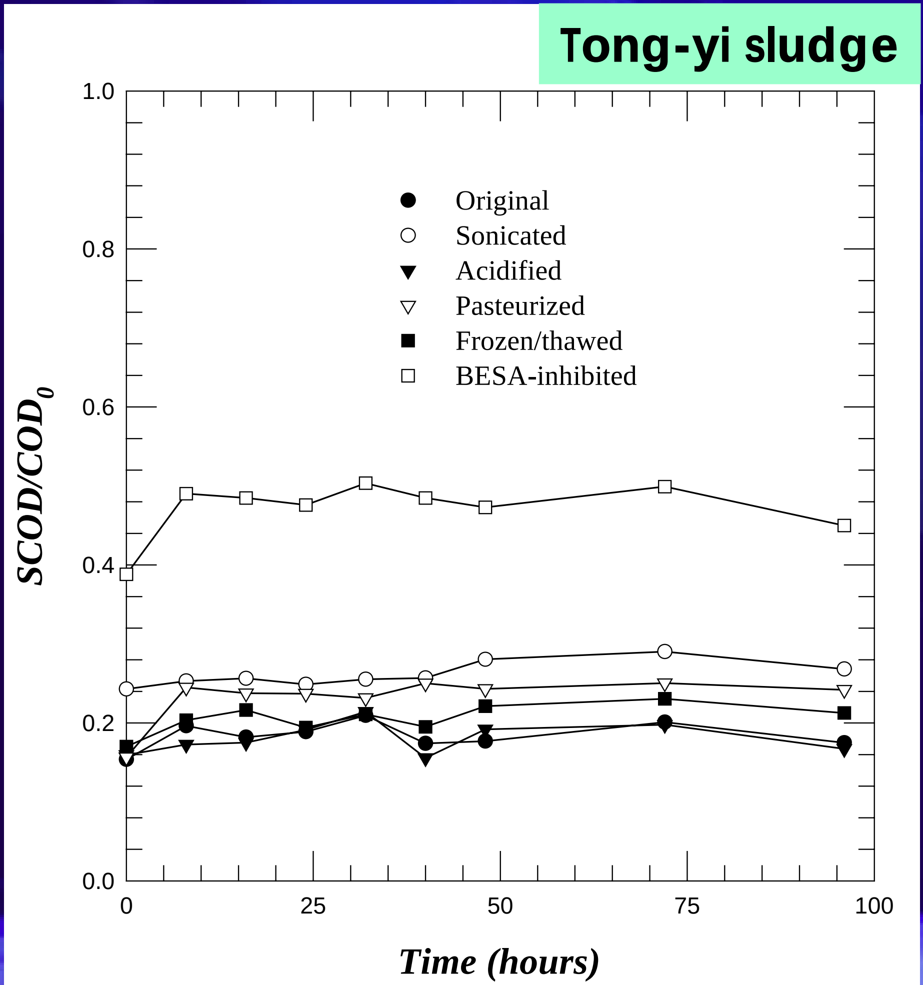
Pretreatment flow chart



Sludge fermentation test - COD

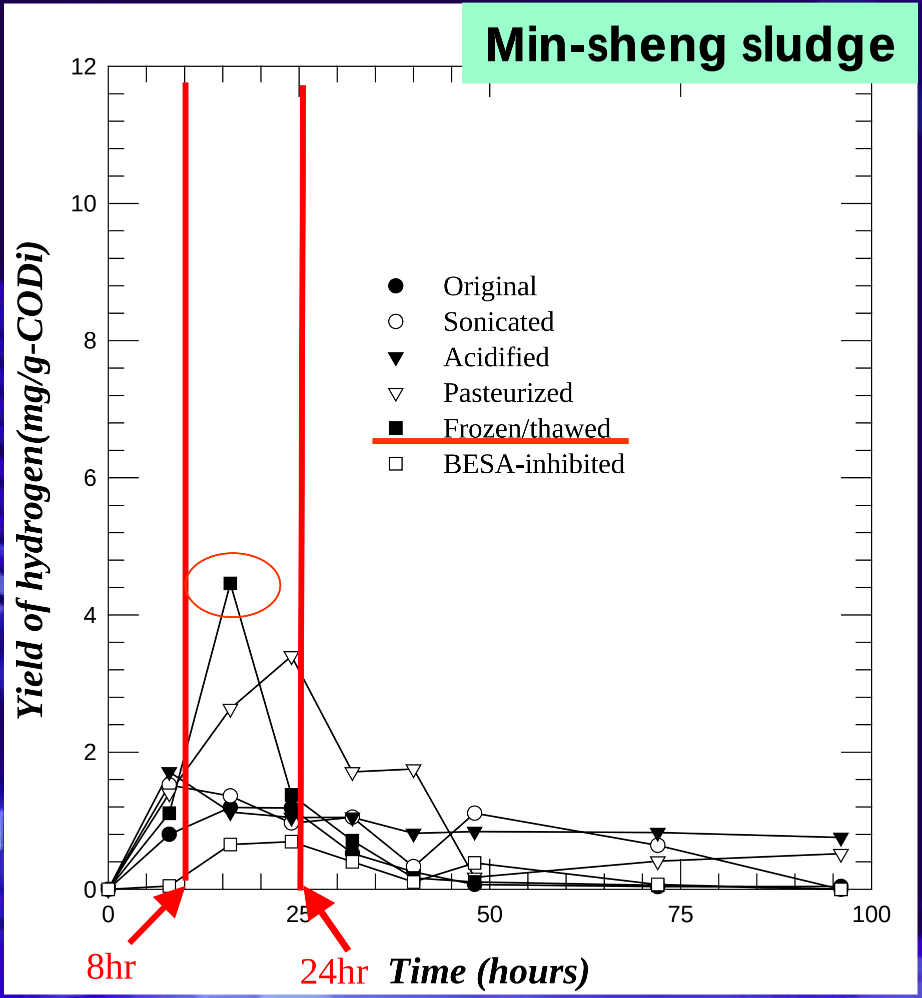
COD0 – COD of original biosolid
SCOD – Soluble COD

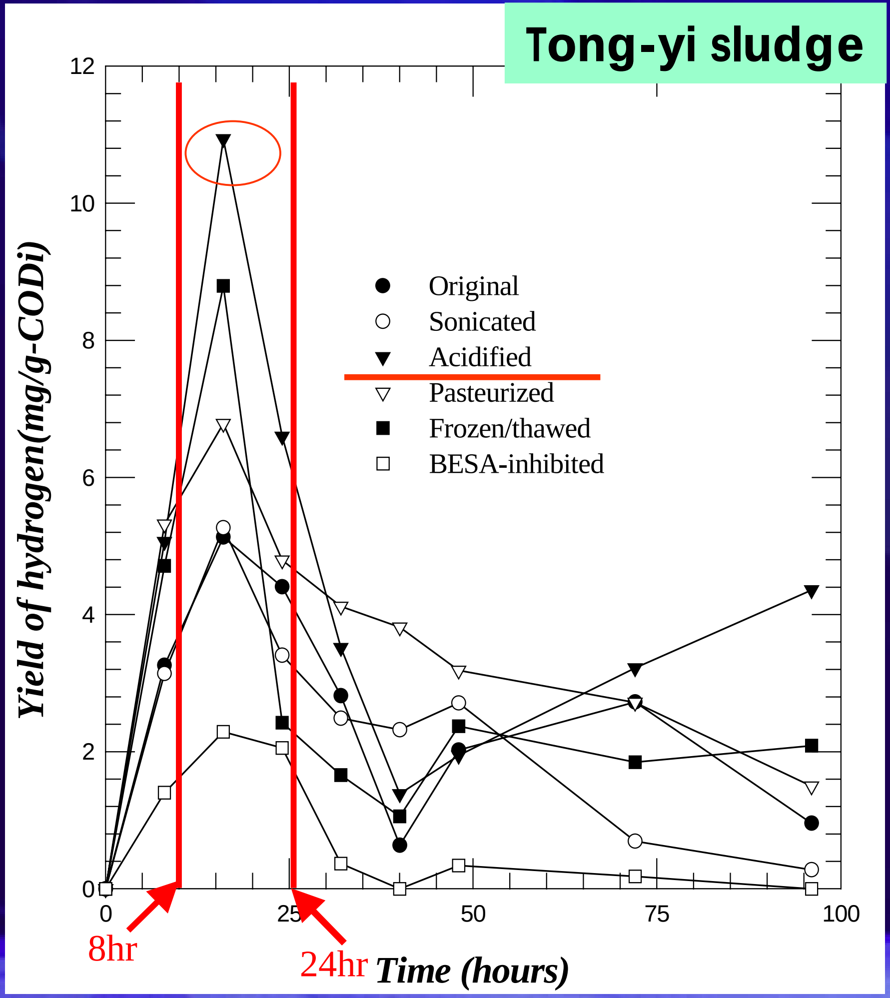




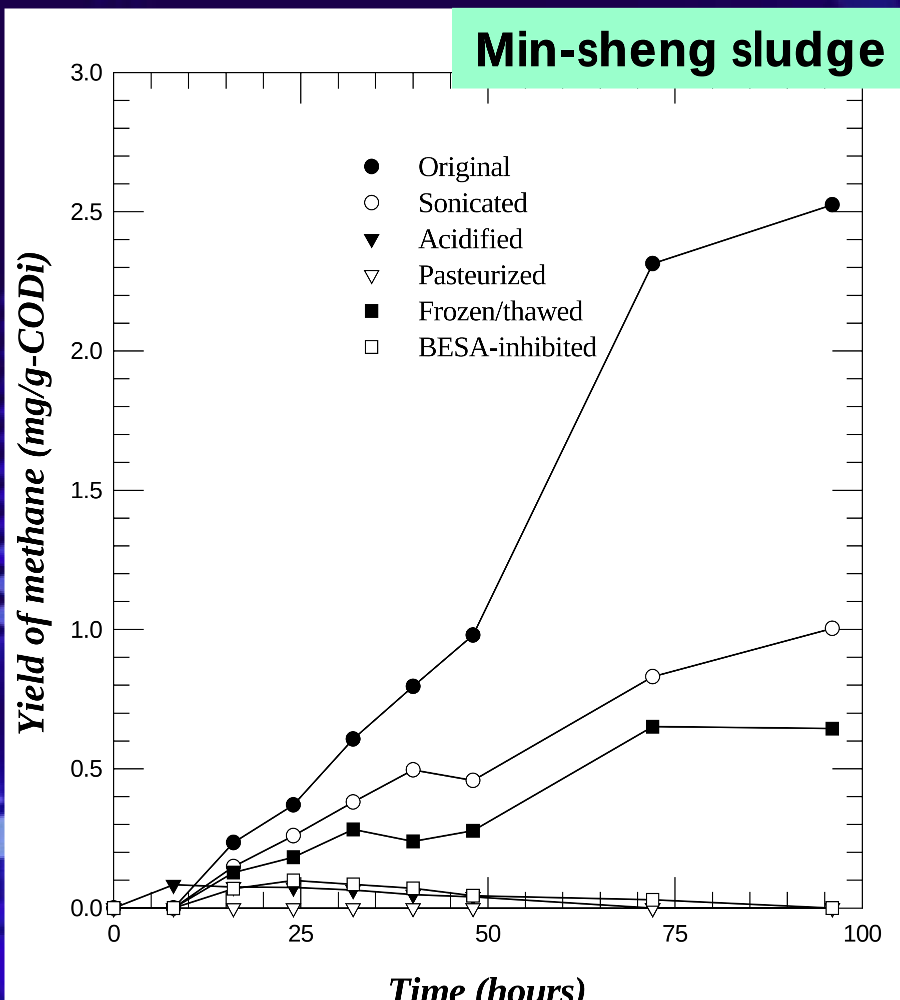
Sludge fermentation test – Hydrogen production

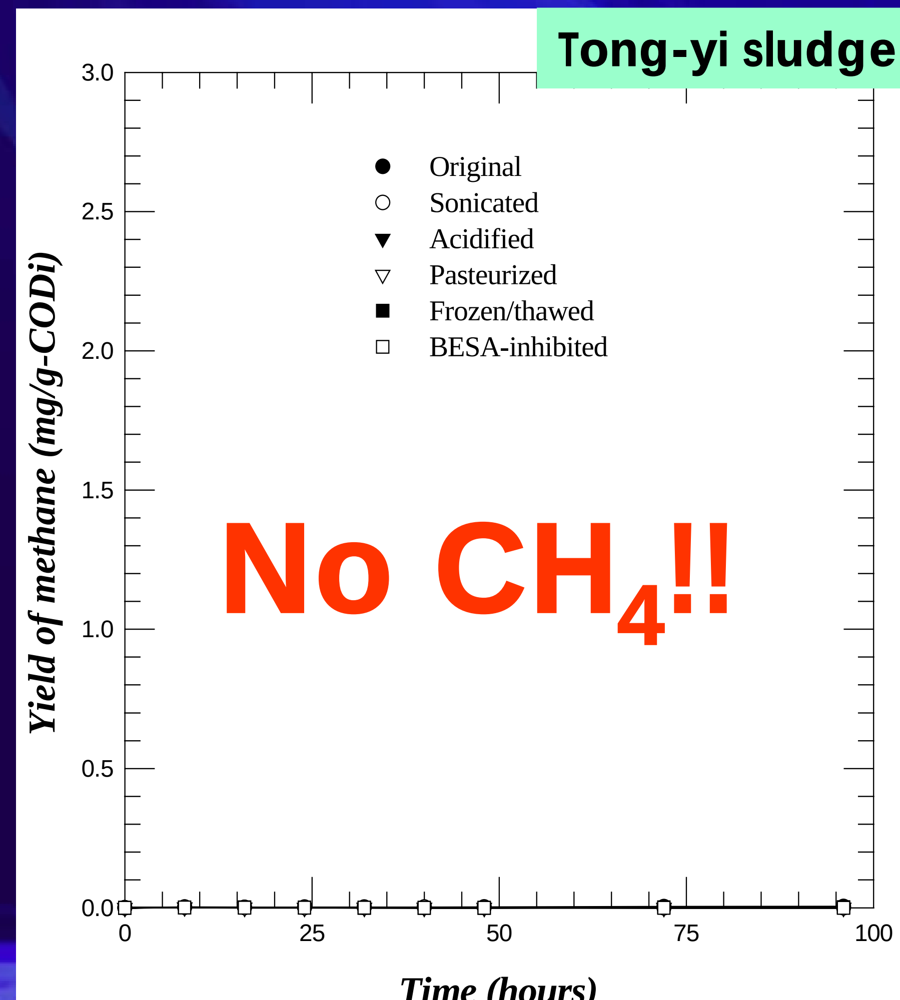
CODi – COD of the substrate before testing



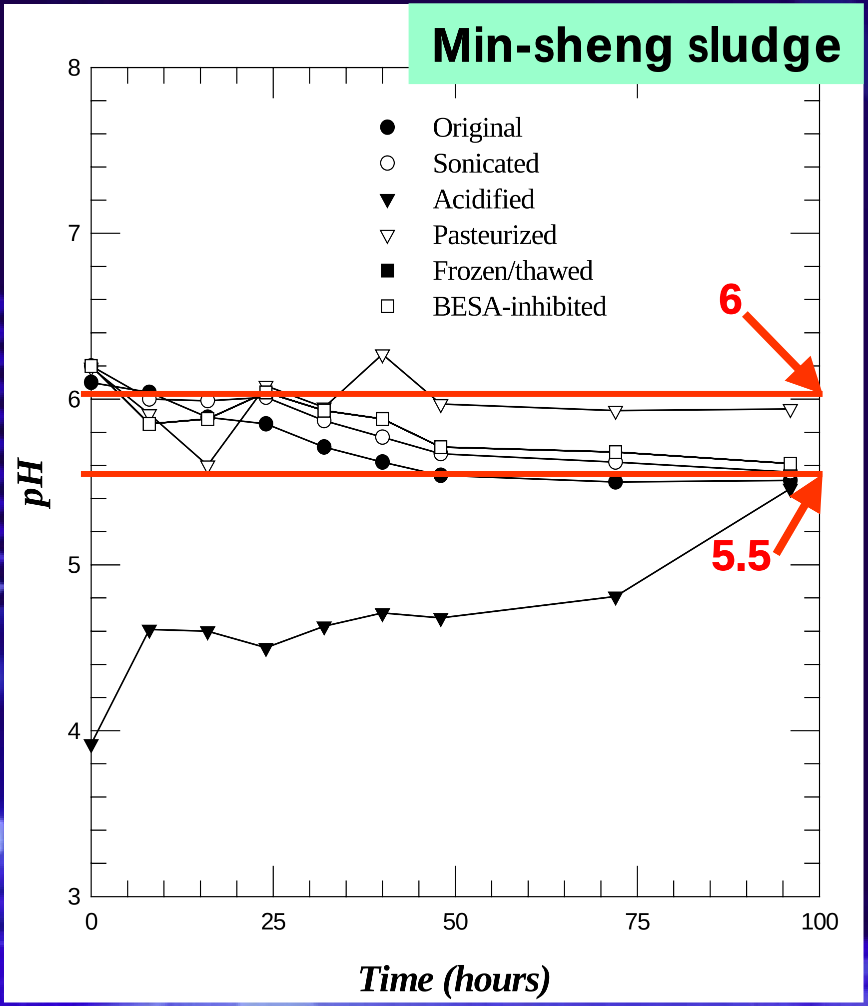


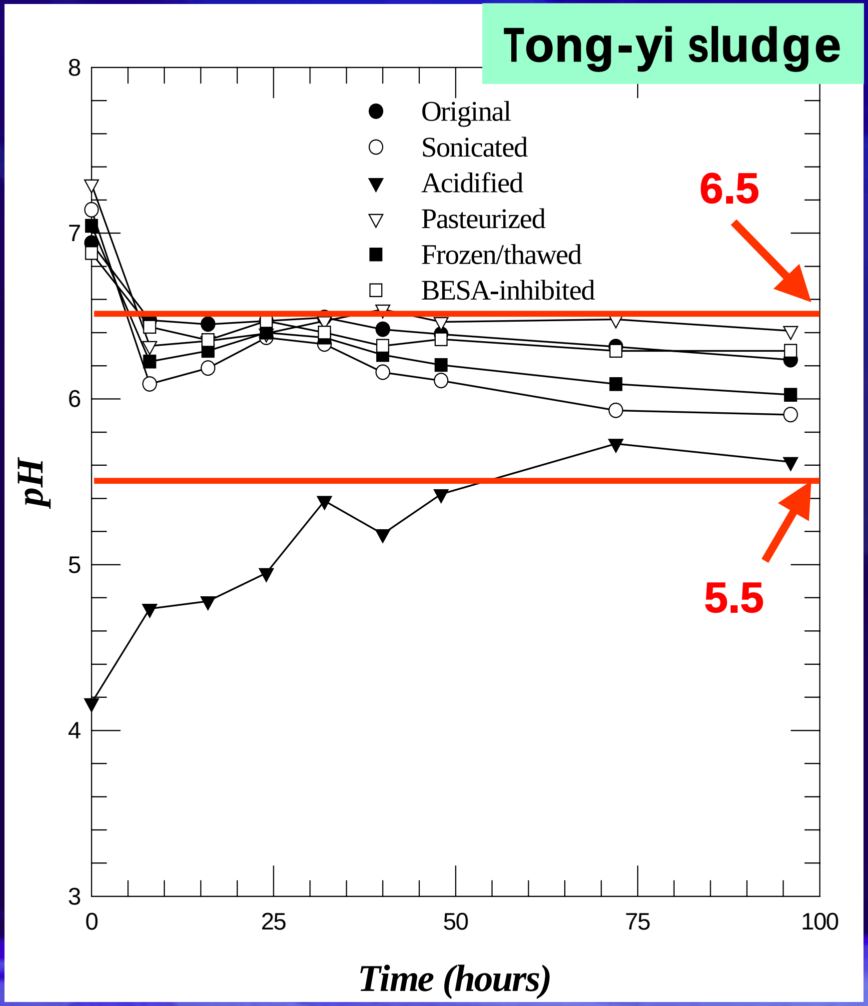
ludge fermentation test –
ethane production



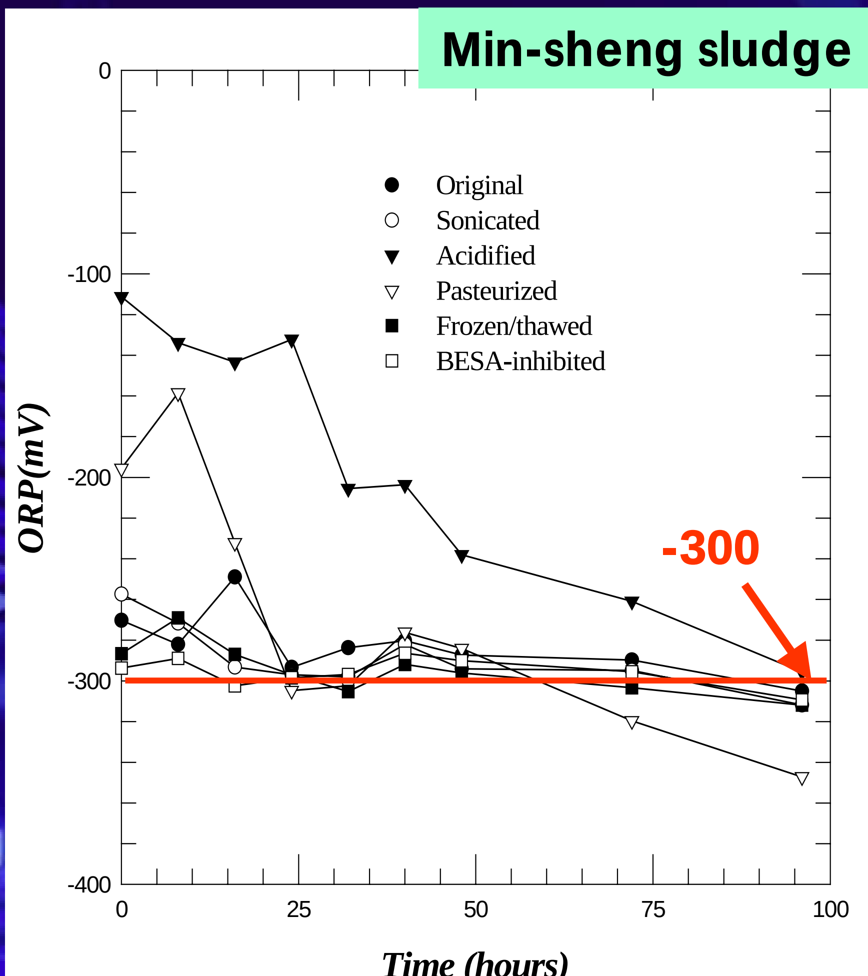


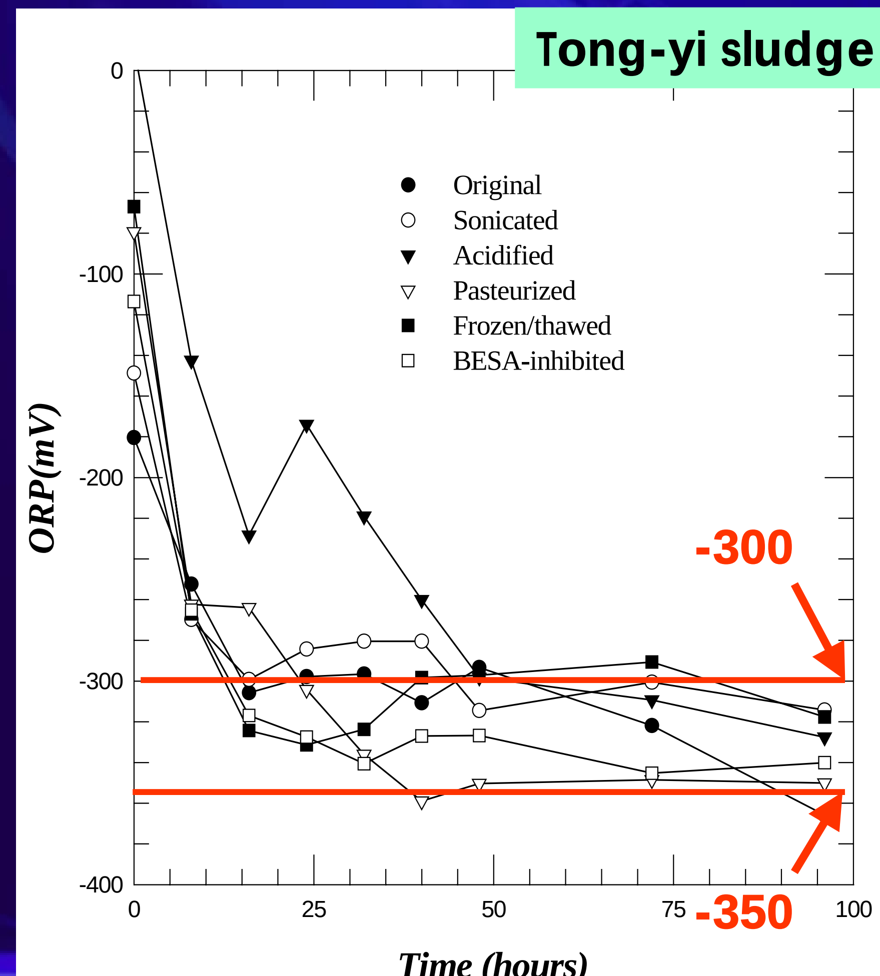
Sludge fermentation test – pH measuring



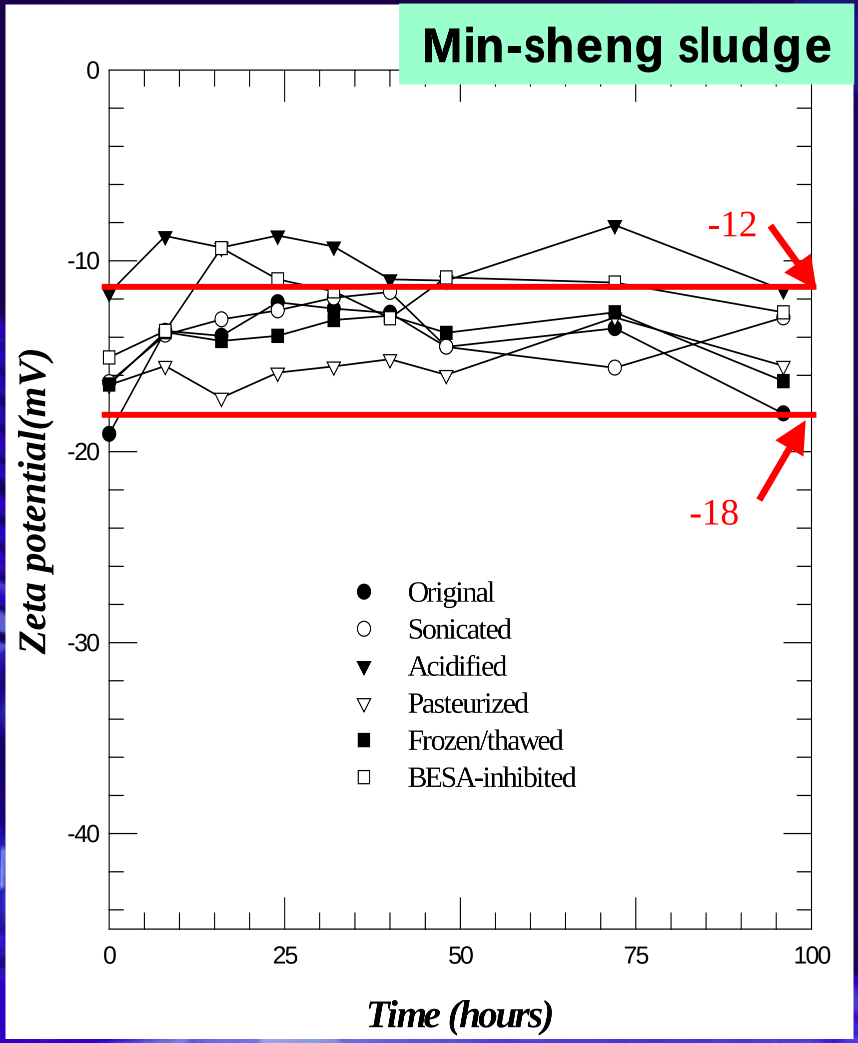


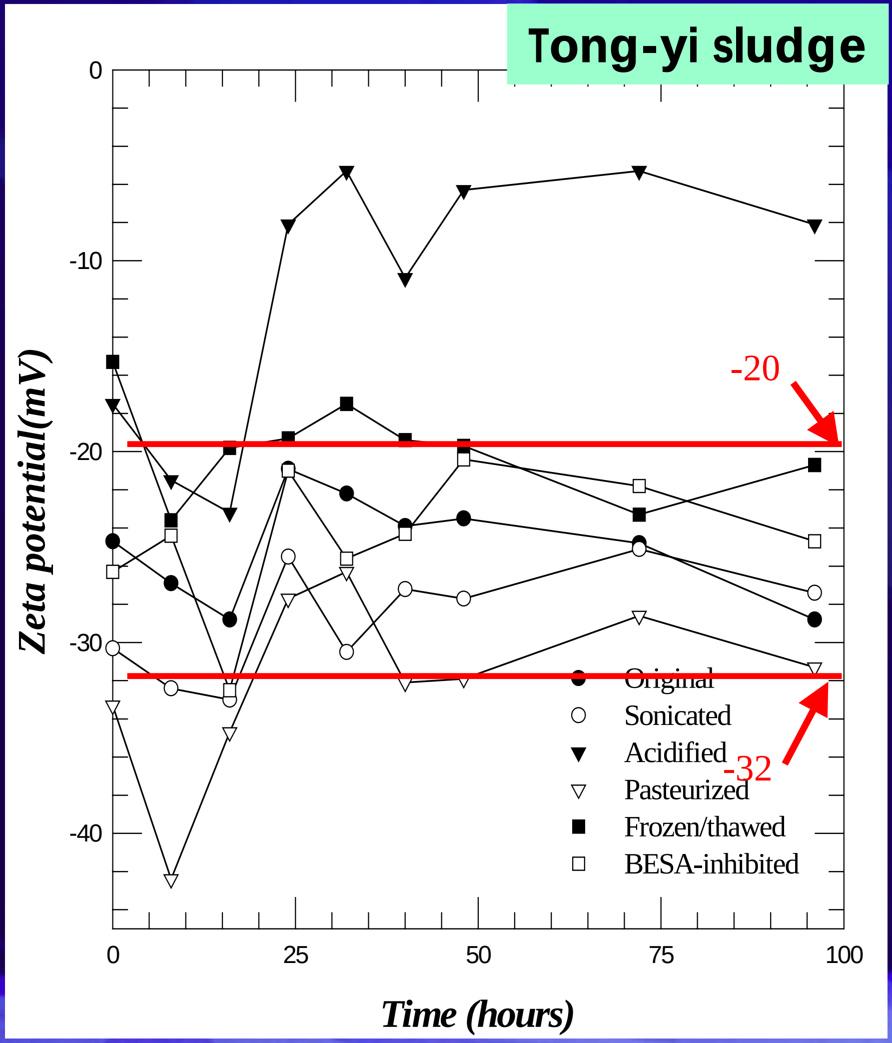
Sludge fermentation test - ORP



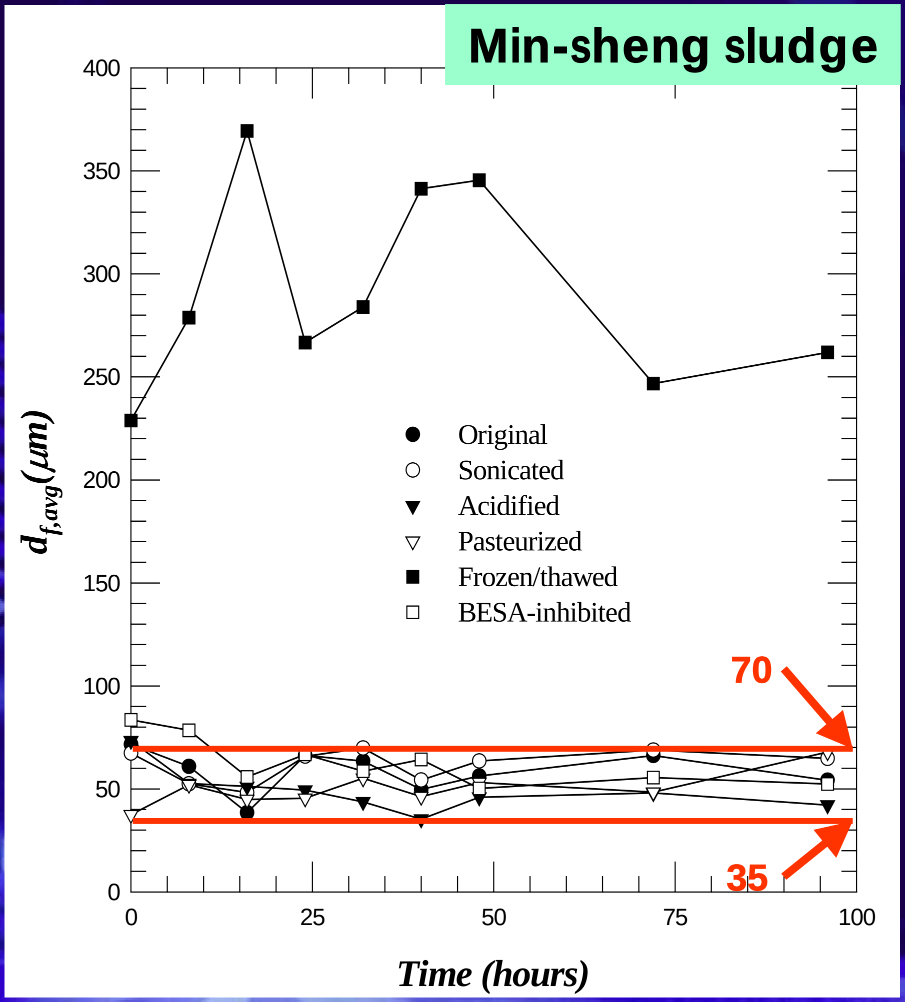


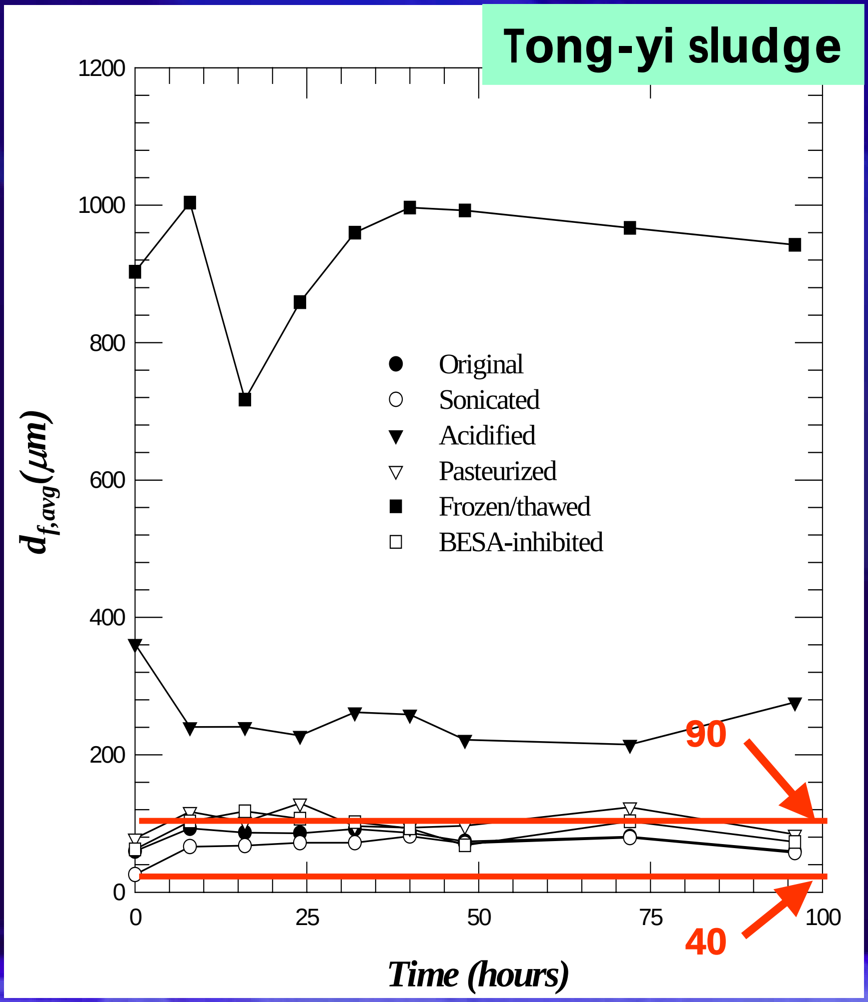
Sludge fermentation test –
Zeta potential



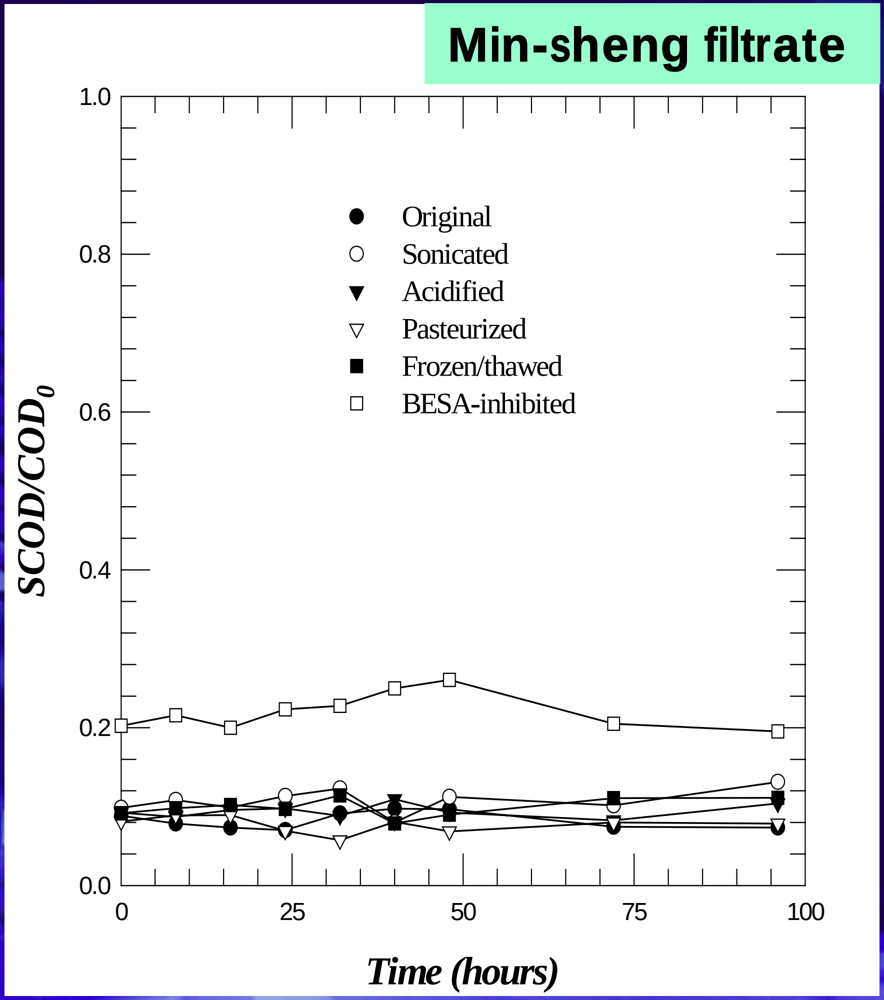


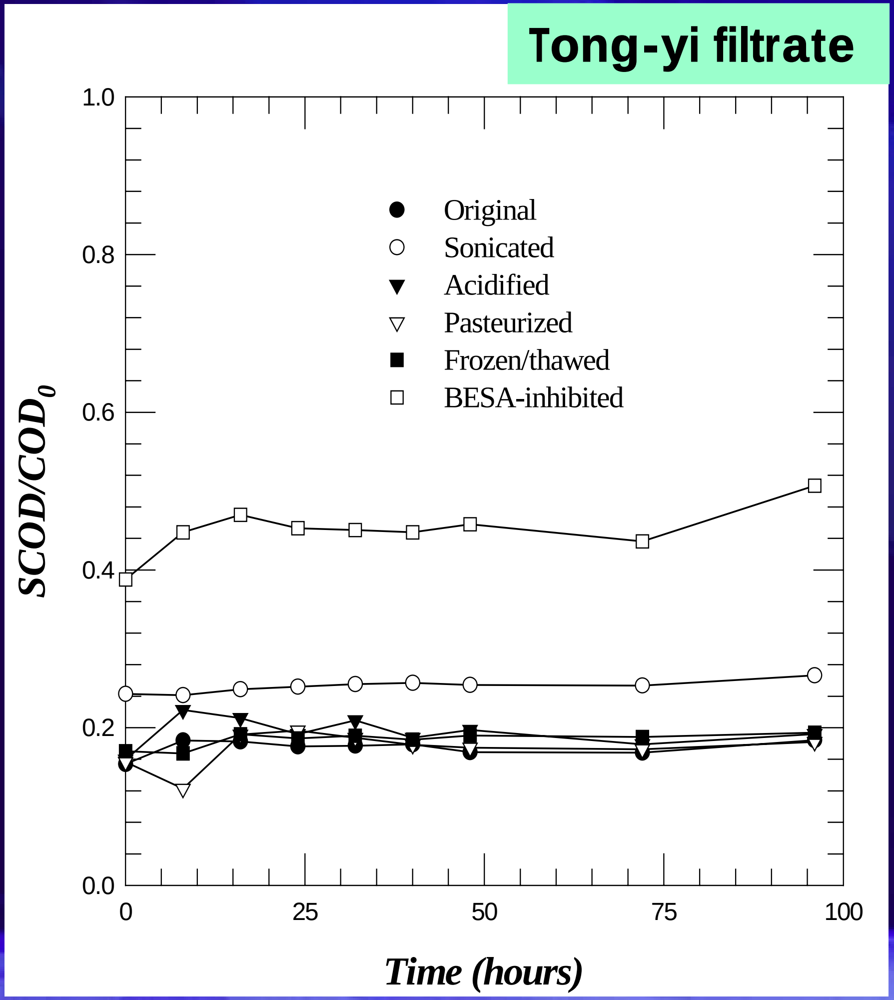
Sludge fermentation test –
Particle size distribution





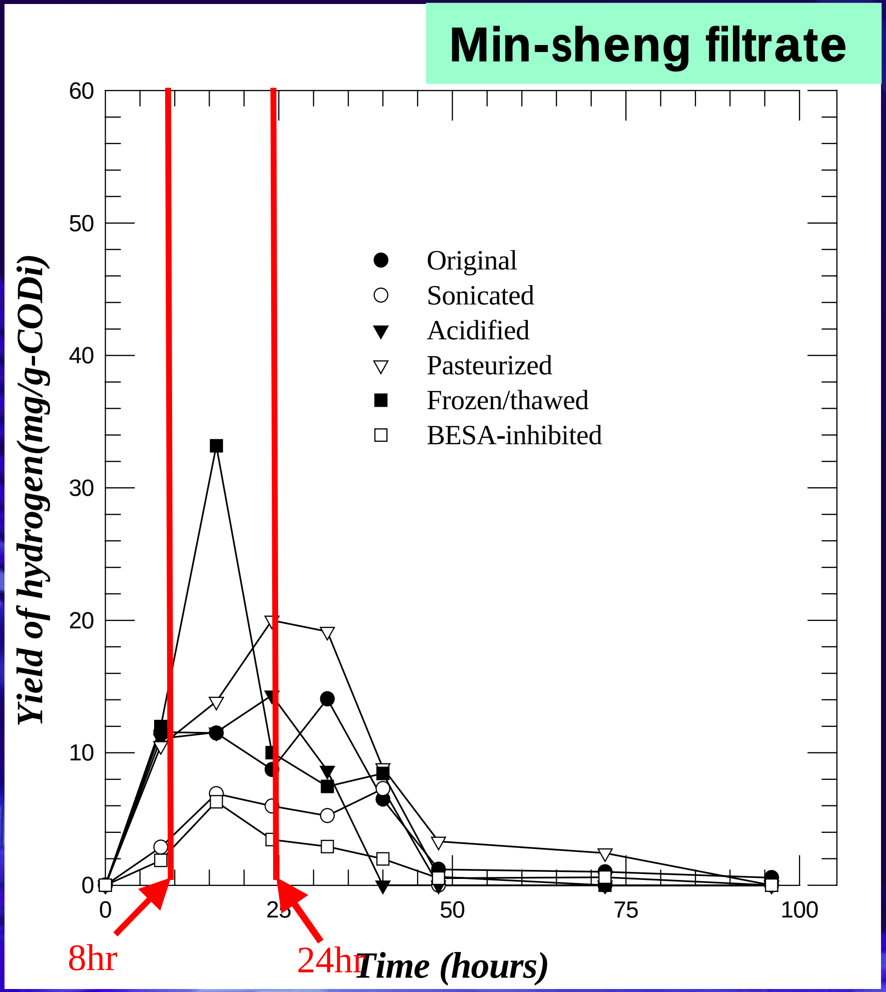
Filtrate fermentation test - COD

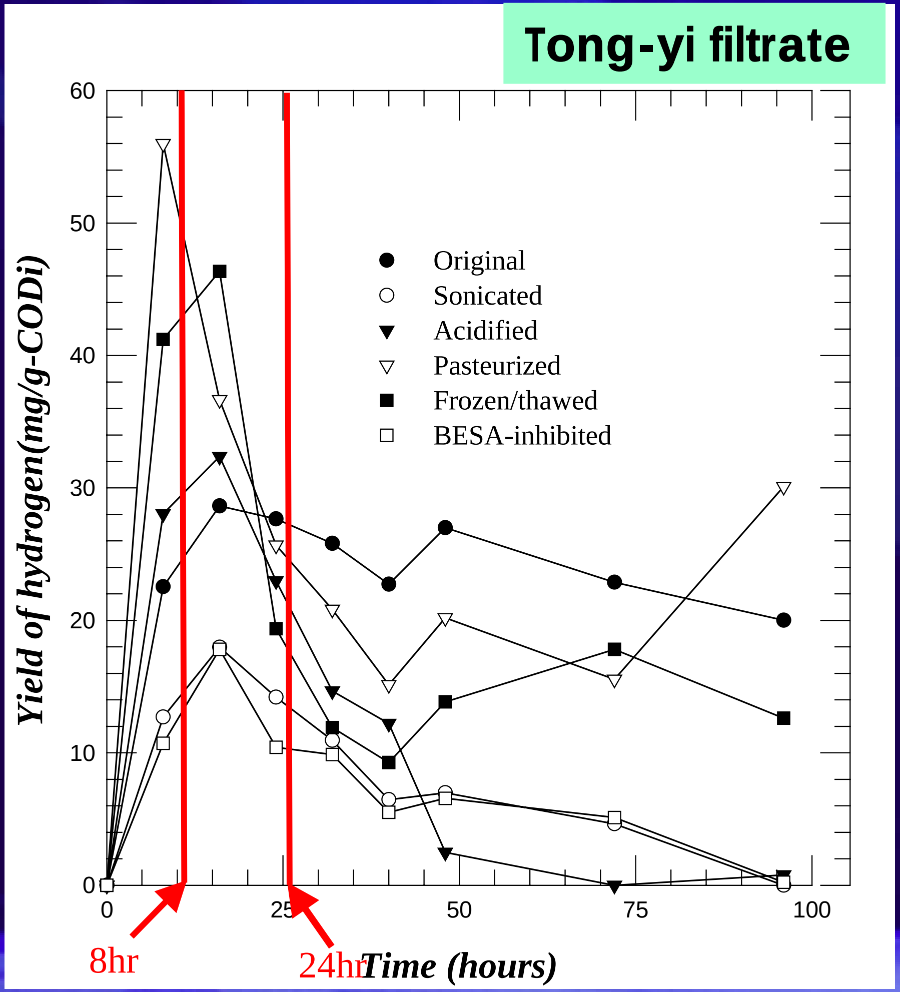




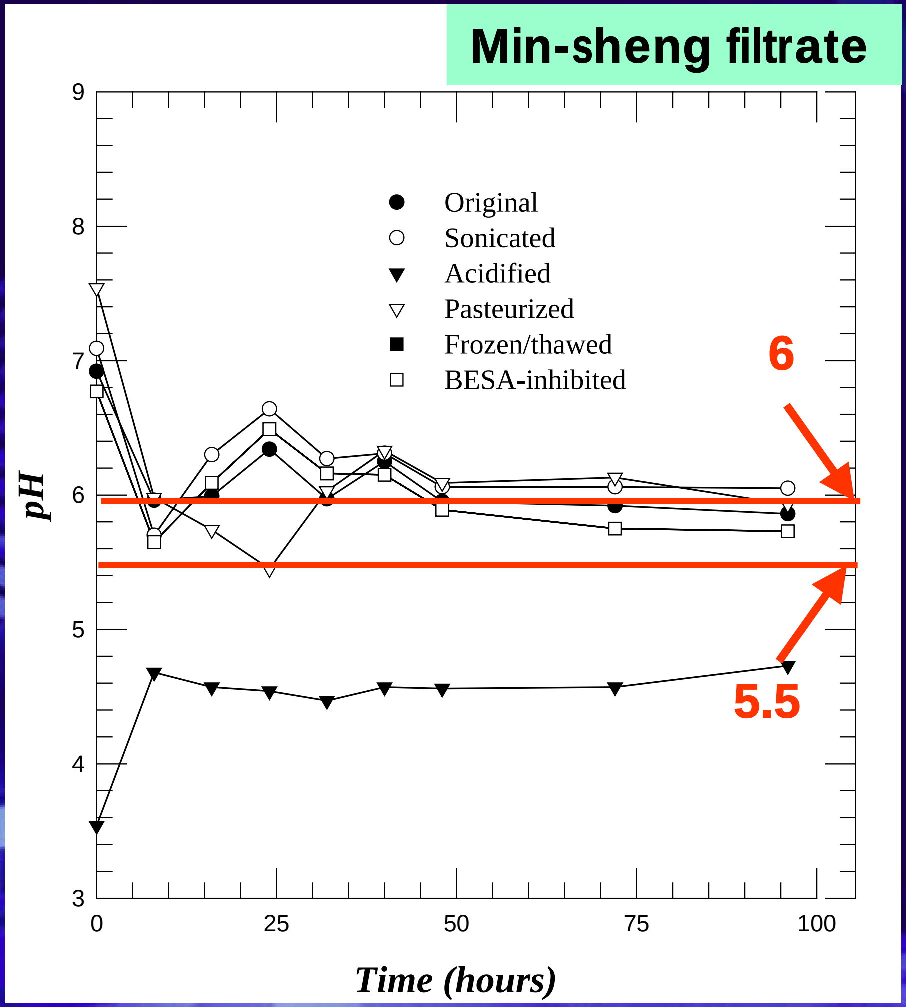
Filtrate fermentation test –

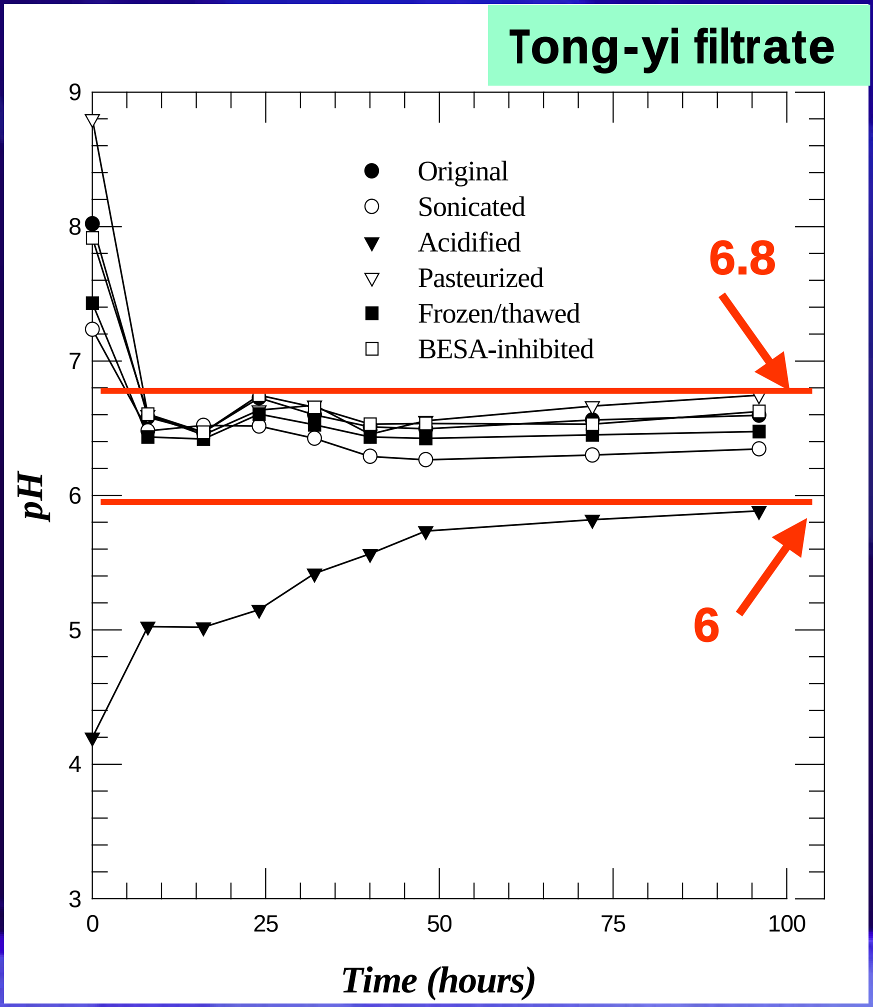
Hydrogen production



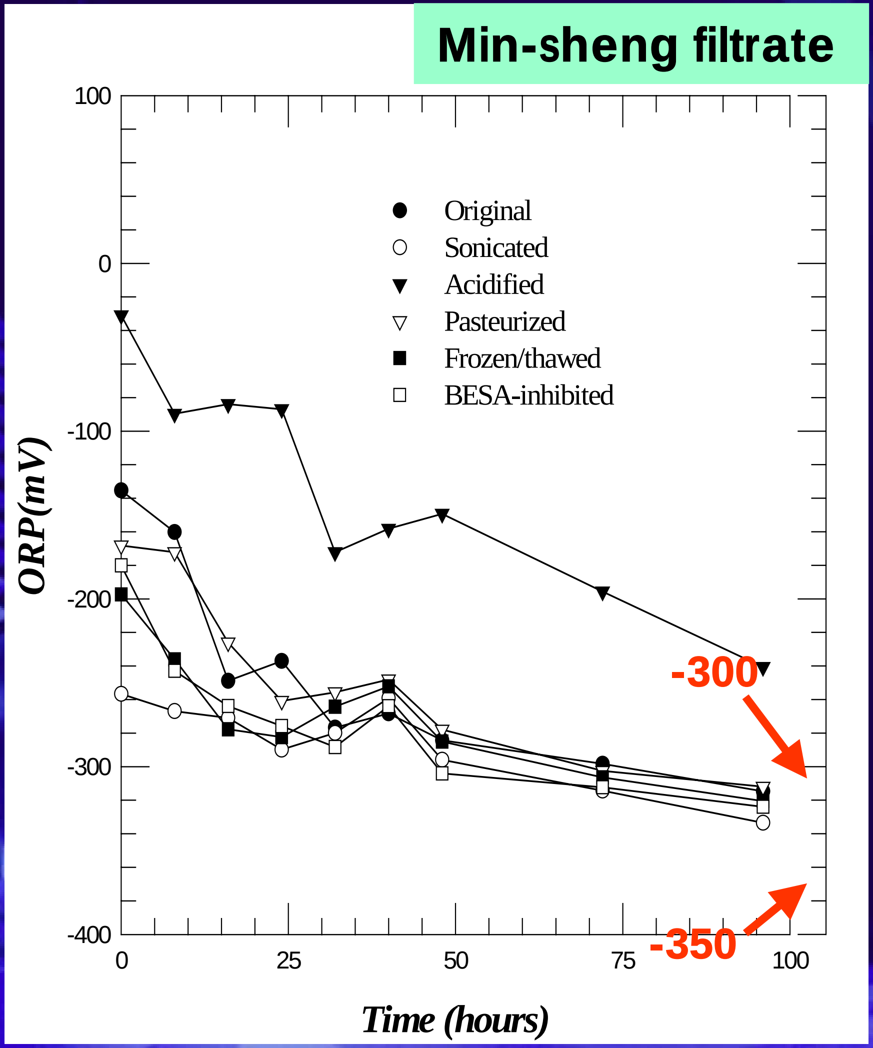


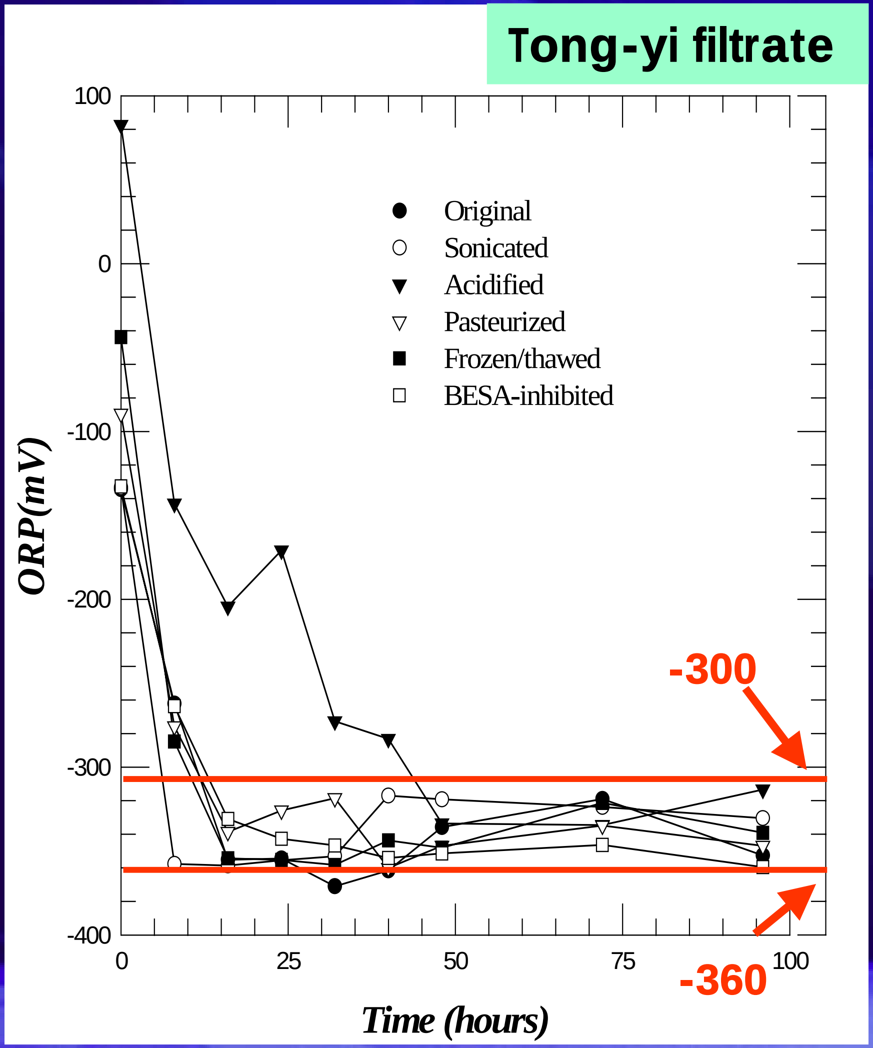
Filtrate fermentation test –
pH measuring





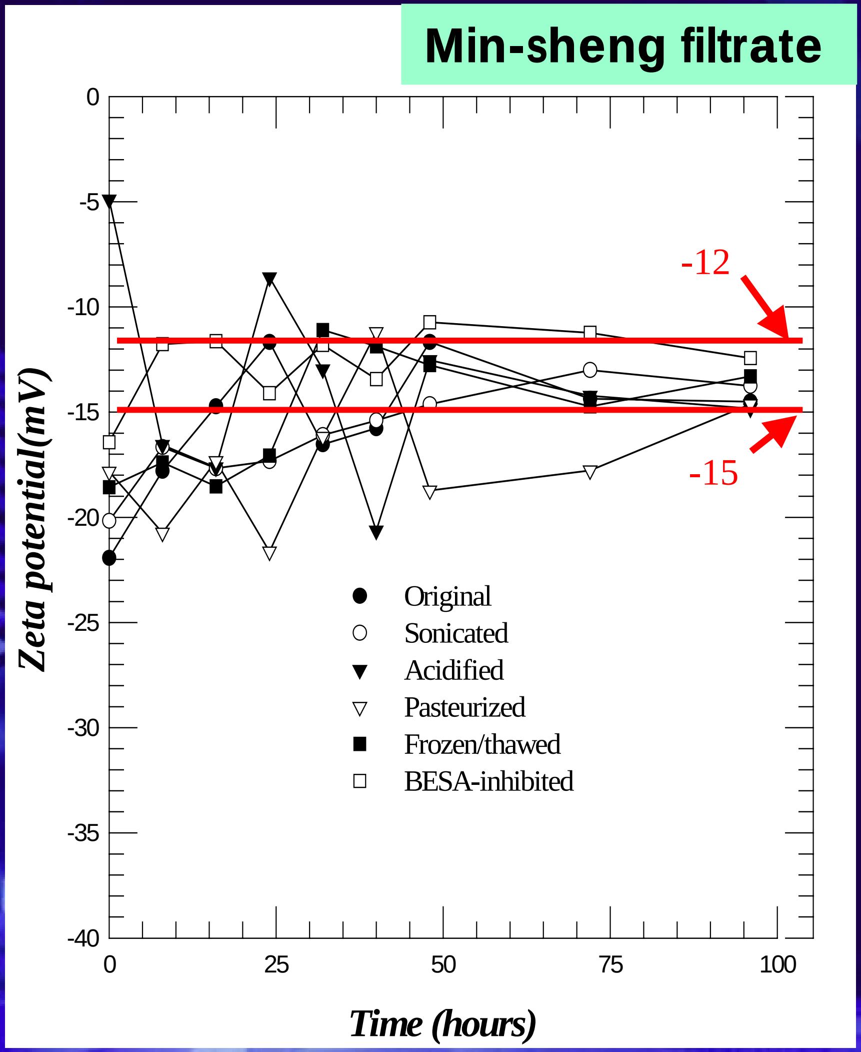
Filtrate fermentation test – ORP

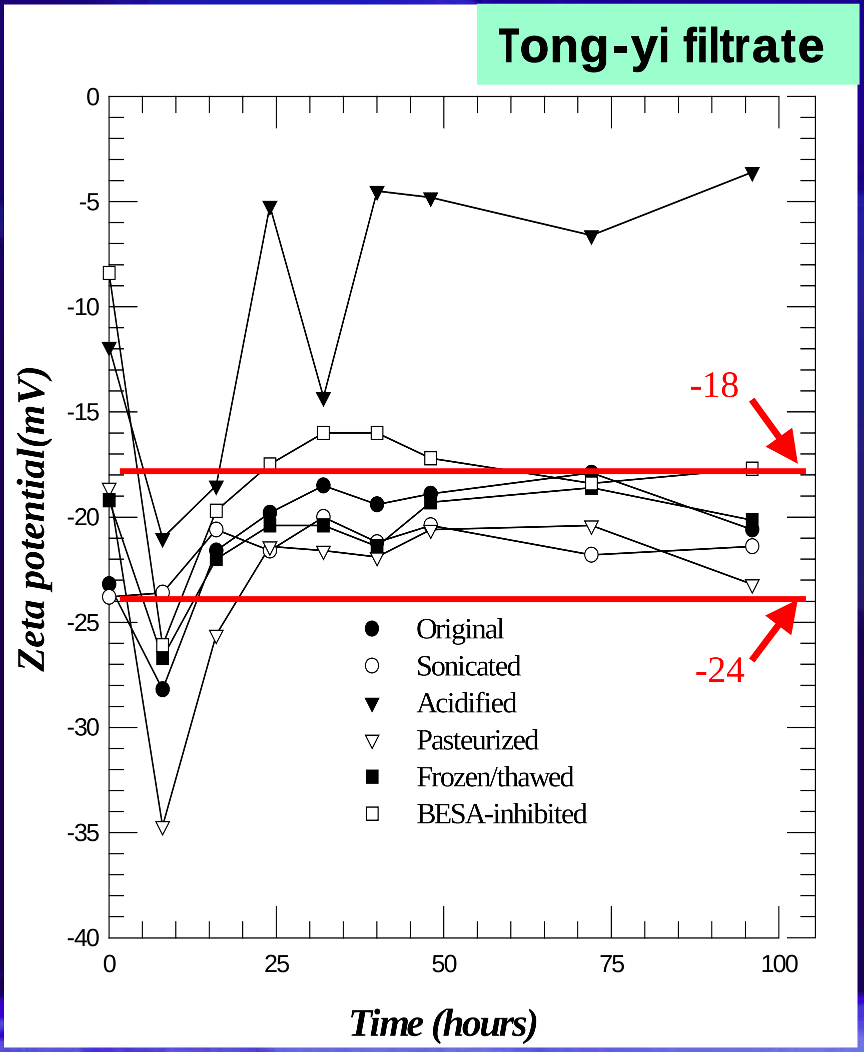




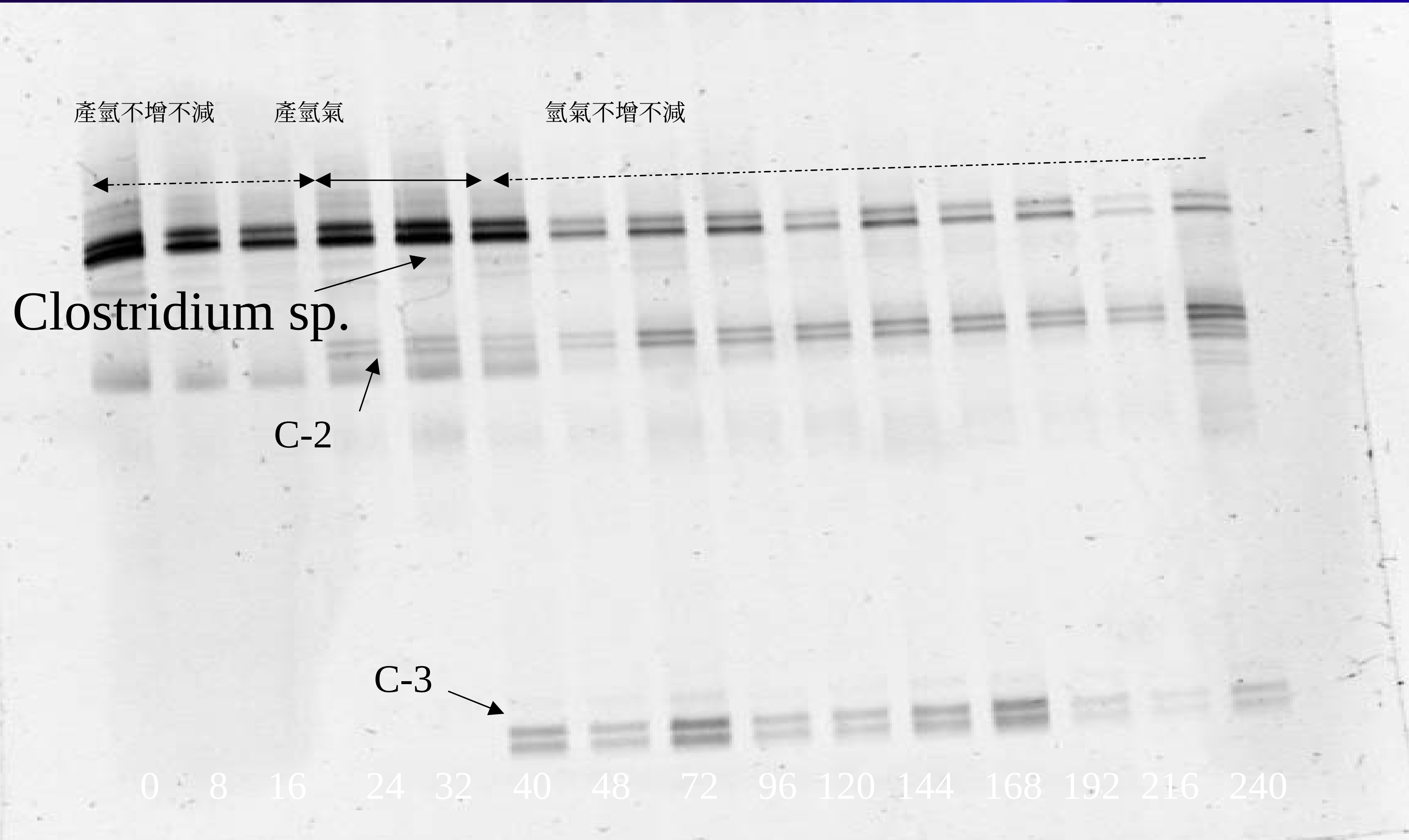
Filtrate fermentation test –

Zeta potential





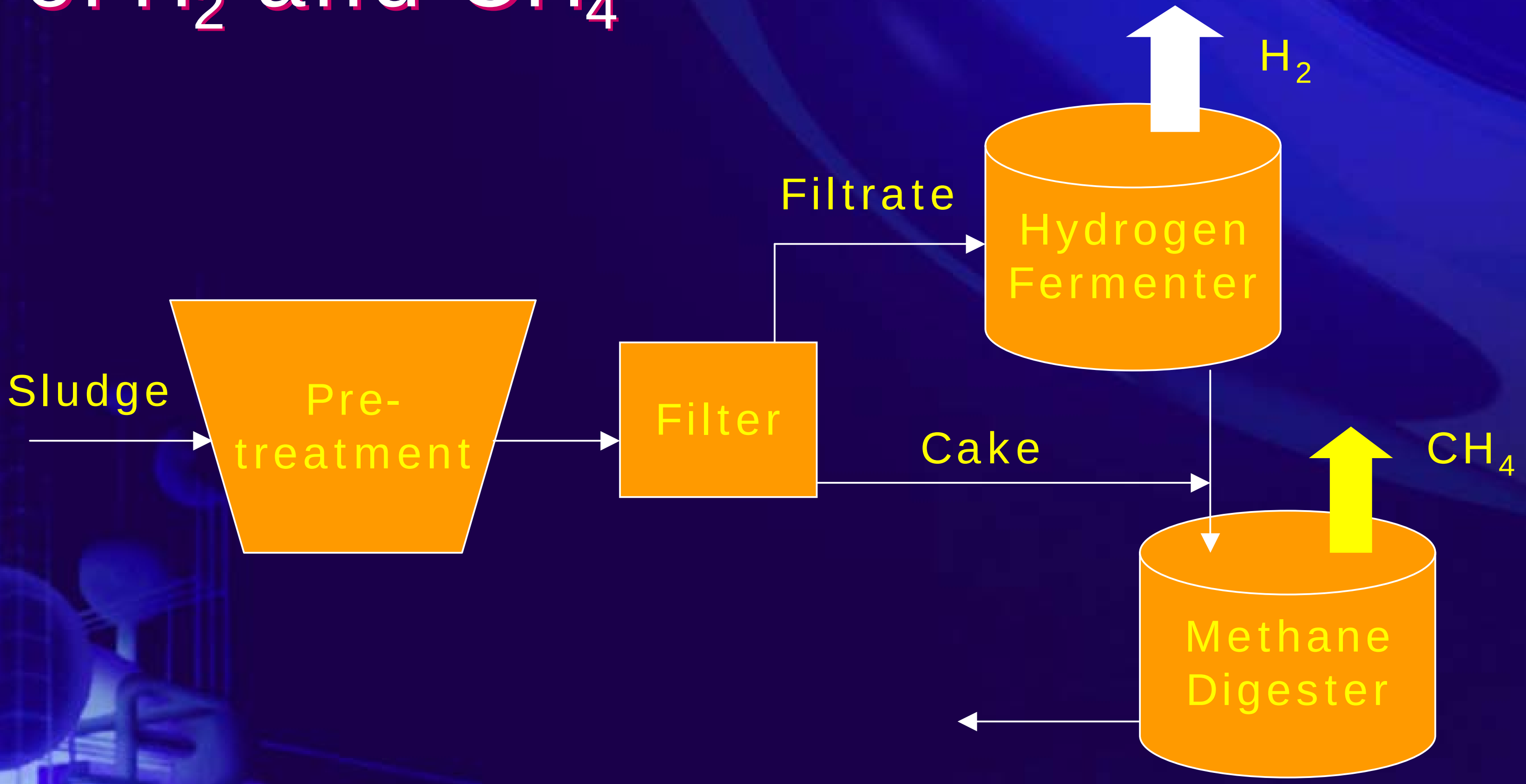
Clostridium inoculum



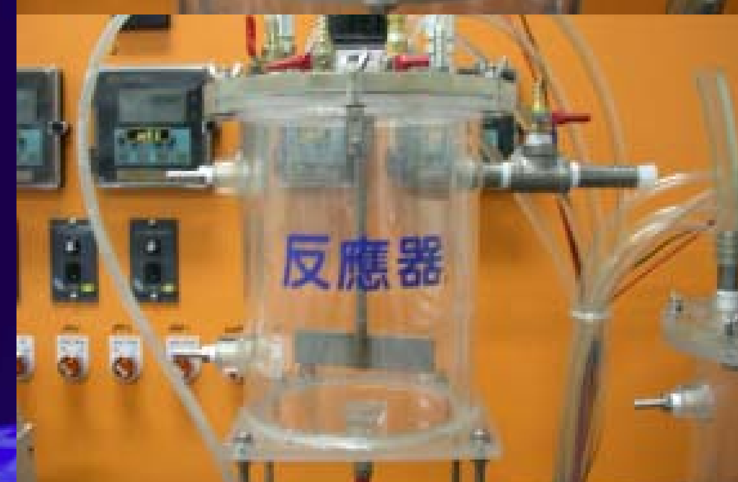
So…

- All pretreatments can assist hydrolysis of organic materials effectively. But not all of them help in producing hydrogen.
- The production of hydrogen increases markedly over 8-24 hr, and is consumed afterward.
- Freezing-thawing, pasteurization, and acidification assist hydrogen production. But adding BESA and ultrasonication retard it.
- Hydrogen production reaction occurs in liquid phase, while the existence of sludge would in some sense consumes the hydrogen.

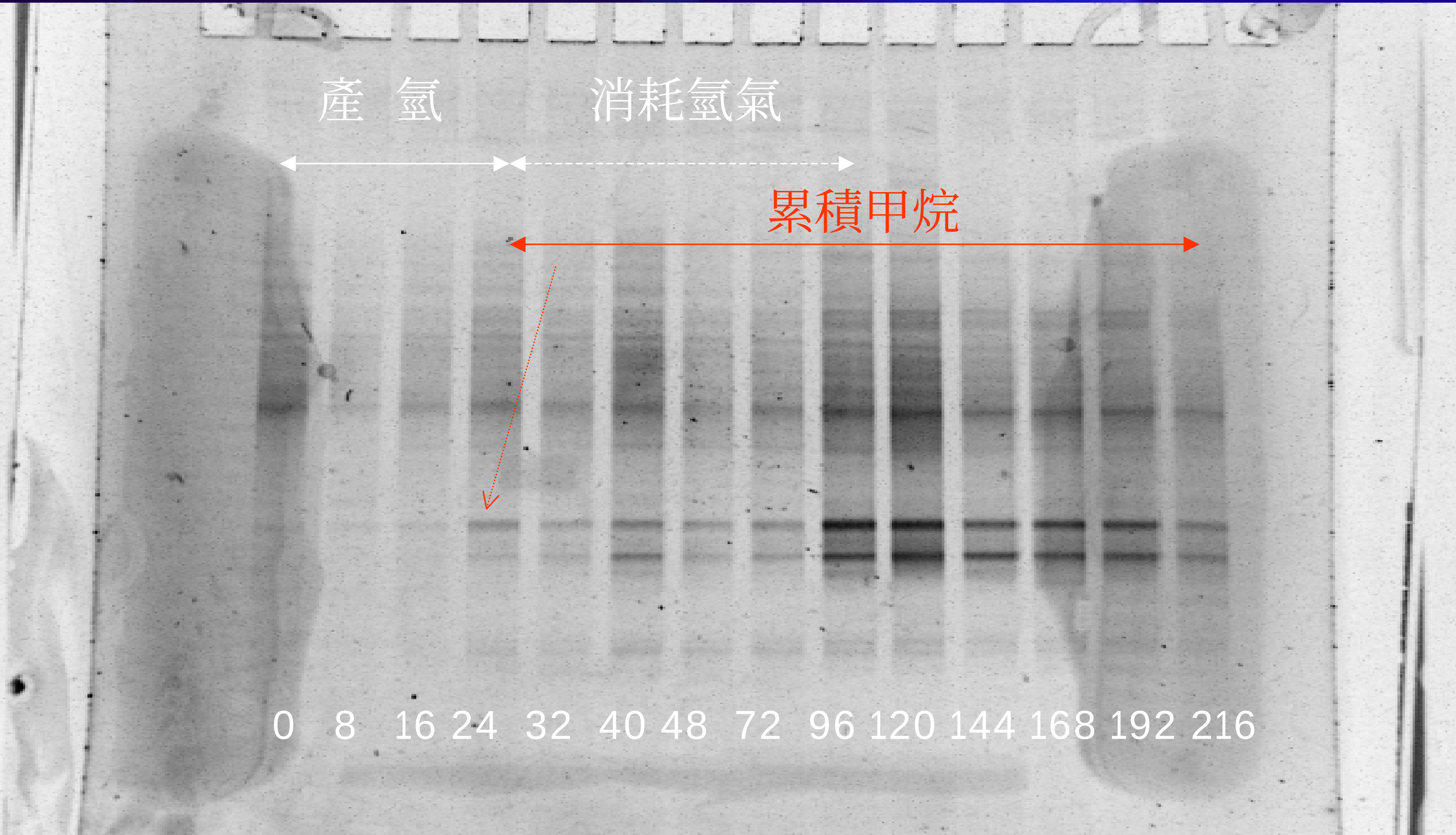
Co-Production of H_2 and CH_4

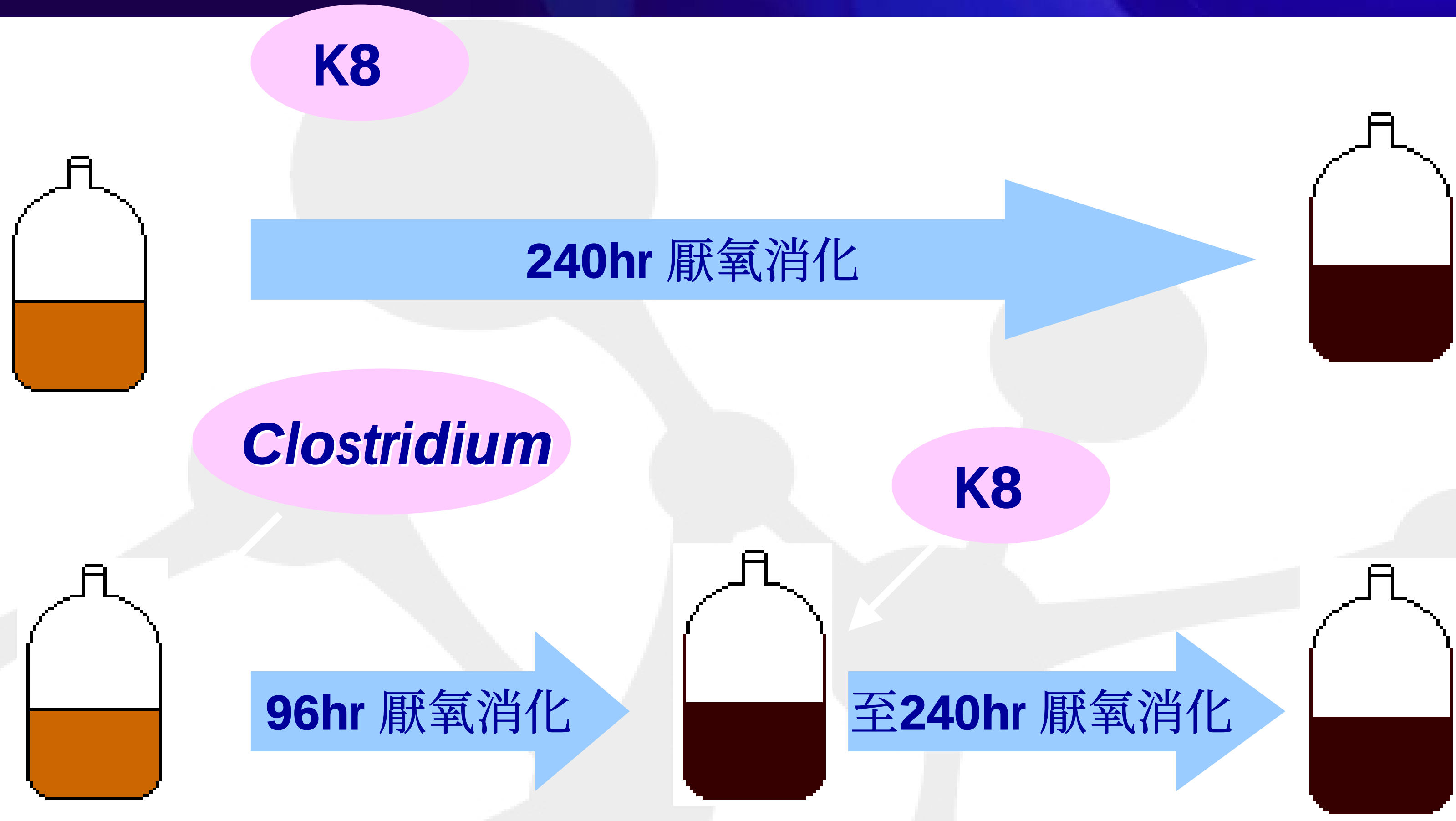


Twin Fermentors

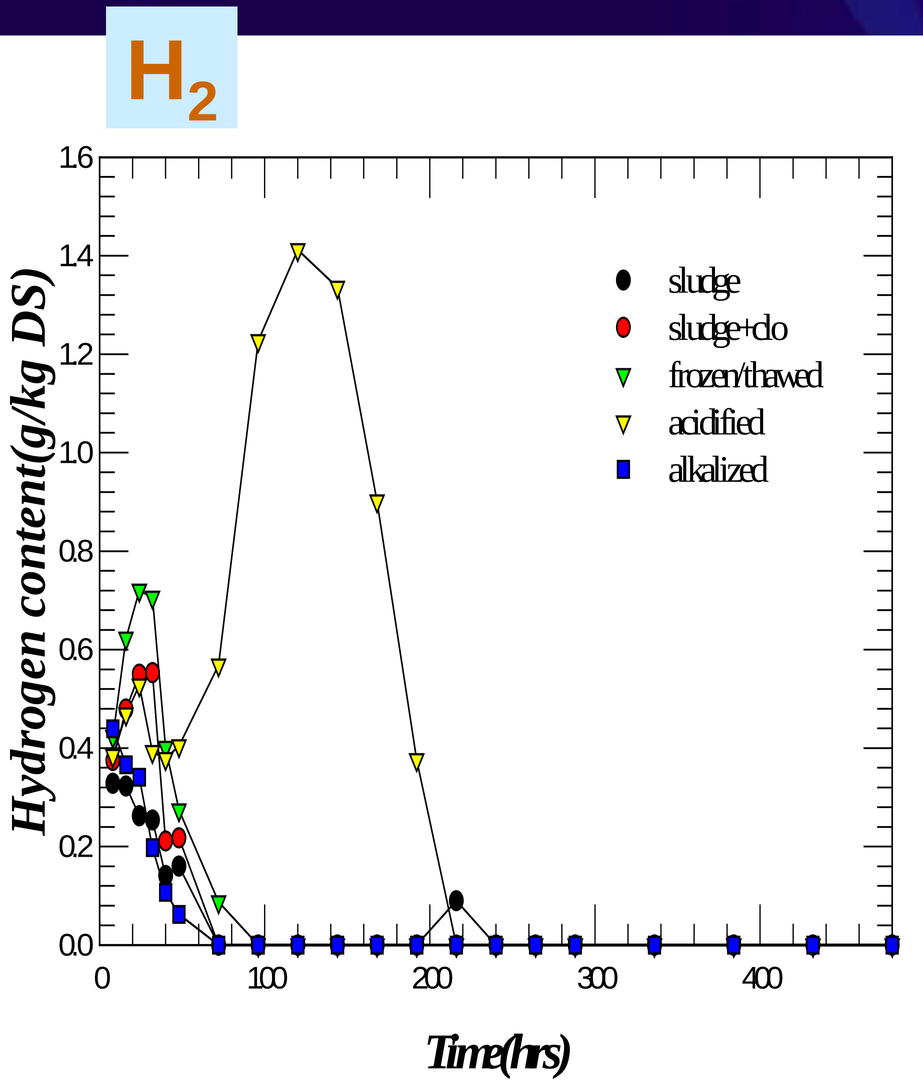


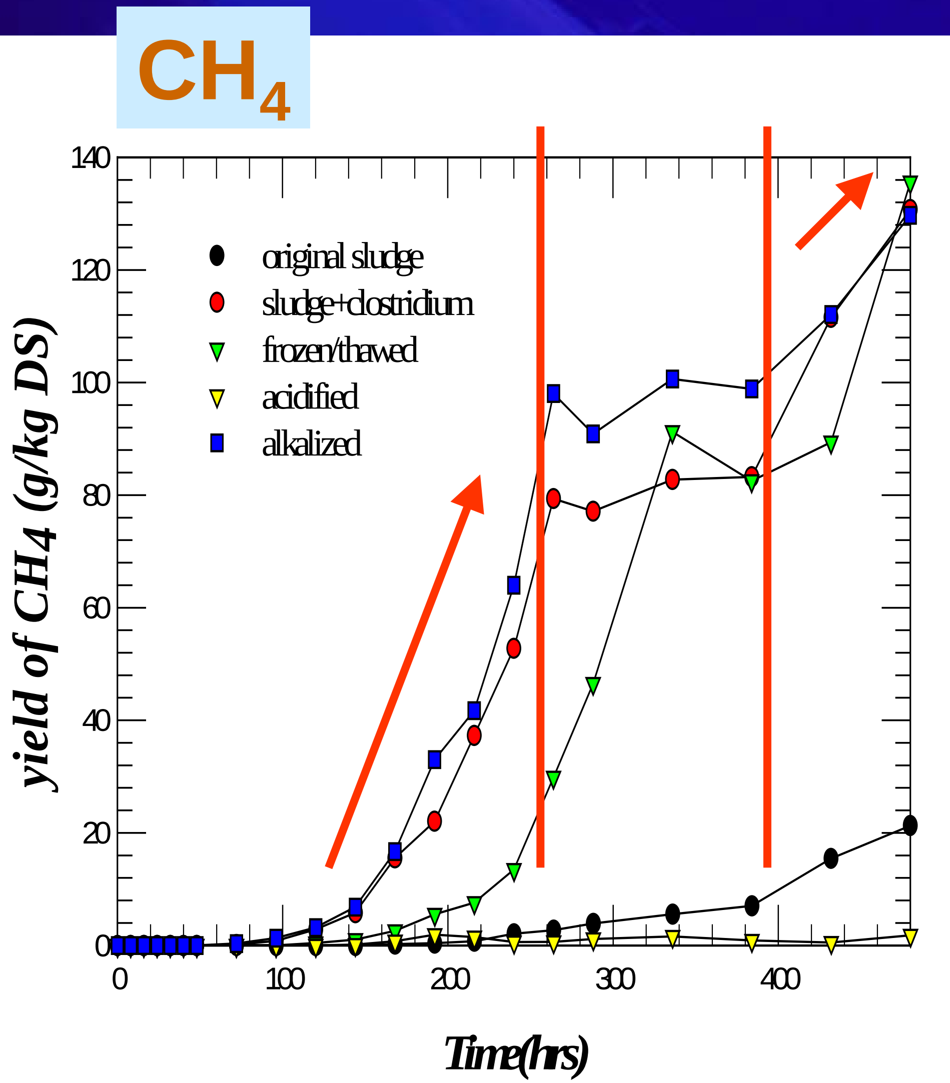
K8 inoculum

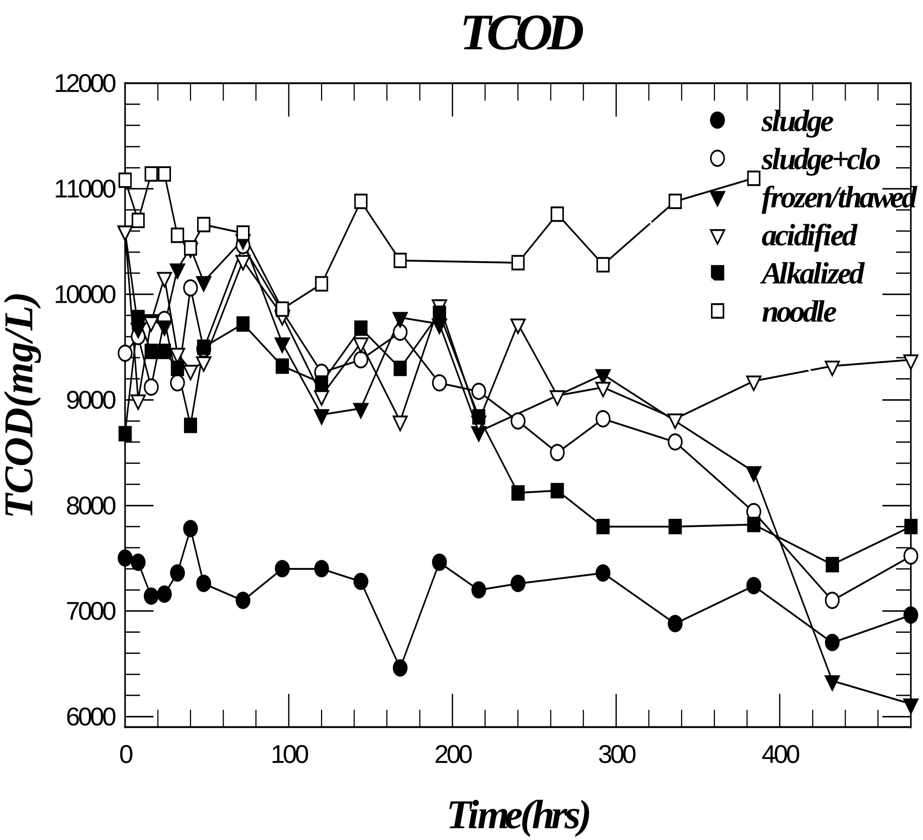


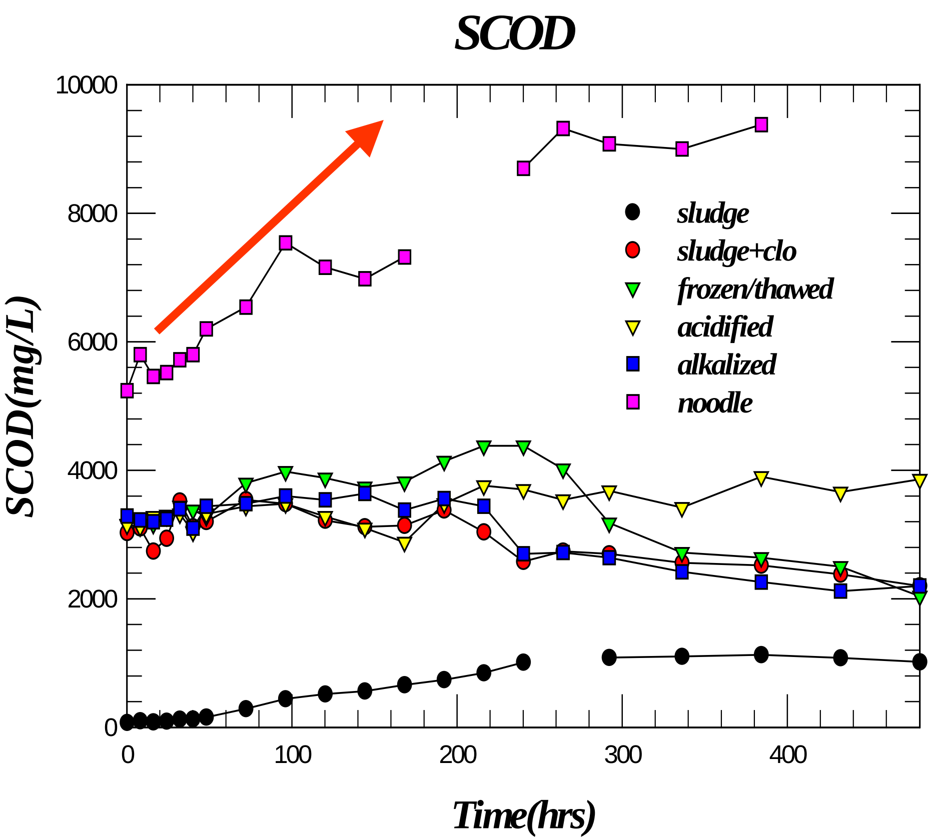

K8
240hr 厭氧消化
Clostridium
K8
96hr 厭氧消化
至240hr 厭氧消化

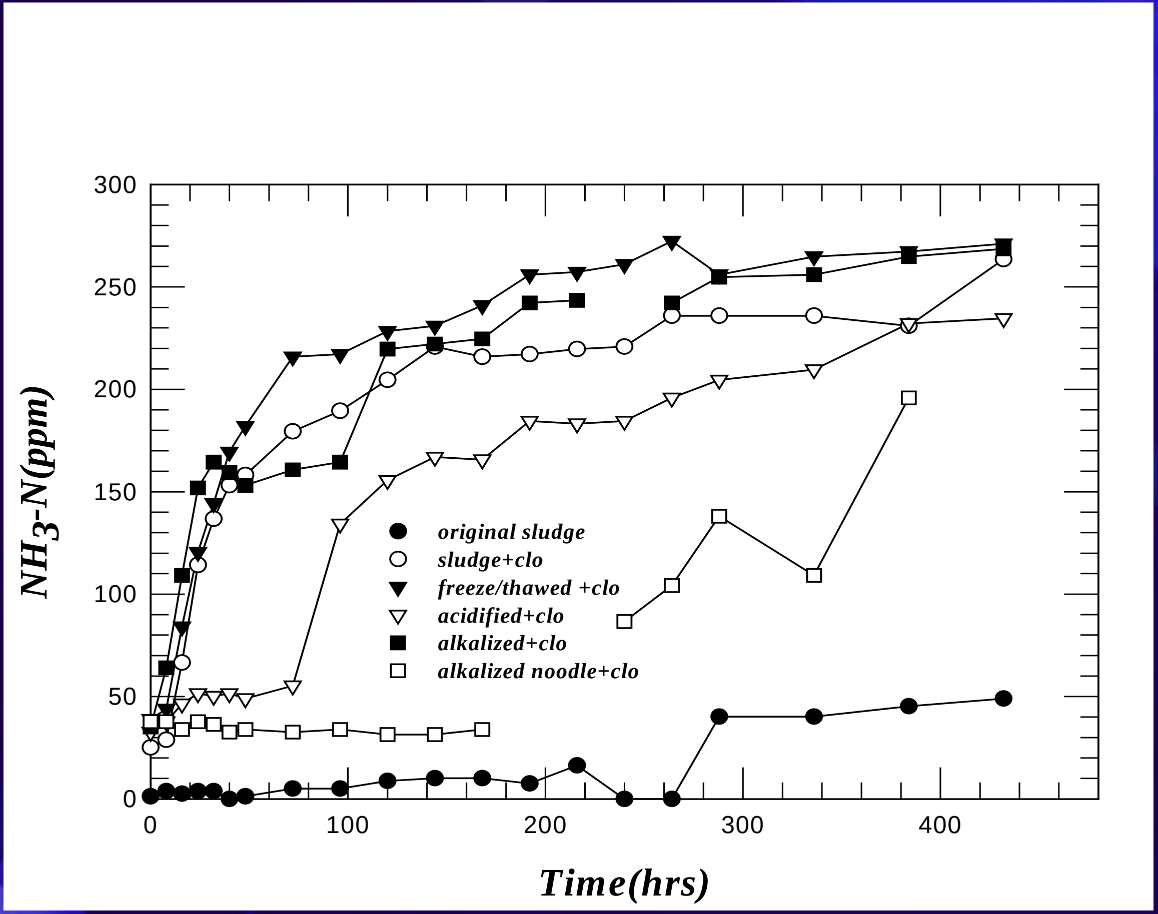
Co-Production





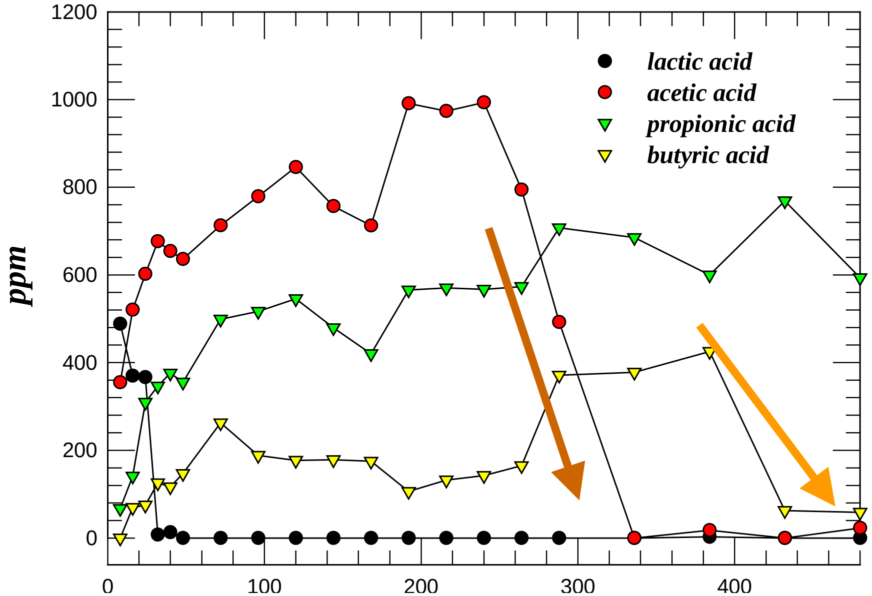

TCOD
12000
11000
10000
9000
8000
7000
6000
0
100
200
300
400
TCOD(mg/L)
Time(hrs)
sludge
sludge+clo
frozen/thawed
acidified
Alkalized
noodle


SCOD
10000
8000
6000
4000
2000
0
0
100
200
300
400
SCOD(mg/L)
Time(hrs)
sludge
sludge+clo
frozen/thawed
acidified
alkalized
noodle

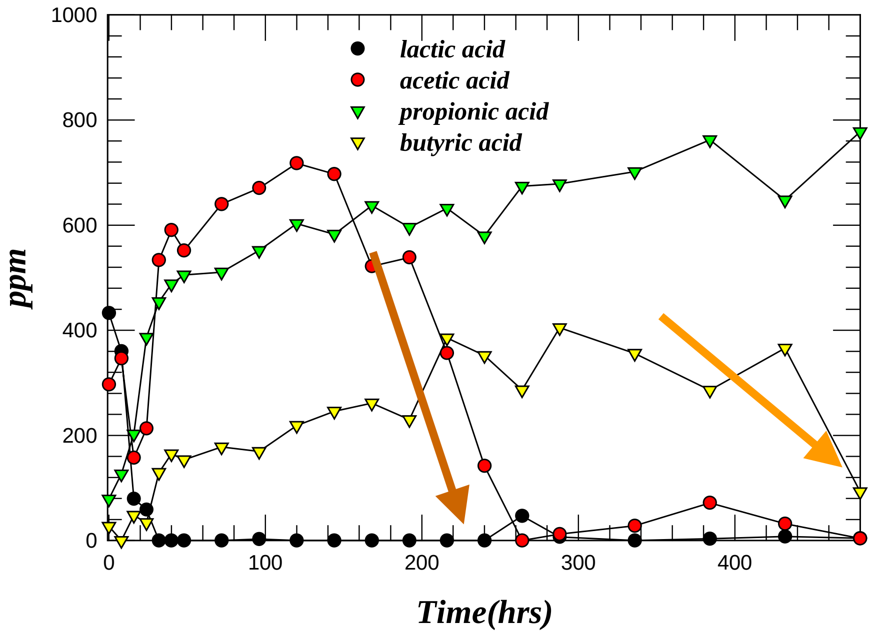


300
250
200
150
100
50
0
0
100
200
300
400
NH_3-N(ppm)
Time(hrs)
original sludge
sludge+clo
freeze/thawed +clo
acidified+clo
alkalized+clo
alkalized noodle+clo

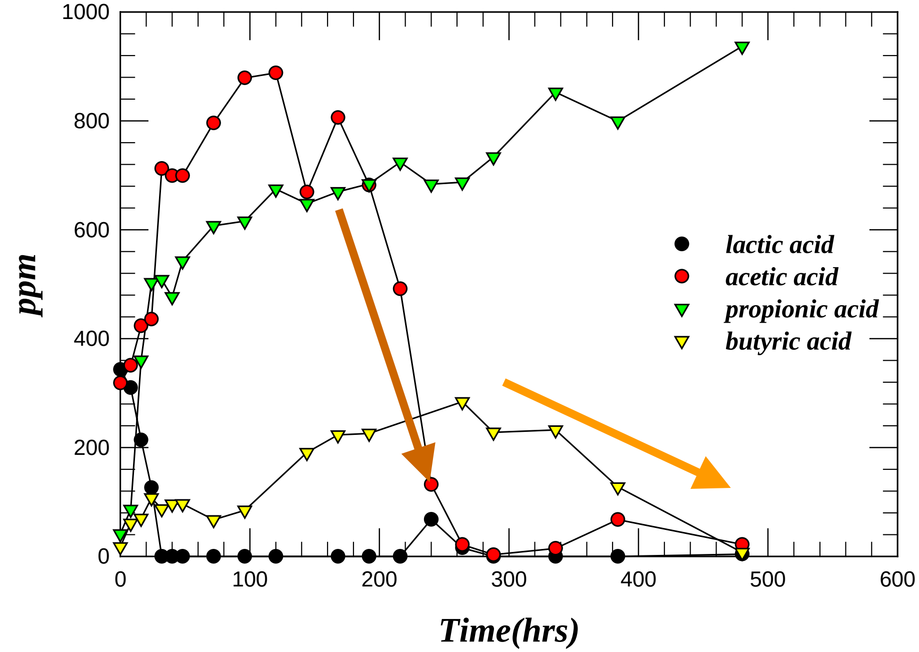
Fre/thaw



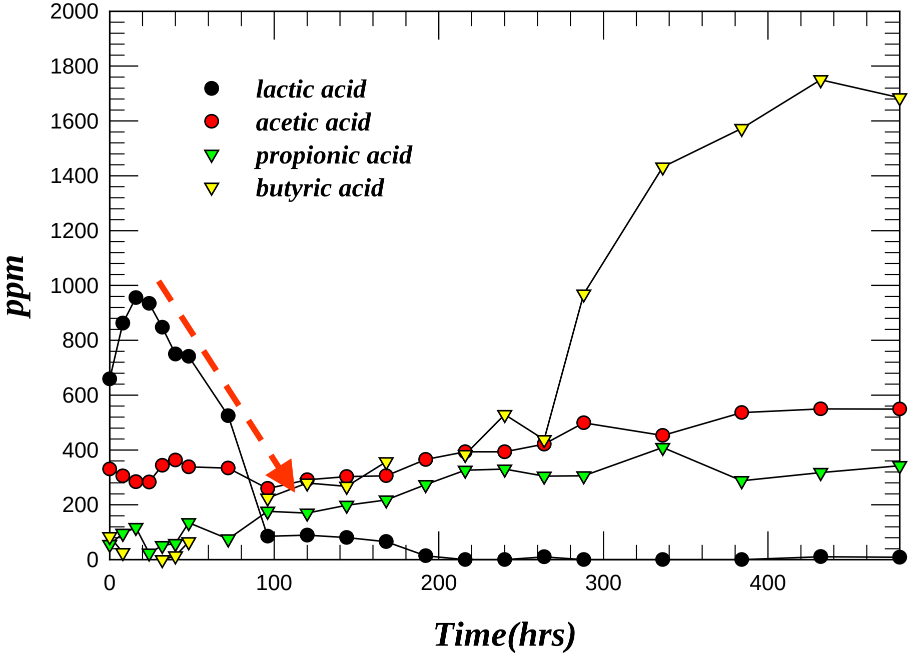
Ori+clo



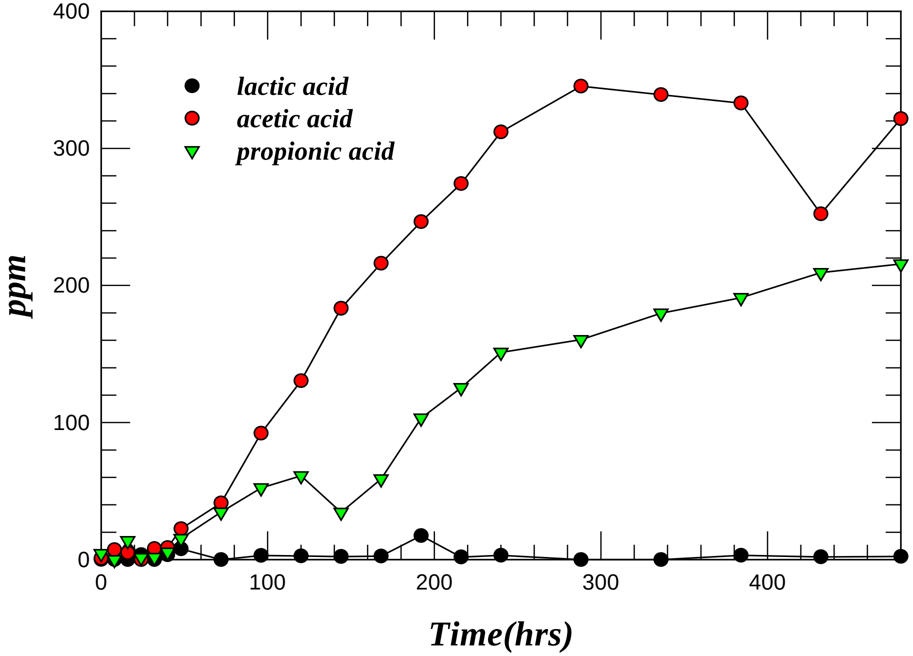
Alkalized

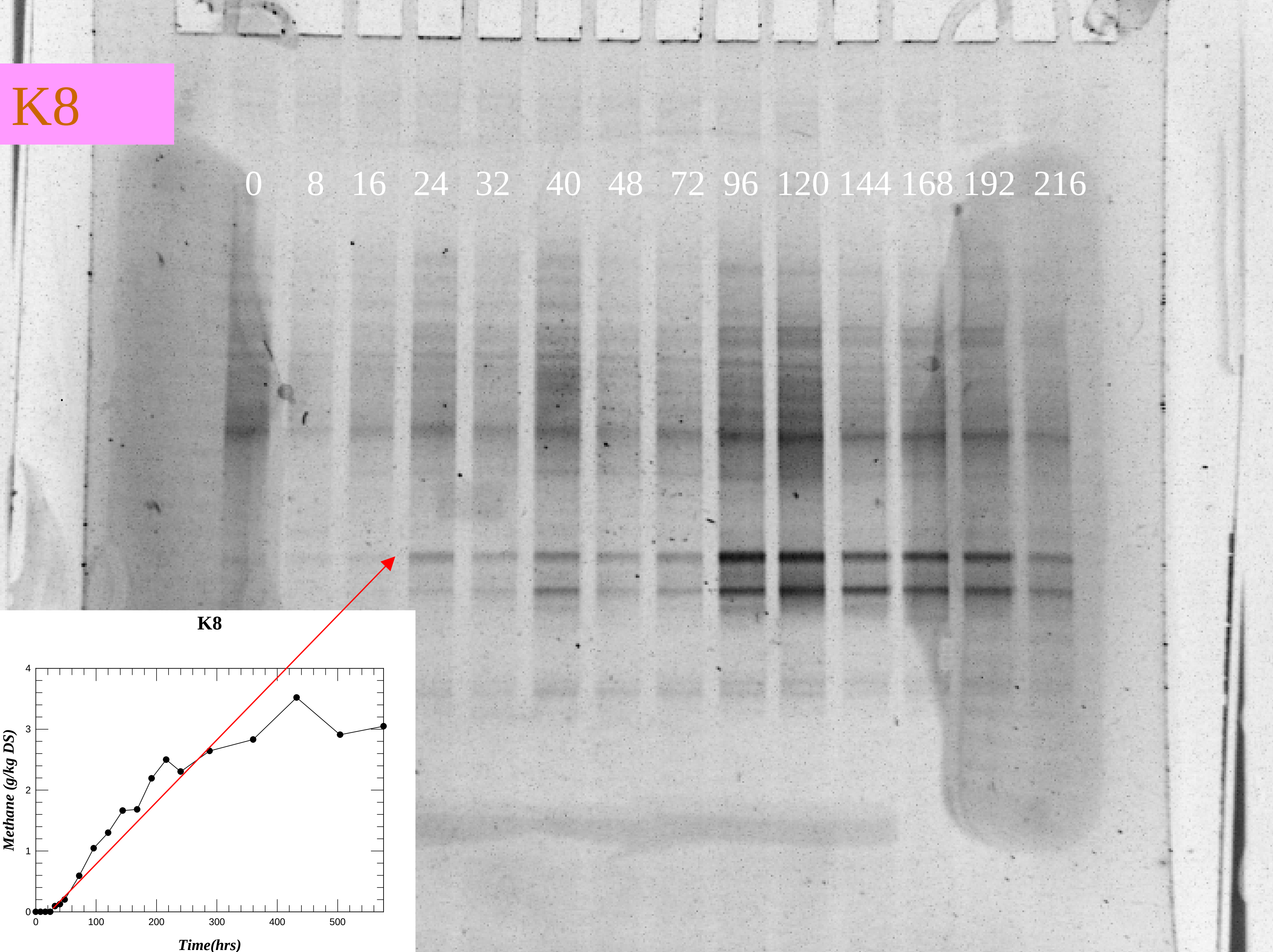


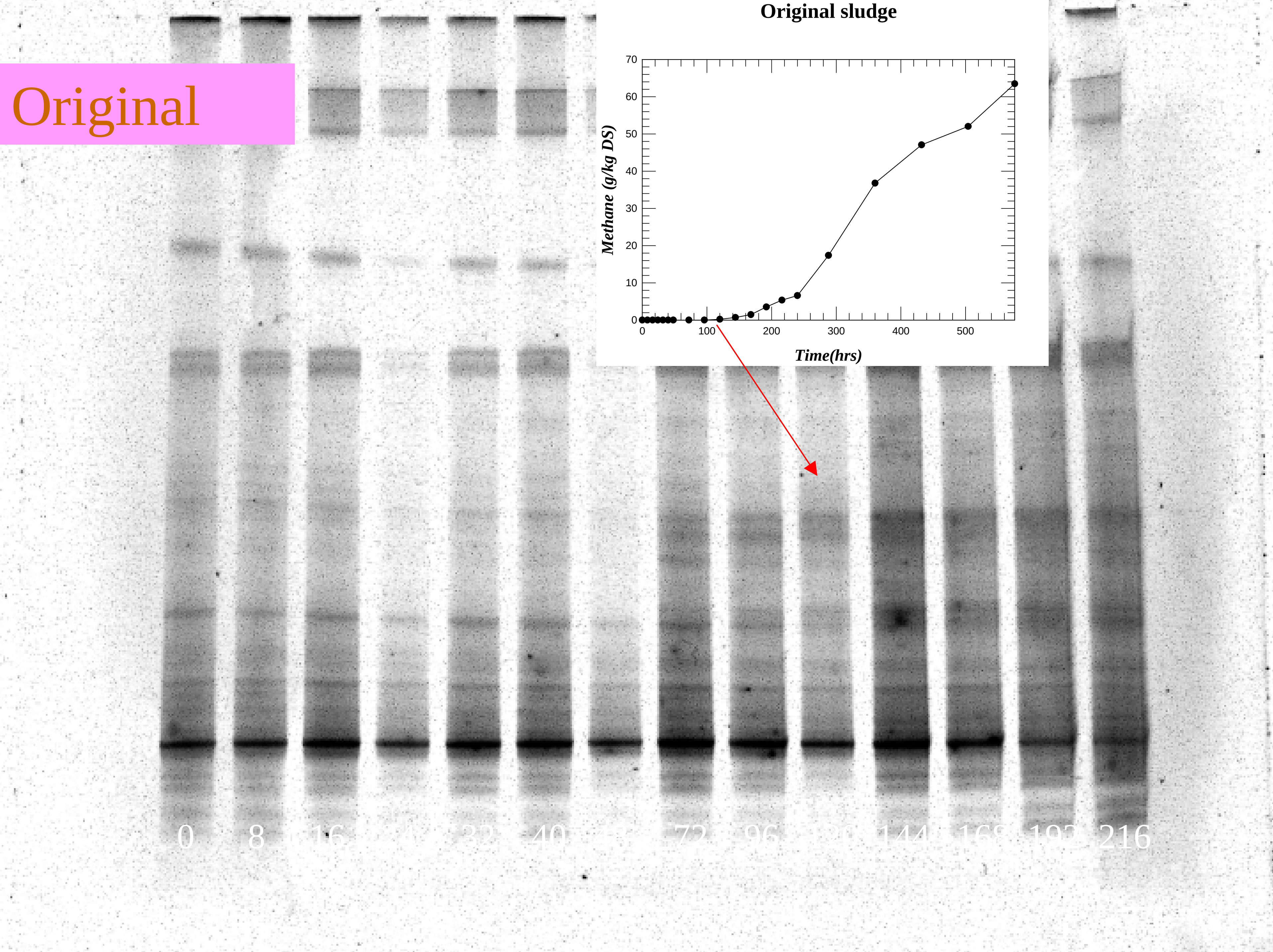
Acidified



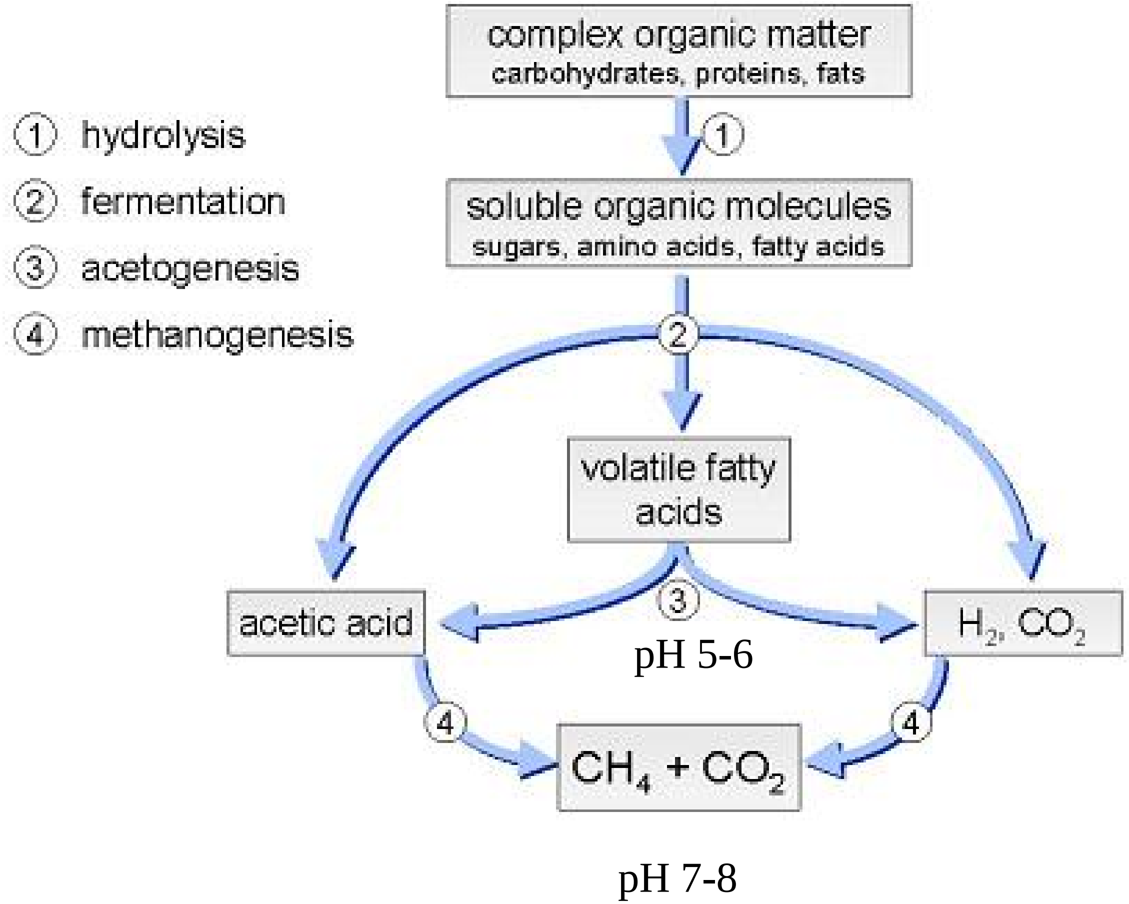
Original




K8
0 8 16 24 32 40 48 72 96 120 144 168 192 216
K8
Methane (g/kg DS)
Time(hrs)
0 1 2 3 4
0 100 200 300 400 500


Original
Original sludge
Methane (g/kg DS)
70
60
50
40
30
20
10
0
0
100
200
300
400
500
Time(hrs)
0
8
16
40
72
96
144
168
216

SUMMARY



complex organic matter
carbohydrates, proteins, fats
1
soluble organic molecules
sugars, amino acids, fatty acids
2
volatile fatty acids
3
acetic acid
H_2, CO_2
4
4
$CH_4 + CO_2$
1 hydrolysis
2 fermentation
3 acetogenesis
4 methanogenesis
pH 5-6
pH 7-8