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Bio-upgrading of syngas into renewable natural gas (methane)

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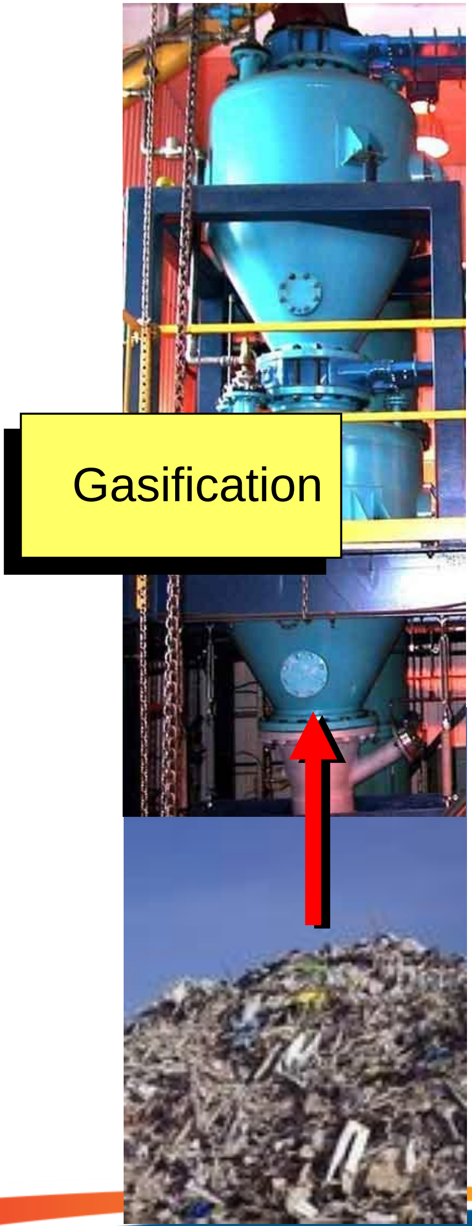
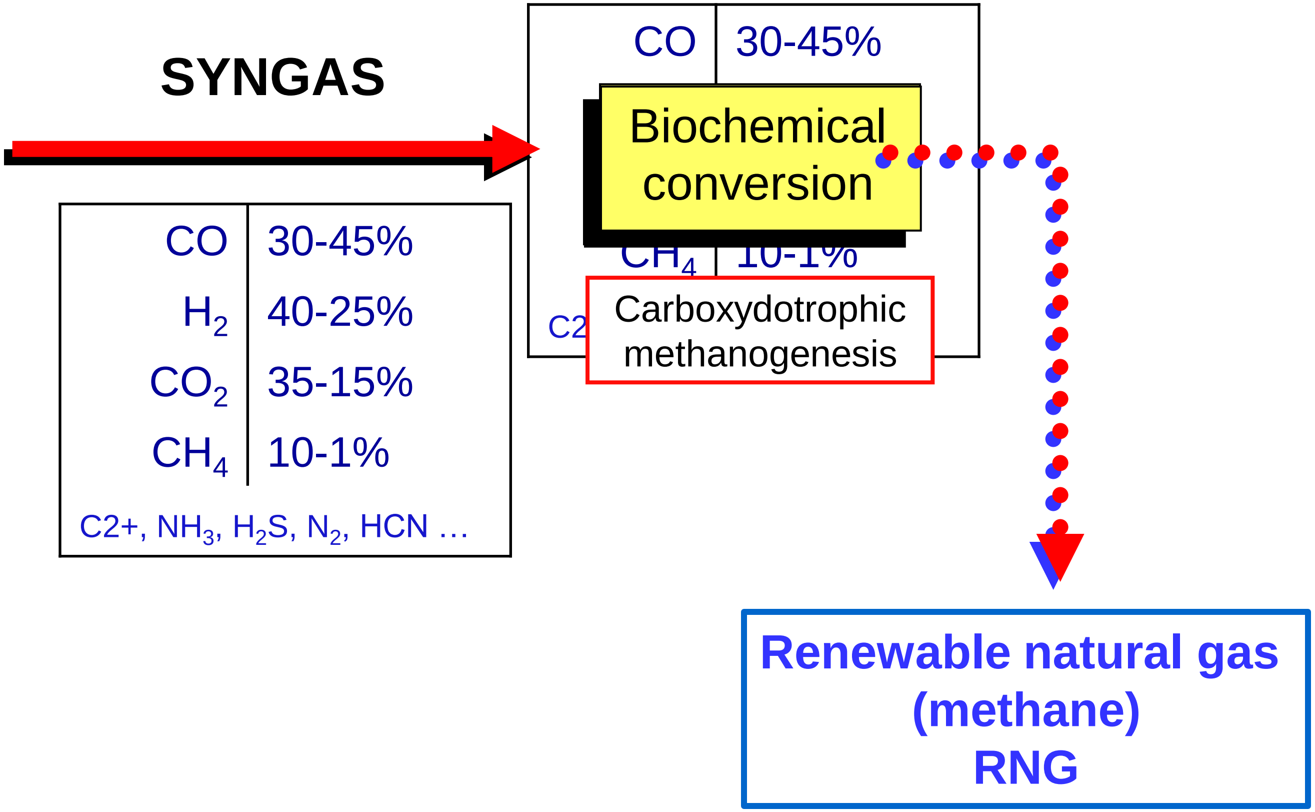
Syngas catalytic methanation / biomethanation





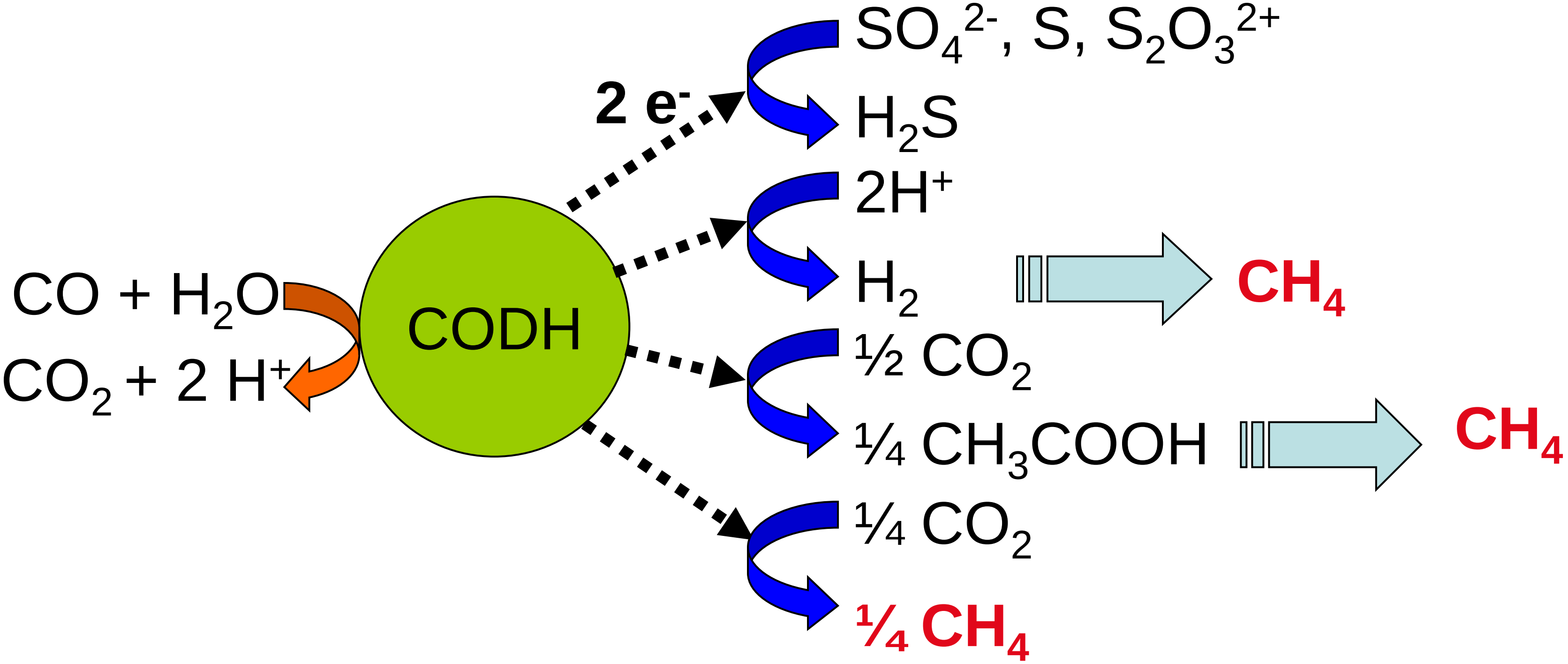
SYNGAS

CO	30-45%
H_2	40-25%
CO_2	35-15%
CH_4	10-1%

C2+, NH_3, H_2S, N_2, HCN …

Renewable natural gas (methane) RNG

Key enzyme : CO-dehydrogenase



$CO + H_2O$

$CO_2 + 2\ H^+$

CODH

2 e$^-$

SO_4^{2-}, S, $S_2O_3^{2+}$

H_2S

$2H^+$

H_2

CH_4

½ CO_2

¼ CH_3COOH

CH_4

¼ CO_2

¼ CH_4

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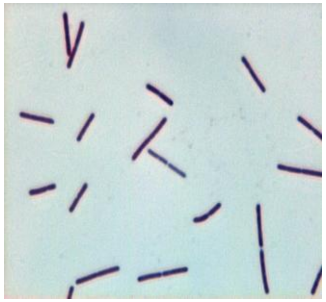
Biochemical pathways



Hydrogenotrophic methanogenesis

✓ $\mathbf{CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O}$ ($\Delta G^{\circ\prime} = -130$ kJ/mol CH_4)

Carboxydotrophic methanogenesis

➢*Methanocaldococcus jannaschii, Methanopyrus kandleri* (85-98ºC)

➢*Methanobacterium thermoautotrophicum, Methanothermobacter wolfeii, Methanosaeta thermophila* (55-65ºC)

➢*Methanobrevibacter arboriphilicus, Methanosarcina acetivorans, M. barkeri (35-40ºC)*

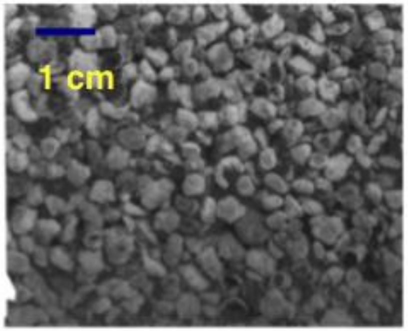
✓ $\mathbf{4\ CO + 2\ H_2O \rightarrow CH_4 + 3\ CO_2}$ ($\Delta G^{\circ\prime} = -211$ kJ/mol CH_4)

✓ $\mathbf{CO + 3\ H_2 \rightarrow CH_4 + H_2O}$ ($\Delta G^{\circ\prime} = -151$ kJ/mol CH_4)

Biochemical pathways II

- **Indirect pathways (consortium)**
  - ✓ CO-hydrogenogens + CO-methanogens

$$\begin{array}{l} 3\,CO + 3\,H_2O \rightarrow 3\,H_2 + 3\,CO_2 \\ \underline{CO + 3\,H_2 \qquad \rightarrow CH_4 + H_2O} \\ 4\,CO + 2\,H_2O \rightarrow CH_4 + 3\,CO_2 \end{array}$$



- ✓ CO-hydrogenogens + hydrogenotrophic methanogens

$$\begin{array}{l} 4\,CO + 4\,H_2O \rightarrow 4\,H_2 + 4\,CO_2 \\ \underline{CO_2 + 4\,H_2 \qquad \rightarrow CH_4 + 2\,H_2O} \\ 4\,CO + 2\,H_2O \rightarrow CH_4 + 3\,CO_2 \end{array}$$

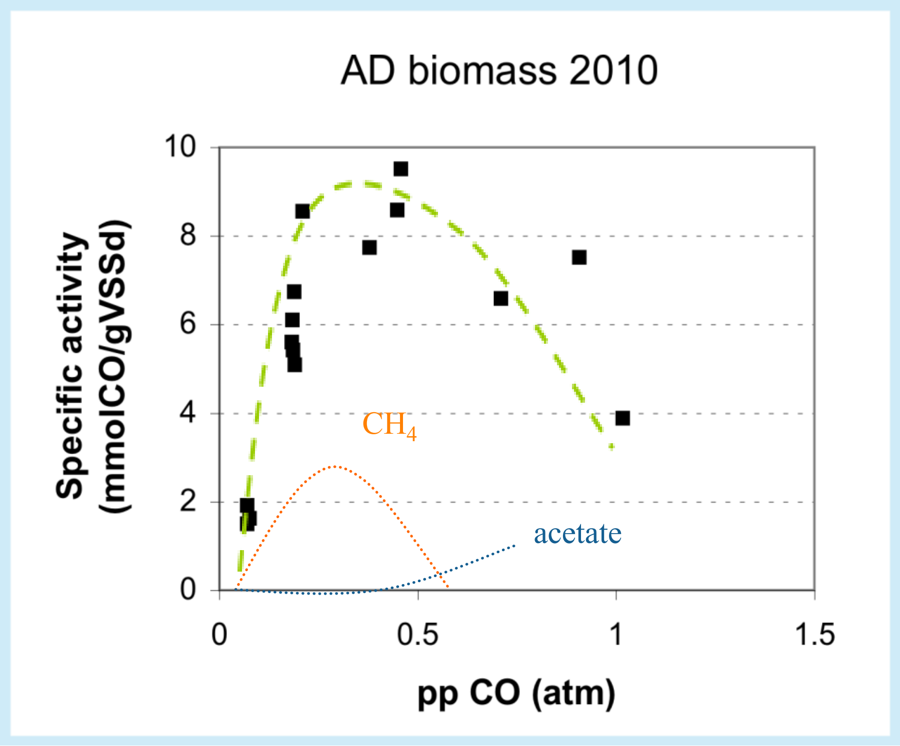
- ✓ CO-homoacetogens + acetoclastic methanogens

$$\begin{array}{l} 2\,CO + 2\,H_2 \rightarrow CH_3COOH \\ \underline{CH_3COOH \qquad \rightarrow CH_4 + CO_2} \\ 2\,CO + 2\,H_2 \rightarrow CH_4 + CO_2 \end{array}$$

Theoretical yield

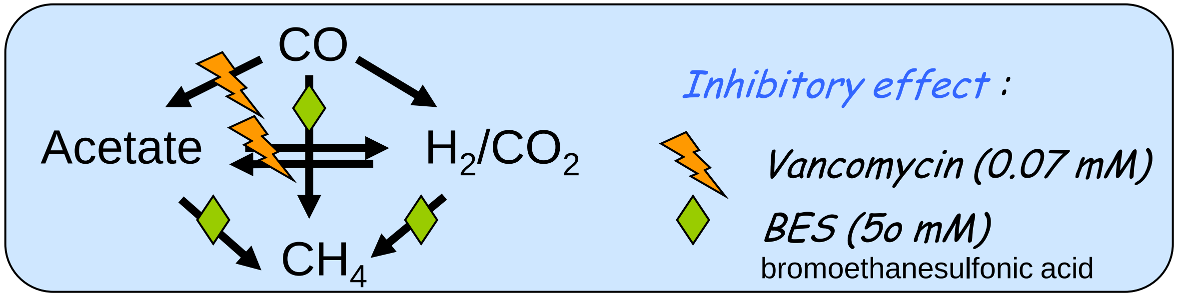
- ➢ CO alone
  - ✓ 1/4 mol CH_4 per mol CO
- ➢ CO & H2
  - ✓ 1/4 mol CH_4 per mol CO + 1/4 mol CH_4 per mol H_2

Kinetics of carboxydotrophic methanogenesis / mixed population



- specific activity optimal at p_{CO} ~ 0.3 atm
- high CH_4 yield (VFA between 0.2 & 5% CO input) up to p_{CO} ~ 0.3 atm
- methanogenesis inhibited above p_{CO}~ 0.5 atm
- carboxydotrophy redirected to mainly acetate

Predominant carboxidotrophic routes to methane in a mixed consortium



CO

Acetate

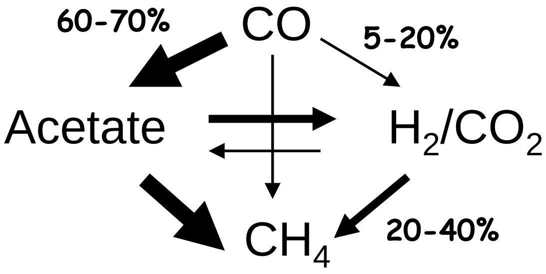
H_2/CO_2

CH_4

Inhibitory effect :

Vancomycin (0.07 mM)

◆ *BES (5o mM)*
bromoethanesulfonic acid

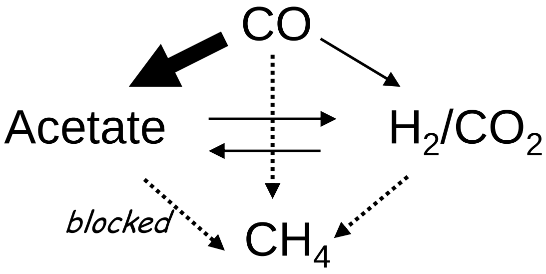


60-70% CO **5-20%**

Acetate H_2/CO_2

CH_4 **20-40%**

low p_{CO} (< 0.5 atm)

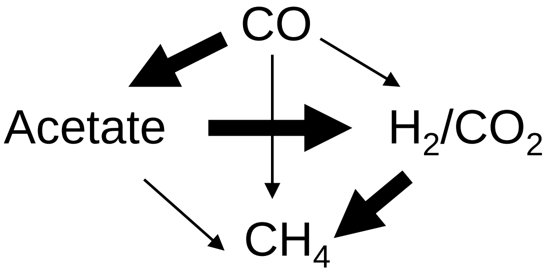


CO

Acetate H_2/CO_2

blocked CH_4

high p_{CO} (> 0.5 atm)



CO

Acetate H_2/CO_2

CH_4

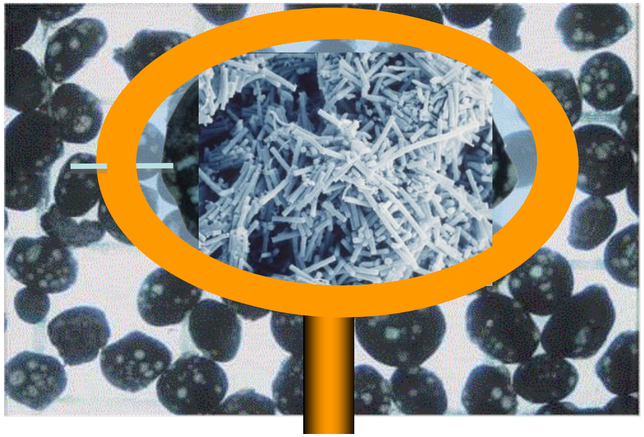
after acclimation (100% CO)

Predominant carboxidotrophic routes to methane in a mixed consortium

- ✓ Direct methane production from CO appears to be negligible: CO was converted (CO acetogenesis) mainly to acetate, which was further transformed to methane.
- ✓ The optimal methanogenic activity achieved under mesophilic conditions was observed at P_{CO} in the gas phase lower than 0.3 atm, and further increase in the amount of CO supplied lead to the inhibition of methanogenesis. However, it was possible to achieve methane production at high P_{CO} through the sludge's adaptation to CO.
- ✓ At high CO partial pressure, CO conversion shifted to hydrogen which was then used to reduce CO_2 into methane.
- ✓ Importance of hydrogenotrophic methanogenesis, as H_2 accumulated at high p_{CO} with non-adapted sludge.
- ✓ Long-term exposure to high CO concentrations, enrichment in hydrogen consumers ⇒ driving oxidation of acetate (as the major intermediate product) : $CH_3COOH + 2\ H_2O \rightarrow 2\ CO_2 + 4\ H_2$ ⇒ significant pathway for CH_4 production followed by hydrogenotrophic methanogenesis.
- ✓ This allows bypassing substrate and impurity inhibition of the acetoclastic methanogenesis route.

Engineering challenge : reactors and conditions to significantly improve gas-to-liquid mass transfer rate

Because the aqueous solubility of CO and H2 is low, syngas bioconversions are typically limited by the gas-to-liquid mass transfer rate which may represent the major engineering challenge for development of large-scale syngas bioconversion facilities



An approach : to use industrial wastewater-treating anaerobic granules = robust microbial populations densely packed, adapted to harsh conditions, massively available, with free/ low cost.

Reactors investigated for the conversion of CO on the continuous mode:

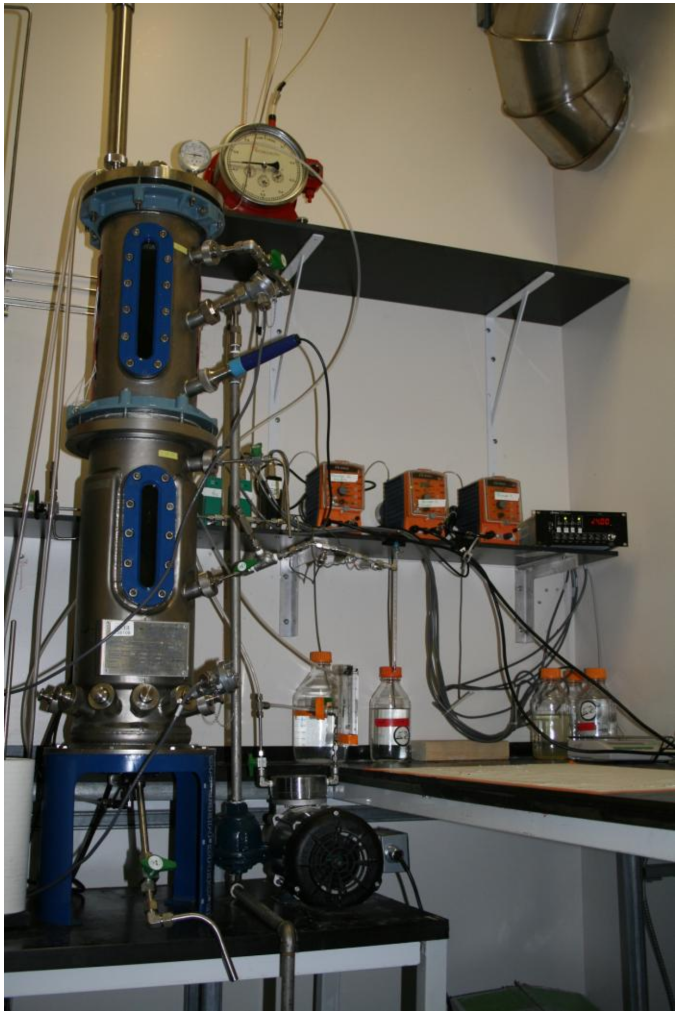
- closed-loop gas lift reactor (GLR)
- bubble column reactor (BCR)

similar gas-liquid transfer rates (k_La) ranging between 2 and 6 h^{-1}

- completely stirred tank reactor (CSTR)

k_La 5-120 h^{-1}

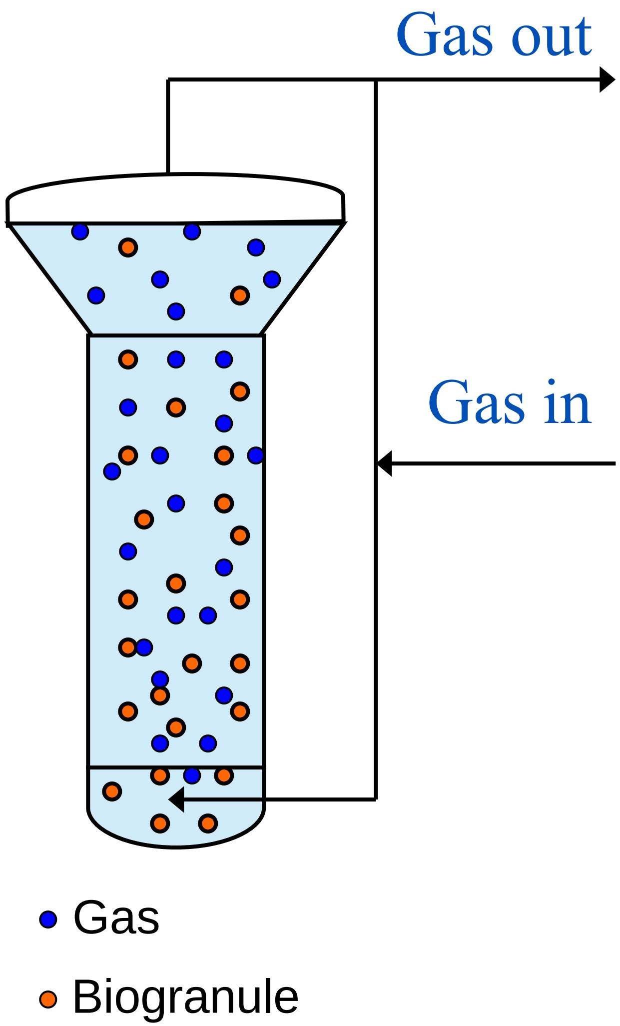
Carboxydotrophic methanogenesis in a closed-loop gas-lift reactor, 30 L, anaerobic granules 4 g VSS/L



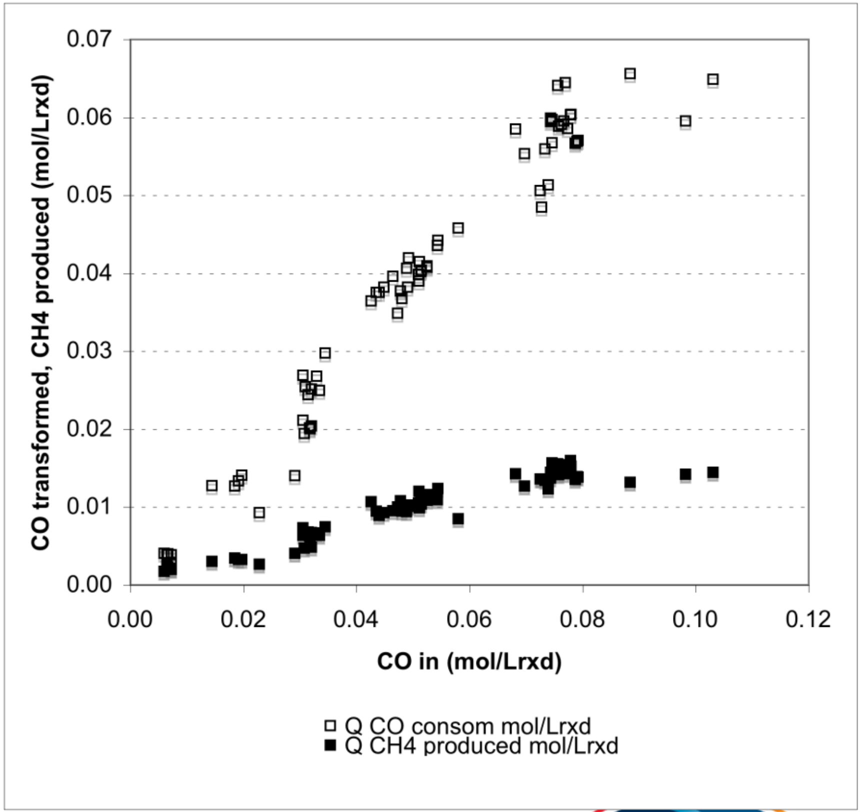
Volumetric load (mmol CO/L_{rxr}·d) **(L_{CO}/L_{rxr}·d)**	**60** **1.6**
CO loading rate (mmol/g VSS·d)	**17**
Gas recirculation ratio	**20:1**
p_{CO} in gas feeding (atm)	**0.62**
CO transfer rate (L_{CO}/L_{rxr}·d)	**1.2**
CO transferred (%)	**75**
CO consumed (mmol/g VSS·d)	**13**
Yield CH_4/CO (% theor)	**95**
Yield H_2/CO (% theor)	0.1
Yield Acetate/CO (% theor)	0

Limiting step : Mass transfer (gas holdup) and biomass activity

Bubble column reactor (BCR)

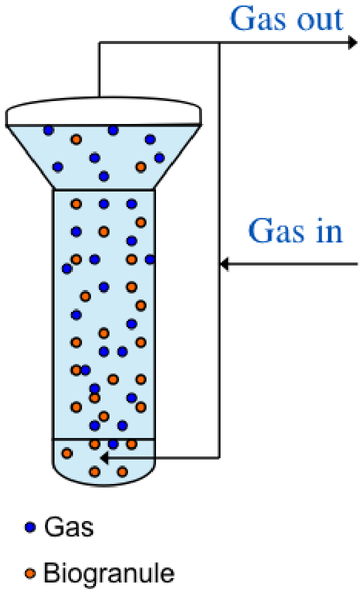


Reactor volume : 9.7 L
Inoculum, anaerobic biogranules: 7 g VSS/L)
20 experimental phases over a 189 days period
CO flow rate > 7 L/d
Gas recirculation rate > 1200 L/d)



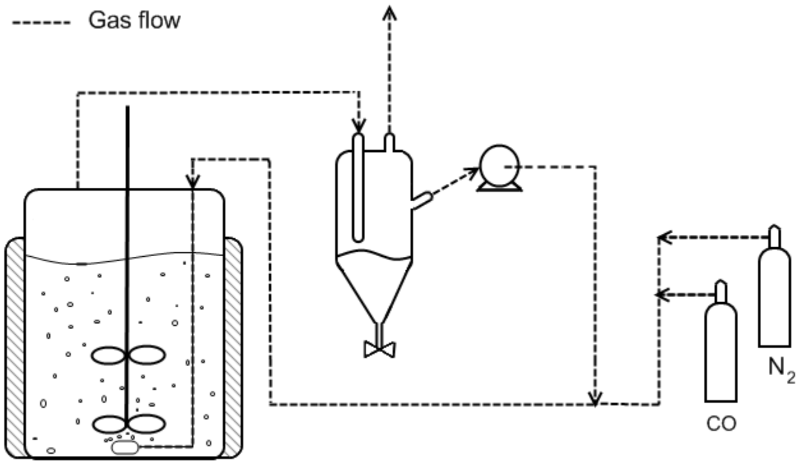
Bubble column reactor (BCR) - II

Volumetric load (mmol CO/L_{rxr}·d) **(L_{CO}/L_{rxr}·d)**	**100** **2.3**
CO loading rate (mmol/g VSS·d)	**14**
Gas recirculation ratio	**170:1**
p_{CO} in gas feeding (atm)	**1.62** (100% CO)
Retention time (d)	**1**
CO transfer rate (L_{CO}/L_{rxr}·d)	**1.9**
CO transferred (%)	**85**
CO consumed (mmol CO/L_{rxr}·d)	**86**
CO consumed (mmol/g VSS·d)	**12**
Yield CH_4/CO (% theor)	**100**
Yield H_2/CO (% theor)	0.1
Yield Acetate/CO (% theor)	0



Limiting step : enzymatic kinetics (biomass activity) rather than gas-liquid mass transfer rate

Completely Stirred-Tank Reactor (CSTR)



Liquid volume 2.2 L
100 rpm
k_La 20 h^{-1}
35ºC
Biomass 6 g VSS/L

Most stable results, not the highest	
Volumetric load (mmol CO/L_{rxr}·d) **(L_{CO}/L_{rxr}·d)**	**165** **3.7**
Sp. CO loading rate (mmol/g VSS·d)	**28**
Gas recirculation ratio	**16:1**
p_{CO} in gas feeding (atm)	**1.2**
Retention time (d)	**0.3**
CO transfer rate (L_{CO}/L_{rxr}·d)	**3**
CO transferred (%)	**81**
CO consumed (mmol CO/L_{rxr}·d)	**134**
CO consumed (mmol/g VSS·d)	**23**
Yield CH_4/CO (% theor)	**100**

Limiting step : biomass activity (granules dismantled, more sensitive to CO toxicity)

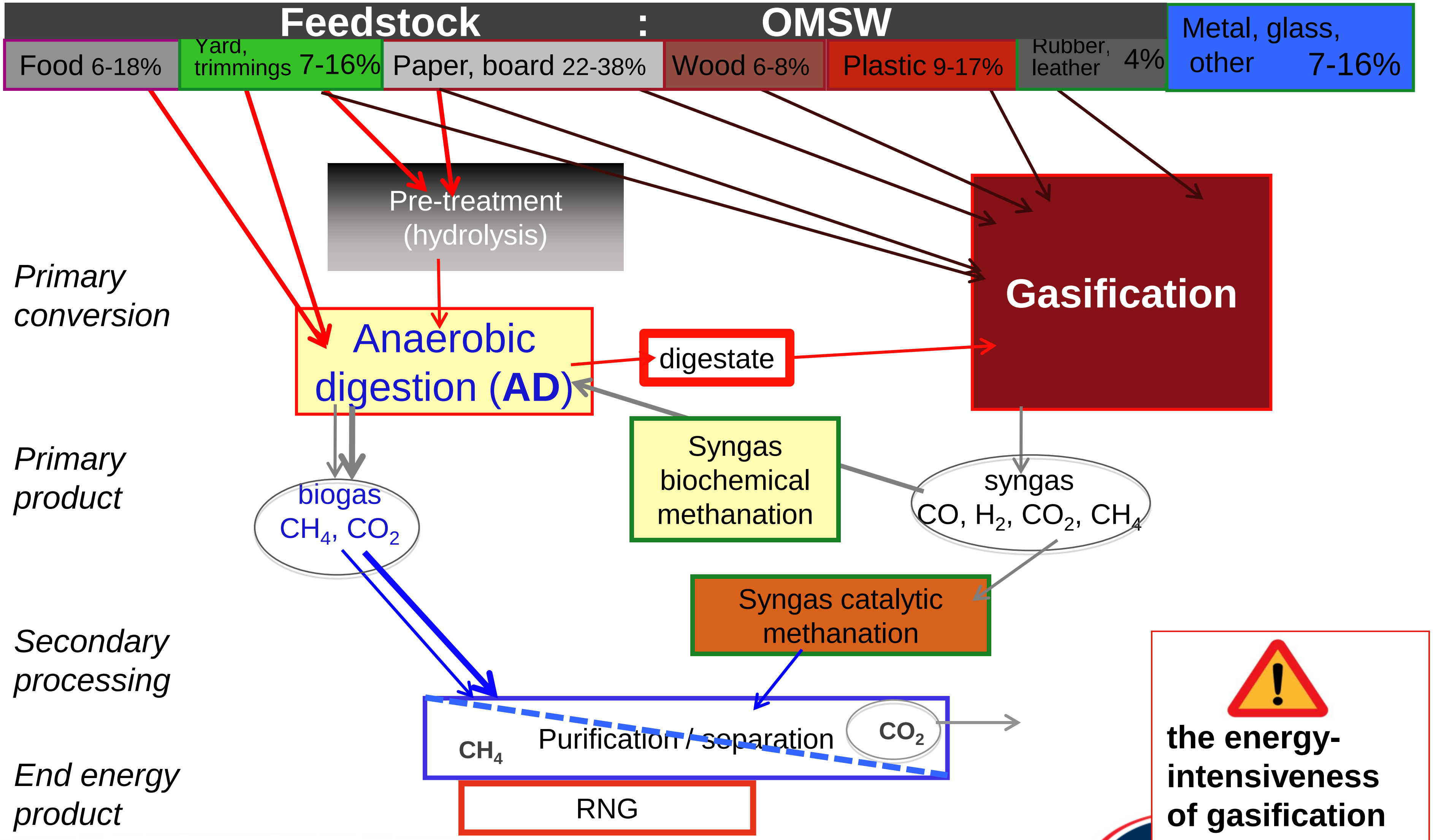
Conclusions / Prospectives, for large scale

For similar mass transfer conditions and methane yields, the CO-consuming volumetric activity of BCR was twice that of GLR (also inoculated with anaerobic granules, and with comparable specific activities in the range of 9-10 mmol CO/g VSS·d).

Potential for large-scale syngas biomethanation is realistic
•in the hypothesis that mass transfer efficiency could be maintained at 80% at large scale, with a specific potential of 60 mmolCH4/gVSS·d (thermophilic, adaptation)
•productivity higher than 40 m^3 STP CH_4/m^3 reactor·d to be expected in a thermophilic UASB-like reactor retrofitted for syngas treatment.

Despite more limited (unstable), the CSTR yet remains a viable alternative since CSTR showed high bioactivity and gas-liquid mass transfer potential and will allow for integration of syngas biomethanation with solid biowaste anaerobic digestion.

Waste-to-energy platform → RNG



Feedstock : OMSW

Food 6-18% | Yard, trimmings 7-16% | Paper, board 22-38% | Wood 6-8% | Plastic 9-17% | Rubber, leather 4% | Metal, glass, other 7-16%

Primary conversion

Pre-treatment (hydrolysis)

Anaerobic digestion **(AD)**

digestate

Gasification

Syngas biochemical methanation

Primary product

biogas CH_4, CO_2

syngas CO, H_2, CO_2, CH_4

Syngas catalytic methanation

Secondary processing

CH_4 Purification / separation CO_2

End energy product

RNG

the energy-intensiveness of gasification may mitigate the net energy output

Thank you!

Questions – comments ?