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IEA Bioenergy

Biofuels & Bioenergy: A Changing Climate
August 23-26, 2009
Vancouver, BC, Canada

ANAEROBIC DIGESTION AS A BIOFUEL PRODUCTION TECHNOLOGY FROM CROPS

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AD : yields - in theory

AD can use many different input streams, carrying the majority of the “electron freight” into methane independent of the chemistry of the feedstock (virtually all organics, but lignin)

Theoretical biochemical methane potential, from elemental formulas :

CARBOHYDRATES : $(CH_2O)_n \rightarrow n/2\ CH_4 + n/2\ CO_2$

$Y_{CH4} = 0.37\ Nm^3$ / kg sugar

PROTEINS : $C_{3.12}H_{4.94}ON_{0.82}S_{0.03} + 2\ H_2O \rightarrow 1.61\ CH_4 + 1.51\ CO_2 + 0.82\ NH_3 + 0.03\ H_2S$

$Y_{CH4} = 0.51\ Nm^3$ / kg protein

FATS : $C_8H_{15}O + 3.74\ H_2O \rightarrow 5.62\ CH_4 + 2.38\ CO_2$

$Y_{CH4} = 1\ Nm^3$ / kg fat

R. Braun. 2007. In: Improvement of crop plants for industrial uses (Ed. R. Paolo). Springer, Dordrecht, Netherland pp. 335-416

AD : yields - in practice

Feedstock	Conversion %	Methane Yield Nm^3 CH_4/wet t. (/dry t.) add
MSW-OF	50-70	100 (350)
Secondary sludge	30-60	70 (318)
Slaughterhouse residue	60-85	140 (550)
FOG	> 80	ND (1010)
Bovine manure	33	25 (~115)
Switchgrass	30-75	162 (377)

(1) Frigon & Guiot. 2005. Water Sci. Technol. 52(1-2):561-566
(2) Kabouris et al. 2008. Wat. Res. 80(3):212-221
(3) Salminen and Rintala. 2002. Wat. Res. 36(13): 3175-3182

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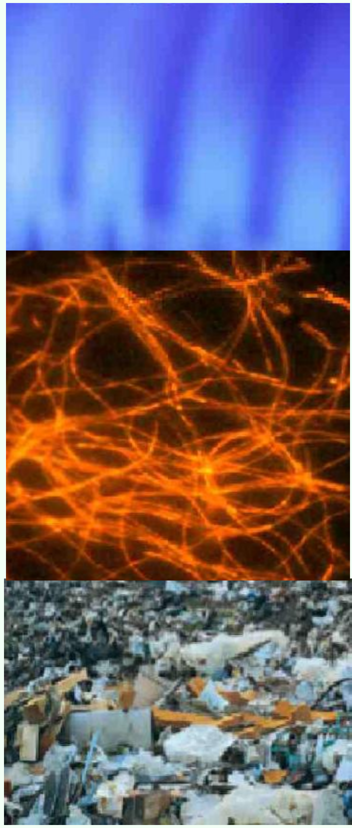
AD enhancement
Limiting step / Hydrolysis

Integration of hydrolytic pretreatment techniques

- **soft chemical options** (ammonia, dilute acid, sulfur dioxide, soda, lime [slower])
- **enzymatic hydrolysis**
  - commercial enzymes (dosage **optimization** for high yields with low enough costs)
  - developing **new enzymes**, namely in the thermophilic range



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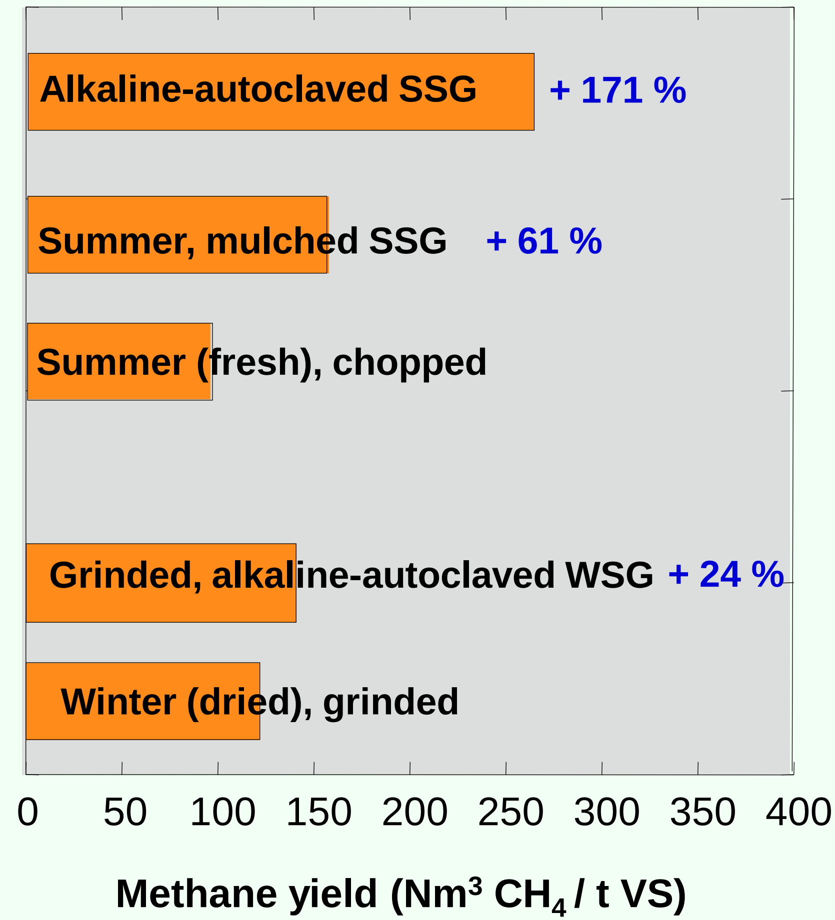
Thermochemical pretreatment

switchgrass

- Intensive mechanical pre-treatment: 1.6 X CH_4
- Mechanical + chemical: ~ 3 X CH_4
- Better fresh than dried
- Conversion: around 74% of biodegradable organics



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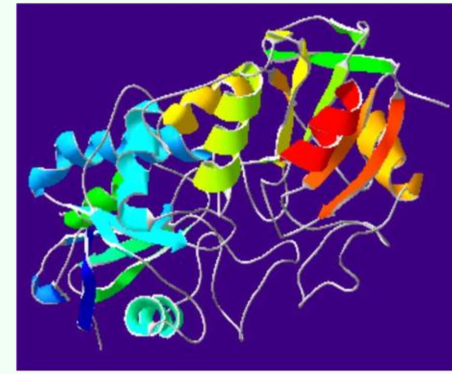
Enzymatic pretreatment



summer harvested switchgrass

Enzymes	Increase in methane yield	
Control 160 NL_{CH4}/kgVS added	Enzyme only	Enzyme & NaOH
Lignin peroxidase	+29 %	+5 %
Mn peroxidase	+42 %	+22 %
Control 190 NL_{CH4}/kgVS added	Low dosage	High dosage
Pectate-lyase (lo 1260 U; hi 6310 U)	No	+40 %
Poly-galacturonase (lo 10 U; hi 50 U)	No	+72 %

Positive effect of enzyme, no further improvement with NaOH, when compared with control SHS + NaOH

Significant impact only at high enzyme dosage.

Optimization needed, as well as cost-effectiveness analysis.

AD COST/PROFIT

Per ton of MSW-OF

Conversion by AD (%)	50	80	
Methane potential (Nm^3/ton)	63	101	
Electricity generated (kWh/ton)	182	271	
Commercial value ($/kWh)	0.147		
Revenue from energy produced ($/ton)	+ 23	+ 34	
Tipping fees ($/ton)	+ 46		
GHG reduction (t eCO_2/ton)	1.30	1.94	
Revenue from CO_2 credit (@ 5$/ton eCO_2) ($/ton)	+ 6	+ 10	
Capital & operation AD ($/ton)	– 75	– 86	– 75
Overcost [–]/benefit [+] ($/ton)	0	+ 3	+ 14

Digestion: Dryness : **28%** – **VS/TS :** 90% – **Yield : 0.5** Nm^3 CH_4 / kg SV degraded

Conversion to electricity : 9.6 kWh/Nm^3 CH_4
Efficiency : 30% – Cost: 0.8 ¢/kWh

GHG reduction based on
- **2.35 t eCO_2/ton landfilled w/LFG collect (baseline)**
- **0.85 t eCO_2/dt AD**
- **GHG displaced : 1.8 t eCO_2 displaced/1000** Nm^3 CH_4 **combusted**

AD unit cost (capital [7 yr] + operation) : 30 ↔ 270 $/ton ⇢ 75 $/ton (50 000 ton/yr capacity)

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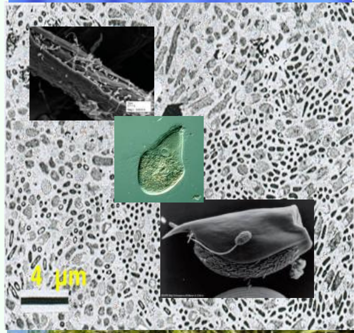
AD *in situ* enhancement
Limiting step / Hydrolysis

Target : *consolidated bioprocessing* (CBP) ~ hydrolysis & fermentation/1 step

Paradigm : Capitalize on robustness of AD communities : "Communities that carry out methanogenesis have evolved over millions of years, and in the interest of efficiency, it is likely best to leave them intact." Buckley & Wall. 2006. Microbial energy conversion. A Report of the American Academy of Microbiology

- **Microbial consolidation of naturally occurring consortia**
  - **in practice,** e.g. retrofit industrial digesters on the rumen model (highly efficient in methane production from lignocellulosic feed)
    - e.g. controlled microaerobic conditions
    - e.g. adding fungi (anaerobic, aerobic)
    - e.g. retention of limiting microorganisms (uncouple HRT & SRT)



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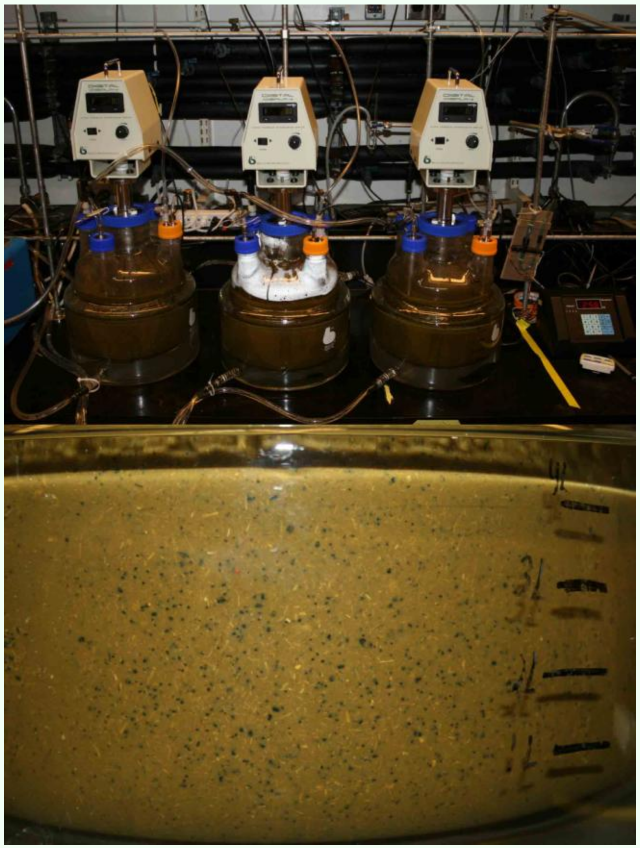
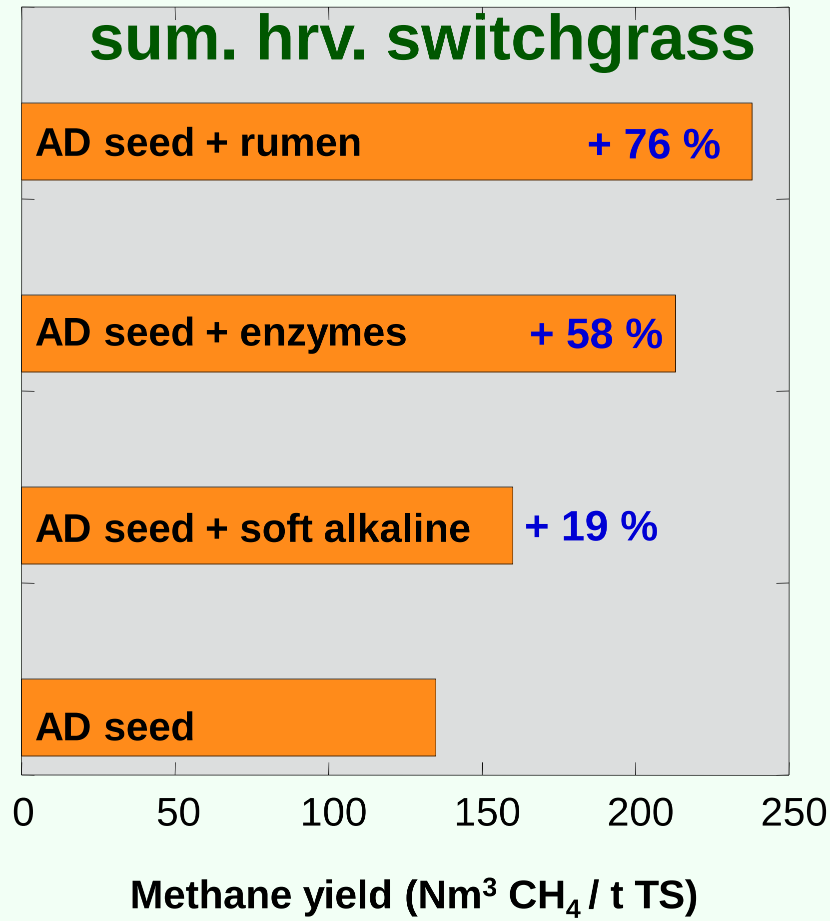
Angelidaki & Ahring. 1992. *Appl. Microbiol. Biotech.* 37: 808
Stams et al. 2003. *Adv. Biochem. Engin. Biotechnol.* 81:151
Mata-Alvarez, Macé & Llabrés. 2000. *Bioresource Techn*. 74: 3

Microbial consolidation





Biomethane *vs* bioethanol / switchgrass

Methane yield		Net energy	
(L /ton VSS_{added})	(m^3/ha)	(GJ/ha)[a]	(MWh/ha)[b]
205	1811	49.7	5.0
315[c]	2783	83.3	8.3

[a] 13 GJ removed from the gross energy yield for growth ad havest of switchgrass, and operation of the digester.
[b] Net electricity generated at 30% efficiency (2.88 kWh/m^3 STP CH_4).
[c] SHS with the best pre-treatment option (mix of pectinases).

Ethanol yield		Net energy
(L /dry ton)	(GJ /dt)	(GJ/ha)
280 [a]	6.6	63
340 [b]	8.0	76

[a] McKendry et al. 2002
[b] Iogen 2009 http://iogen.ca/cellulosic_ethanol/what_is_ethanol/process.html

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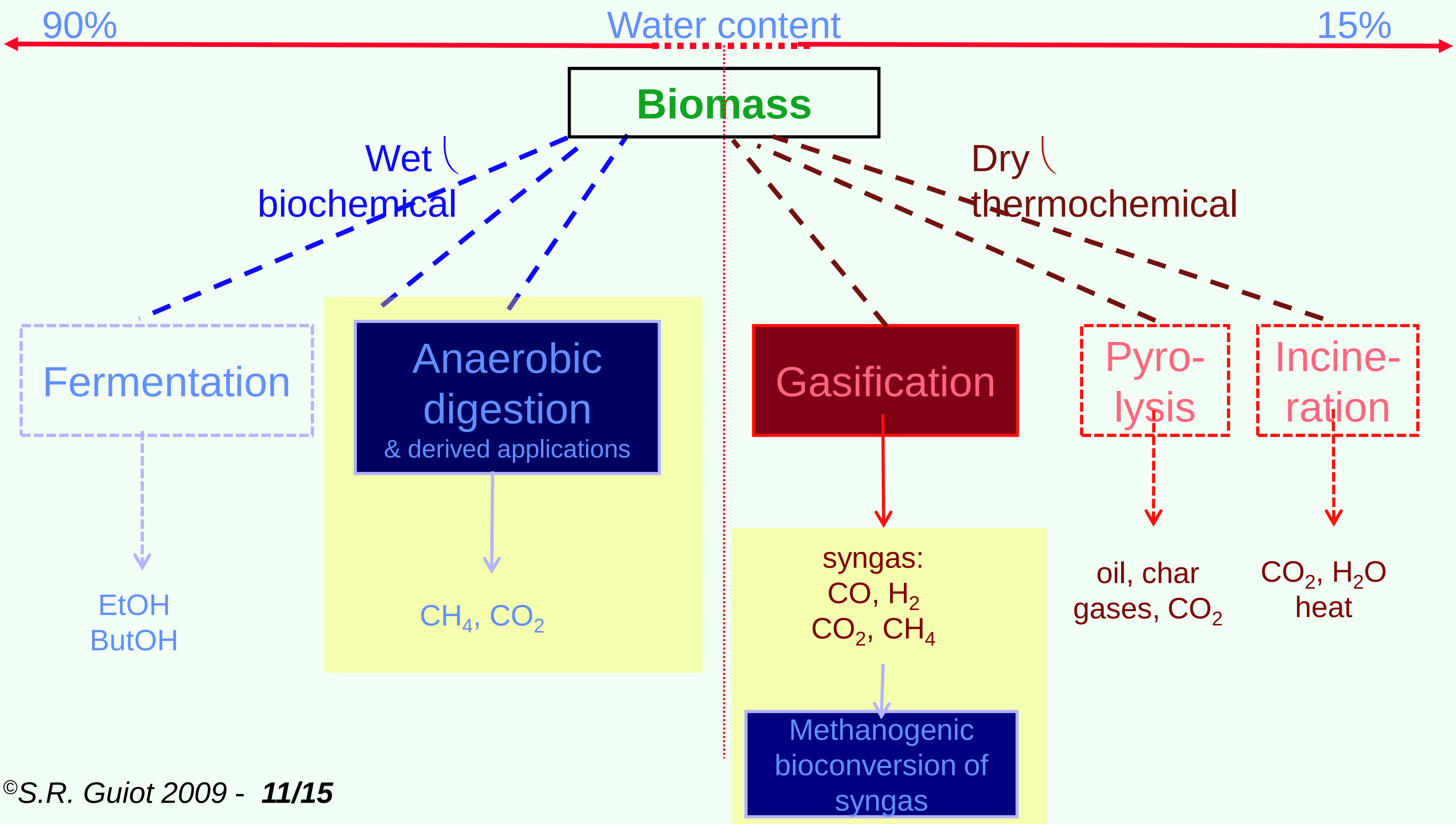
Dry biomass "biomethanisation"



Syngas methanogenic bio-upgrading

- **Carboxydotrophic methanogenesis, to convert syngas compounds into methane**
  - ✓ **Direct :**

    Methanobrevibacter, Methanococcus, *Methanobacterium* spp.

    - **CO_2 + 4 H_2 → CH_4 + 2 H_2O** ($\Delta G°'$ = -245 kJ/mol CO_2)

    Methanobacterium thermoautotrophicus, *Methanothermobacter wolfeii* (55-65ºC)

    - **CO + 3 H_2 → CH_4 + H_2O** ($\Delta G°'$ = -150 kJ/mol CO)
    - **4 CO + 2 H_2O → CH_4 + 3 CO_2** ($\Delta G°'$ = -53 kJ/mol CO

  - ✓ **Indirect** (consortium, with hydrogenogens, homoacetogens, and/or acetoclasts) :
    - **2 CO + 2 H_2 → CH_4 + CO_2**
    - **4 CO + 2 H_2O → CH_4 + 3 CO_2**

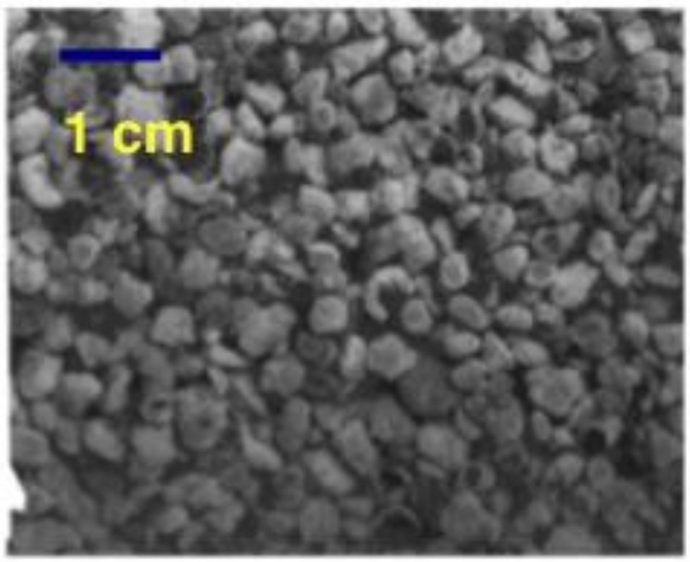
Theoretical yield

- ➢ 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

Syngas methanogenic bio-upgrading (2)

An approach closer to industrial application :

- *to use industrial wastewater-treating anaerobic granules that have the potential to consume CO*
- *a source of microbes already adapted to harsh conditions that would prevail with crude syngas*
- *massively available, free/low cost*



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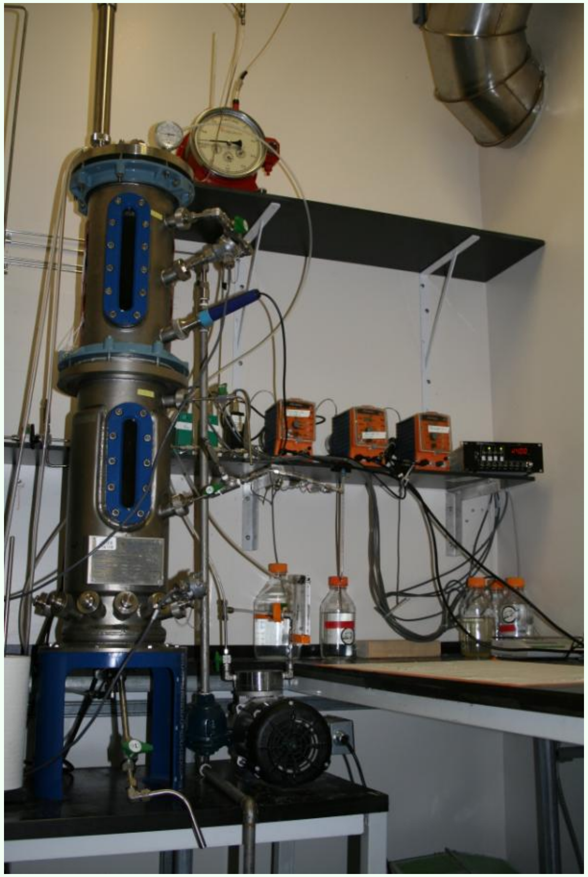
Syngas methanogenic bio-upgrading (3)

Preliminary assays
- *in a closed-loop gas-lift reactor*
- *on the continuous mode*

GAS : 30% CO, balance N_2 ; p_{CO} 0.4 atm
•NO RECIRCULATION : CO transfer efficiency : 4%
•RECIRCULATION RATIO 5:1 : CO transfer efficiency : 51%
•RECIRCULATION RATIO 10:1 : CO transfer eff. : 70%
RECIRC. RATIO 5:1 ; p_{CO} 0.6 atm : CO transfer eff. : 68%
CONVERSION EFFICIENCY / SOLUBLE CO : 100%
CH_4 YIELD (mol CH_4/mol CO) : 24-25%



Challenge : to alleviate
gas/liquid mass transfer limitations

POTENTIAL, W/O MASS TRANSFER LIMITATION : > 30 m^3 $CH_4/m^3_{rx}.d$

Take home

- AD has the potential for an energy yield relatively high, when compared to other biofuels, depending essentially on the **hydrolysis effectiveness** (↑CH_4 yield)

- but AD to be attractive needs more incentives which are likely to be
  - ✓ **energy cost increase**
  - ✓ **government premiums granted for green power**
  - ✓ **CO_2 credits traded on a carbon exchange market**
  - ✓ **R&D: process efficiency enhancement and cost diminution**