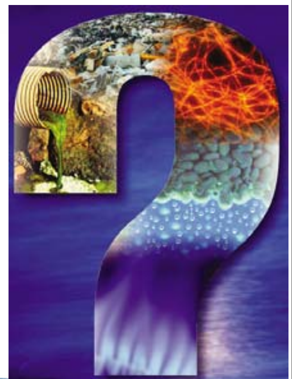
Energy Efficient Wastewater Treatment and Solid Waste Management, Edmonton, AB
April 20, 2011

WASTE-TO-ENERGY: ASSETS & LIMITS OF ANAEROBIC DIGESTION



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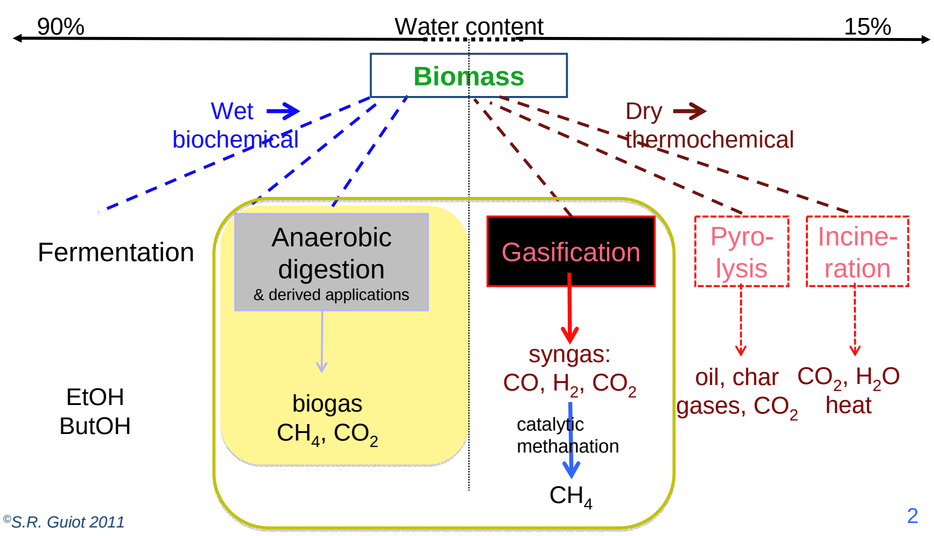
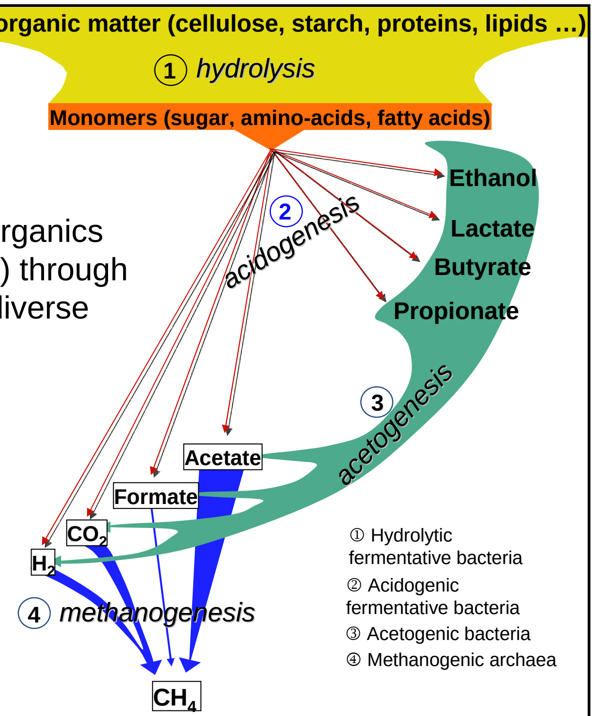
Waste-to-RNG : anaerobic digestion / gasification



Anaerobic digestion (AD)

- AD converts complex organics into biogas (CH_4 + CO_2) through the concerted work of diverse microbial groups
- Fundamentally, the reducing power of the pollution or waste is transferred from one microbial group to the other, to end up into the final product, CH_4



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Anaerobic digestion (AD) unique asset

Biomethane production can be carried out using **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)**. Methane is also relatively easy to harvest since **it distillates off by itself** from the liquid phase. Buckley & Wall. 2006. Microbial energy conversion. A Report of the American Academy of Microbiology.

Theoretical biochemical methane potential, from elemental formulas :

CARBOHYDRATES : $C_6H_{10}O_5 + H_2O \rightarrow 3\,CH_4 + 3\,CO_2$

Y_{CH4} = 0.42 Nm^3 / kg sugar

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

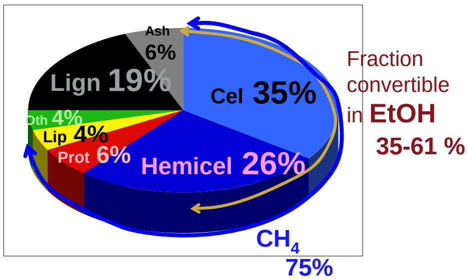
Y_{CH4} = 0.51 Nm^3 / kg protein

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

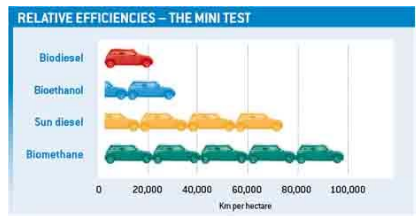
Y_{CH4} = 1 Nm^3 / kg fat

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

Biomethane *vs* bioethanol



T. Evans, Nat. Association of Agricultural Contractors (NAAC) Conference 2007, UK



SENSITIVE ISSUES

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AD yields : in practice

In practice, degradation efficiency hardly exceeds 60%, and Y_{CH4}, 0.3 Nm^3/kg VS added (except some residues (agro-food, slaugterhouse, FOG … > 80%)

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

✓ Limiting step = Hydrolysis

⇒ pre-treatment

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Nutrient balance

Substrates	C:N ≈ 20-30:1	C:P ≈ 250:1	Balance
OF-MSW	40:1 to 100:1	200:1	Small C, P surplus
Primary, secondary sludges	5:1 to 10:1	13:1 to 27:1	Large N, P surplus
FOG	>50 to 100:1	200 to 300:1	C surplus
Manure (pig, cow)	14:1 to 20:1	25:1 to 110:1	N, P surplus
Energy crop (switchgrass)	92:1 to 491:1	624:1 to 2344:1	Large C surplus

⇒ co-digestion

Shin and Park. 1989. Biotechnol. Let. 11(4):293-298
Frigon, Mehta & Guiot. 2011. Biomass Bioenergy, DOI: 10.1016/j.biombioe.2011.02.03

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Inhibition

- Inhibition by accumulation of acid, ↘ pH (organic overload/ unbalance fermentation/methanogenesis)

- Inhibition by ammonia in case of nitrogen surplus, ou production during digestion of proteins (slaughterhouses, manure)

$$\text{(HAc)} \xleftarrow{\text{pH}} Ac^- \qquad NH_4^+ \xrightarrow{\text{pH}} \text{(}NH_3\text{)}$$

The non-ionic form of the acid or ammonia is inhibitory

e.g. 300 mg/L acetate @ pH 5,5 **>** 5000 mg/L @ pH 7

⇒ **pH control and neutralization**

- Other inhibitors : copper sulphate and antibiotics

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H_2S

- Ubiquitous in anoxic systems
- From the reduction of sulfates and sulfites (SO_4^{2-}, SO_3^{2-}) by SRB to sulfides (S^{2-})
- Foul smell : detectable at 0.001 ppm in air
- Highly toxic
- Highly corrosive in humid biogas
- Complete inhibition of methanogens at [H_2S] > 200 ppm

⇒ **removal at the source**

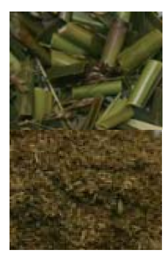
•D.O. is the most effective inhibitor of H_2S formation: returns almost all sulfides to their initial oxidized form
•Small [O_2] are not detrimental to AD

IMPROVEMENTS

AD *ex situ* enhancement

- **Pre-treatment** (vast array of options)
  - Thermochemical options (steam explosion; ammonia explosion, pulsed-electric-field, ultrasound ….)
  - Soft chemical options (dilute acid, sulfur dioxide, soda, lime, ozone, peroxide …)
  - Enzymatic pre-treatment

Model feedstock : switchgrass



- ✓ alkalization alone : $Y_{CH4/Vsad}$ **+19 %**
- ✓ alkalization at high temperature (120 ºC) : **+ 64 %**
- ✓ microwave irradiation (10 min at 120 ºC) : **+ 10 %**
- ✓ peroxidases : lignin (LiP) or manganese peroxidase (MnP) : **+ 29** & **+ 42 %**
- ✓ combination of alkali and MnP : **+ 91%**
- ✓ combination of pectinases (pectate-lyase and poly-galacturonase) : **+ 101 %**
- ✓ cellulases **+ 21%**

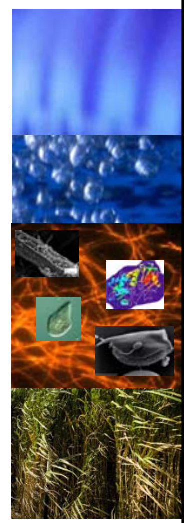
Enzyme pre-treatment seems promising, whereas they are not yet commercially available at a competitive cost

AD *in situ* enhancement

Conventional

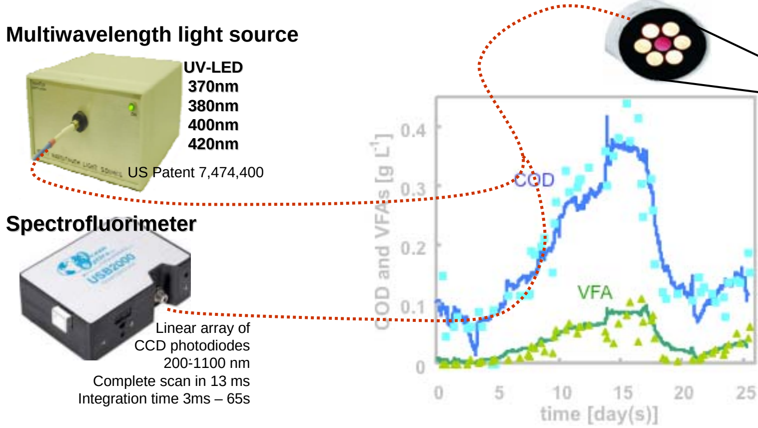
- On-line control
- Temperature
- Retention of limiting microorganisms (dissociate liquid RT from solid and microbes RTs)

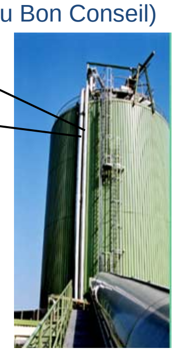
Advanced (consolidated bio-processing ~ CBP)



On-line control

On-line control VFA/liquid / multiwavelength spectrofluorimetry (ex. cheese factory, Agropur, Notre-Dame du Bon Conseil)





Compact
Low cost compared to NIR systems and titration

Temperature

Temperature ranges : psychrophilic (7-25 ºC), mesophilic (27-37 ºC), thermophilic (55-60 ºC)

- ✓ Digestion rate increases with temperature (higher growth rate of microorganisms => higher loads or reduced retention time
- ✓ Efficiency of digestion (% degradation) increases with temperature

Biodegradability improvement

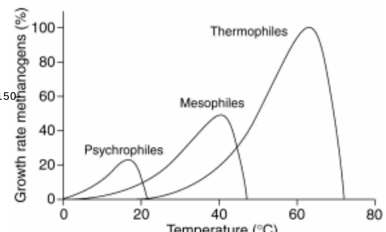
Biosolids (**WAS**) : +20%

Y. Kiyohara, T. Miyahara, O. Mizuno, T. Noike, K. Ono (2000) Water Environment J. 14(2):150-154

OF-MSW : +7% to 35%

J. Mata-Alvarez, S. Macé, P. Llabrés (2000) Bioresource Techn. 74:3-16

↗ deg. proteins(++), lipids(+)



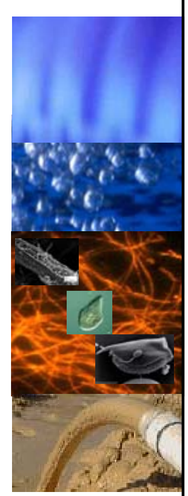
Wiegel J. (1990) Temperature spans for growth: hypothesis and discussion. FEMS Microbiol. Rev. 75:155–170.

C B P

Hydrolysis & fermentation/1 step

Microbial consolidation of naturally occurring consortia

- e.g. co-digestion
- e.g. bioaugmentation → adding protozoa and fungi (anaerobic, aerobic) (cellulases, xylanases and lignases)
- e.g. controlled micro-aerobic conditions (stimulation of added or indigenous hydrolytic aerobic or facultative microorganisms)
- e.g. electrochemically-assisted AD (e.g. electrolysis integrated within AD)



Yang & Wyman. 2008. *Biofuels, Bioprod. Bioref*. 2: 26-40
Lynd et al. 2005. *Curr. Opin. Biotechnol*. 16: 577–583
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

Co-digestion

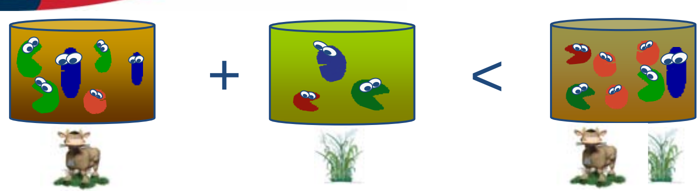
	D 1: dairy manure	D 2 : manure + switchgrass (20% wet ratio)
OLR kg TVS/m^3_{rx}.d	2.1	3.0
TVS degradation efficiency	35%	44%
Yield Nm^3 CH_4/kg TVS added	0.12	0.15
Q_{CH4} Nm^3 CH_4/m^3_{rx}.d	0.32	0.52 **(+63%)**

At a 500 m^3 scale, co-digestion would yield a surplus of 7 GJ/d (i.e. + ~ $30K/yr)

Other advantages : nutrients balance (C:N:P 100:1.6:0.54 for switchgrass versus C:N:P 100:3.6:1.15 for mix) ; dilution

Co-digestion: microbial consolidation

Co-digestion = enhance bacterial cooperation



Substrate (C:N:P balanced, 100:4:1)	Yield (NL_{CH4}/kg TVS added)
Switchgrass (mulched)	**152**±1
Cattle manure	**315**±19
Switchgrass/manure mix (49%/51% dry wt)	
Weighted sum / separately	***235*** *±9*
Actual mix in co-digestion	**288**±31 **(+23%)**

Adapted microorganisms-rich substrates → re/co-inoculate the digester & help to digest target substrate. Cattle manure (cellulolytic & fermentative bacteria, methanogens). Silage (lactic acid bacteria, fermentation bacteria).

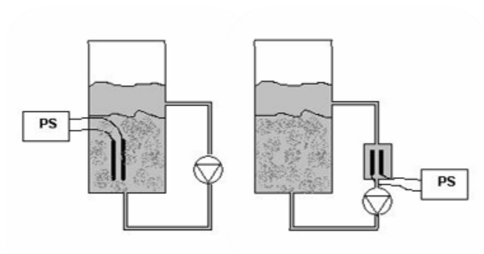
Micro-aeration

Model feedstock : switchgrass

- ✓ lab scale CSTR : HRT 23 days / OLR 3 g VSS/L_{rxr}.d
- ✓ microaerobic conditions at < 0.5% O_2 / headspace
- ✓ biogas production : 2.2 $L.d^{-1}$ in the microaerobic digester against 1.8 $L.d^{-1}$ in the control digester
- ✓ stimulation of enzyme activities
  - ➢ cellulase : 155 in the microaerobic digester *vs* 131 $U.L^{-1}$: + 15%
  - ➢ feruloyl esterase : 4.85 in the microaerobic digester *vs* 3.82 $U.L^{-1}$ i.e. : + 27%
- ✓ facultative populations slightly triggered by microaerobic conditions

Electrolysis-enhanced-AD (eAD)

Concept: integration of electrolysis → O_2 + H_2



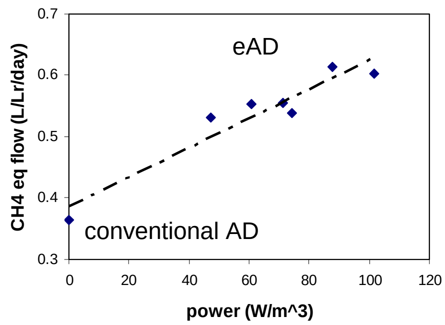
The eAD process uses ***water electrolysis*** at ***low*** applied ***voltages*** and ***current*** densities to facilitate biomethanization of complex organic materials. Electrodes can be installed directly in the anaerobic digester (reactor) or in the reactor external recirculation loop.

- Microaerobic conditions :
  - Stimulation of indigenous hydrolytic, aerobic or facultative microorganisms
  - H_2S removal from biogas
- Partial CO_2 sequestration (through CO_2+H_2 conversion to CH_4)
- Higher CH_4 yield

Tartakovsky & Guiot. Microbially-assisted water electrolysis for improving biomethane production. United States Patent Application 61/213,694. August 24, 2009

eAD (2)

Feedstock: mixture of switchgrass and cow manure / 6 L reactor
two pairs of electrodes, 100-200 mA
methane content, 40-48%, H_2 7-15%, oxygen 0-1.8%



Significant increase in methane production rate because of:

- exogenous H_2
- improved hydrolysis of solid organic matter
- H_2S inhibition (from 0.3% to < 100 ppm) alleviated
- catalytic effect of microbes on the electrochemical reactions (electromethanogenesis) : less power consumption (16-24 Wh/L-CH4eq i.e. 4-6 Wh/LH_2 *vs* > 7 Wh/LH_2 w/H_2O electrolysis)

net energy gain (ΔCH_4 produced *vs* energy consumed)

AD COST/PROFIT

Per tonne of MSW-OF

Conversion by AD (%)	50
Methane potential (Nm³/tonne)	56
Electricity generated (kWh/tonne)	161
Commercial value ($/kWh)	0.07
Co-generation (45% heat) $/GJ NG displaced	-
Revenue from energy produced ($/tonne)	10
Tipping fees ($/tonne)	+ 46
Capital & operation AD ($/tonne)	– 75
(Deficit)/benefit ($/tonne)	(19)

Digestion: Dryness : 28% - VS/TS : 80% - **Yield : 0.5** Nm³ CH_4 / kg SV degraded

Conversion : 9.6 kWh/Nm³ CH_4
Efficiency/electricity : 30% - Cost: 0.8 ¢/kWh
Efficiency/heat : 45% (value $5/GJ)

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

GHG reduction thanks to AD

- **GHG production**
  - GHG generated/landfill : 4.3 t eCO_2/wet ton OSW landfilled (based on UNEP baseline w/o LFG collect)
  - **Baseline in Canada : 2.35 t eCO_2/wet ton landfilled w/LFG collected and flared 8.4 t eCO_2/dry ton (dt) OSW**
  - **GHG generated/AD** (w/E @ 50%) **: 0.34 t eCO_2/dt OSW** (w/80 % VS)
    (considering that AD w/CH_4 recovery generates 0.86 t eCO_2/t VS degraded)

- **Reduction GHG emissions with AD (@ E 50% and 80% VS/OSW)**
  - **Direct : ≈ 3 t eCO_2/dt OSW** (considering that non-digested fraction, 5 t eCO_2 /dt as if landfilled)
  - GHG reduction by fossil fuel displaced : 2 kg eCO_2/Nm^3 CH_4 combusted
  - **Total reduction : 3.4 t eCO_2/dt OSW** (could be 8.5 non-digested fraction composted)

GHG : greenhouse gas
eCO_2 : CO_2-equivalent
OSW : organic solid waste (dt : dry ton)
LFG : landfill gas
E : VS degradation efficiency of AD
VS : volatile solids

AD COST/PROFIT

Per tonne of MSW-OF

Conversion by AD (%)	50		
Methane potential (Nm³/tonne)	56		
Electricity generated (kWh/tonne)	161		
Commercial value ($/kWh)	0.17		
Co-generation (45% heat) $/GJ NG displaced	5		
Revenue from energy produced ($/tonne)	30	30	[illegible]
Tipping fees ($/tonne)	+ 46		
Capital & operation AD ($/tonne)	– 75		
(Deficit)/benefit ($/tonne)	1		23

Digestion: Dryness : **28%** - **VS/TS** : 80% - **Yield : 0.5** Nm^3 CH_4 / kg SV degraded

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Efficiency/heat : 45% (value $5/GJ)

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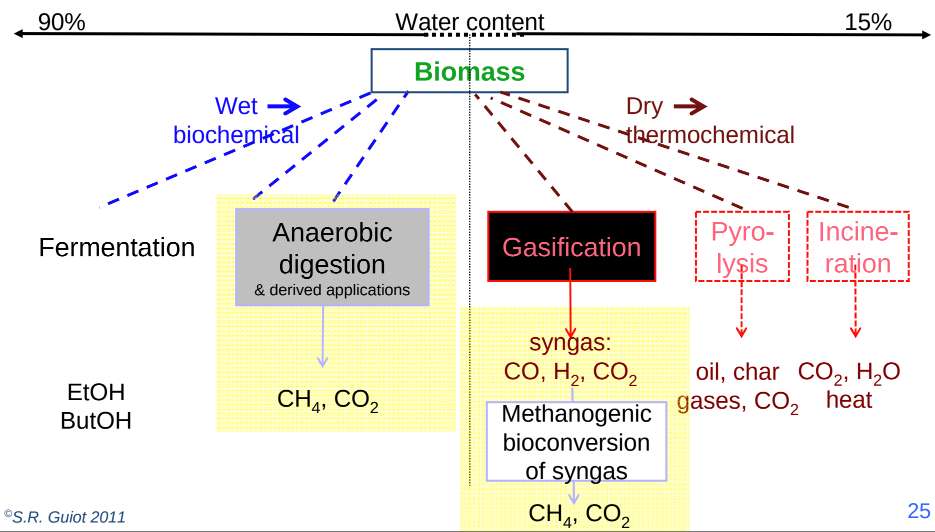
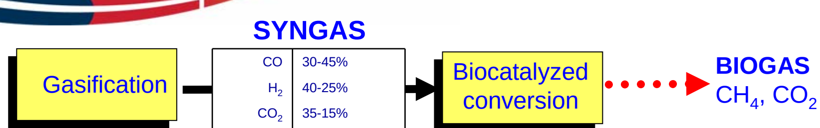
Dry biomass "gasification / biomethanation"

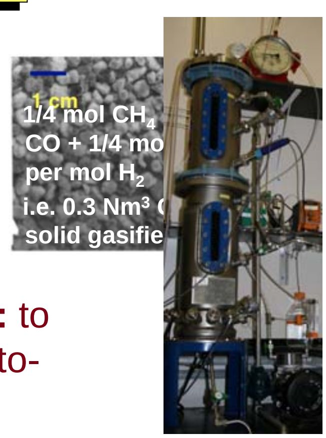


Syngas methanogenic bio-upgrading



CO	30-45%
H_2	40-25%
CO_2	35-15%
CH_4	10-1%
C2+, NH_3, H_2S, N_2, HCN …	

- **Carboxydotrophic methanogenesis, to convert syngas compounds into methane**
  - **$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$** ($\Delta G^{o\prime}$ = -245 kJ/mol CO_2)
  - **$CO + 3\ H_2 \rightarrow CH_4 + H_2O$** ($\Delta G^{o\prime}$ = -150 kJ/mol CO)
  - **$4\ CO + 2\ H_2O \rightarrow CH_4 + 3\ CO_2$** ($\Delta G^{o\prime}$ = -53 kJ/mol CO)



- **Engineering challenge : to significantly improve gas-to-liquid mass transfer rate**

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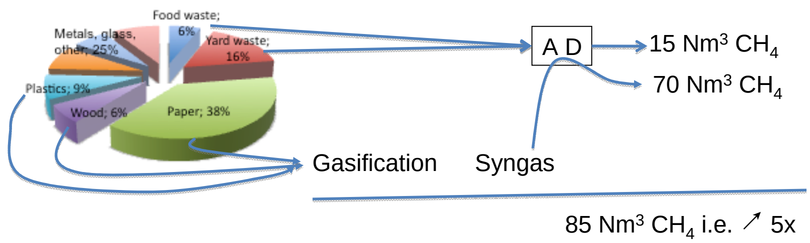
MUNICIPAL SOLID WASTE
AD + gasification

An approach close to industrial application: to use industrial waste/water-treating anaerobic populations (that have the potential to consume CO) and to retrofit AD facilities

MUNICIPAL SOLID WASTE
Composition



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BRI Biotechnology Research Institute
IRB Institut de recherche en biotechnologie

"There should be little doubt that by placing the focus of AD on the production of green energy and clean nutrients, the future of AD will be assured."
W. Verstraete, AD10, Montreal - 2004

Science at work for Canada

National Research Council Canada
Conseil national de recherches Canada
Canada