Air Liquide
creative oxygen

Metrology for bio-methane workshop

Activities on biogas and bio-methane within Air Liquide

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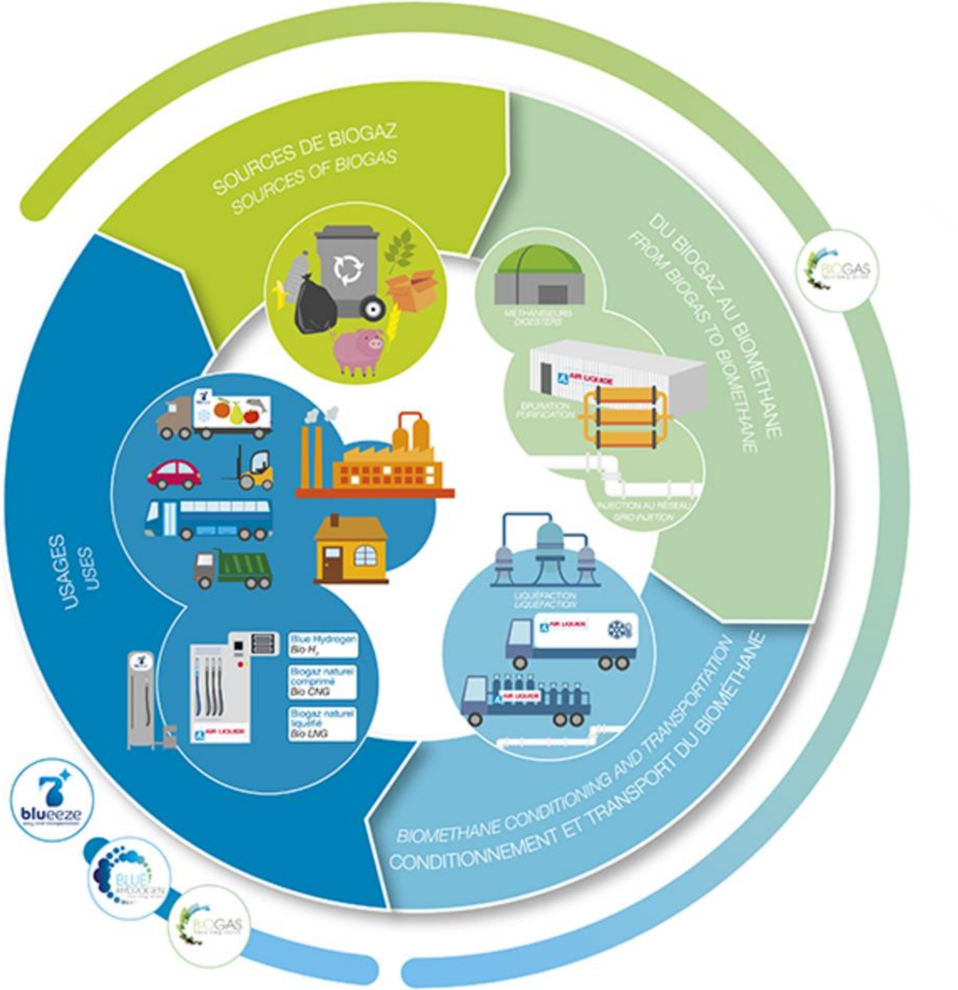

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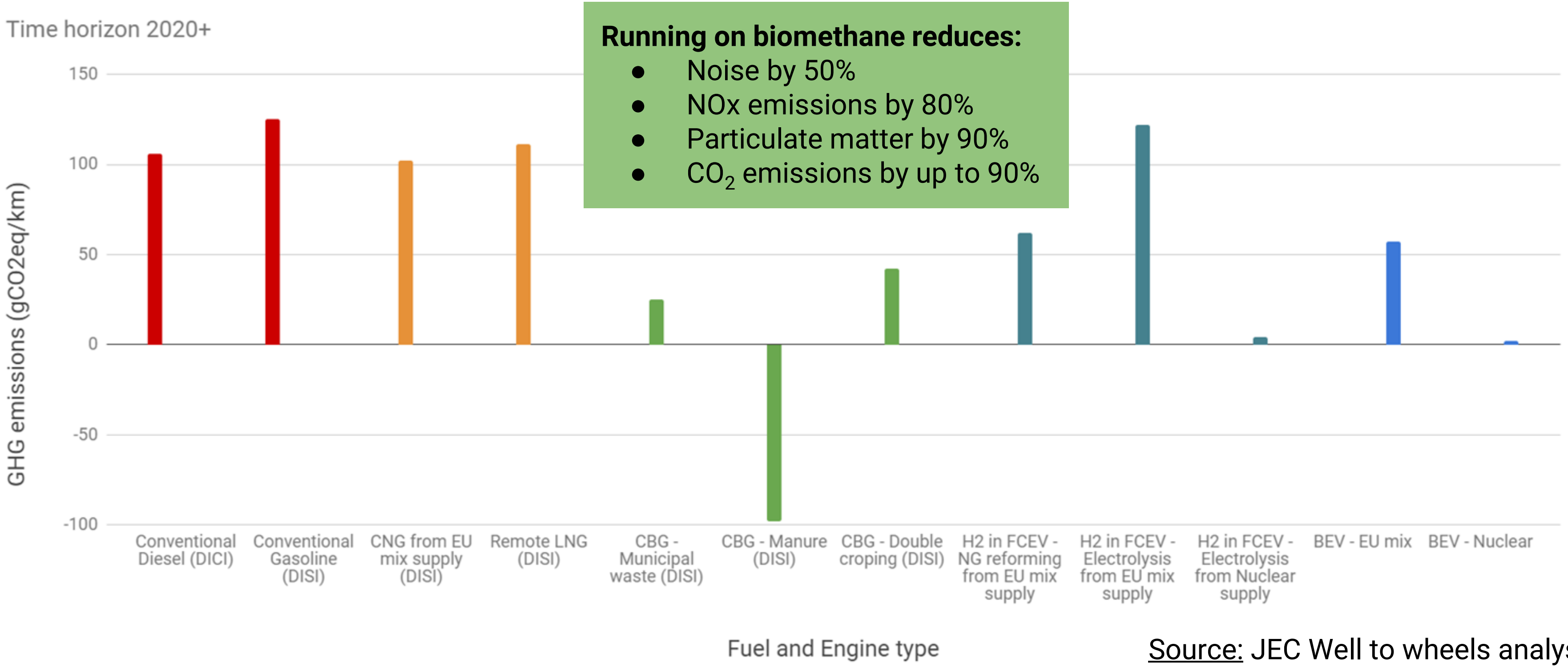
Air Liquide
A main player in bio-methane

LNG/CNG, a solution for clean transportation



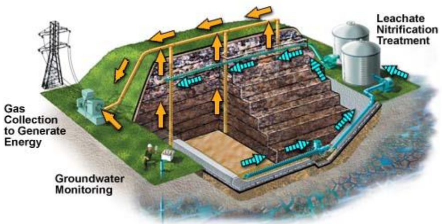
Running on biomethane reduces:

- Noise by 50%
- NOx emissions by 80%
- Particulate matter by 90%
- CO_2 emissions by up to 90%

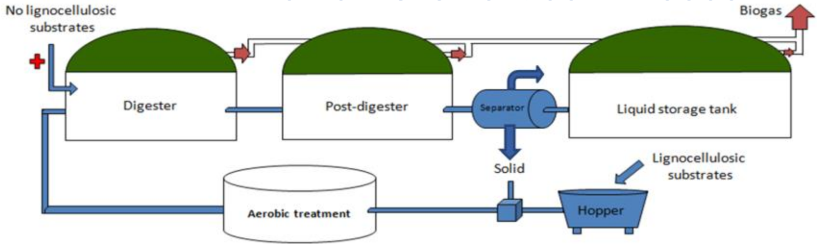
Source: JEC Well to wheels analysis Version 4a - March 2014

Biogas overview

LANDFILL



ANAEROBIC DIGESTION: CONTINUOUS



ANAEROBIC DIGESTION: BATCH

Air Liquide, a main player in bio-methane

50 biogas upgrading units worldwide

- Austria
- Brazil
- Chile
- China
- France
- Germany
- Sweden
- United Kingdom
- USA

10
More than 10 years of experience in biogas upgrading

30
More than 30 years of experience in membrane production

100
More than 100 years of experience in gas separation

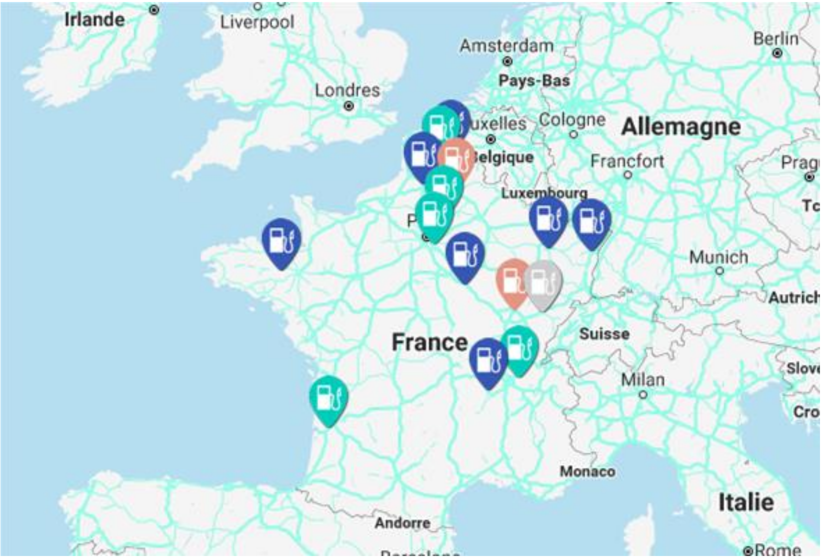
160,000
Air Liquide, world leader in biogas purification, with a capacity of 160,000 m³/h

Air Liquide, a main player in bio-methane

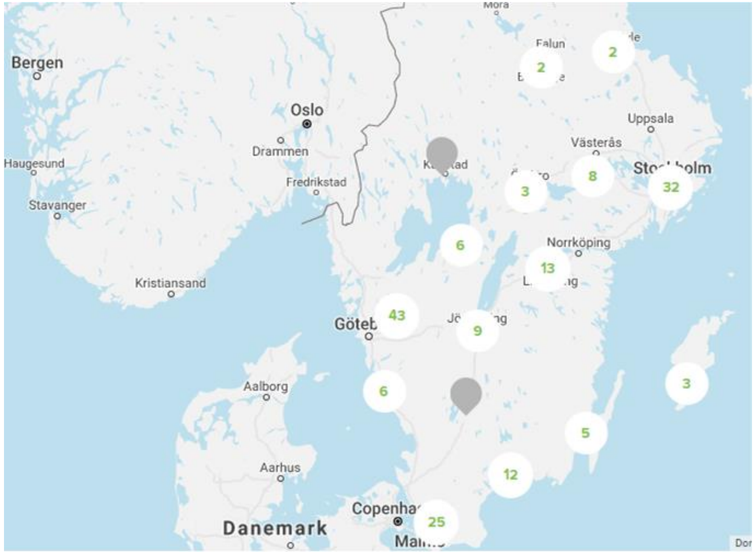
60 bioNGV filling stations in Europe

FordonsGas
an Air Liquide company

10 multi-energy stations (LNG/CNG/H_2 liq) in France and UK



Large grid of bioNGV filling stations in Sweden and Norway



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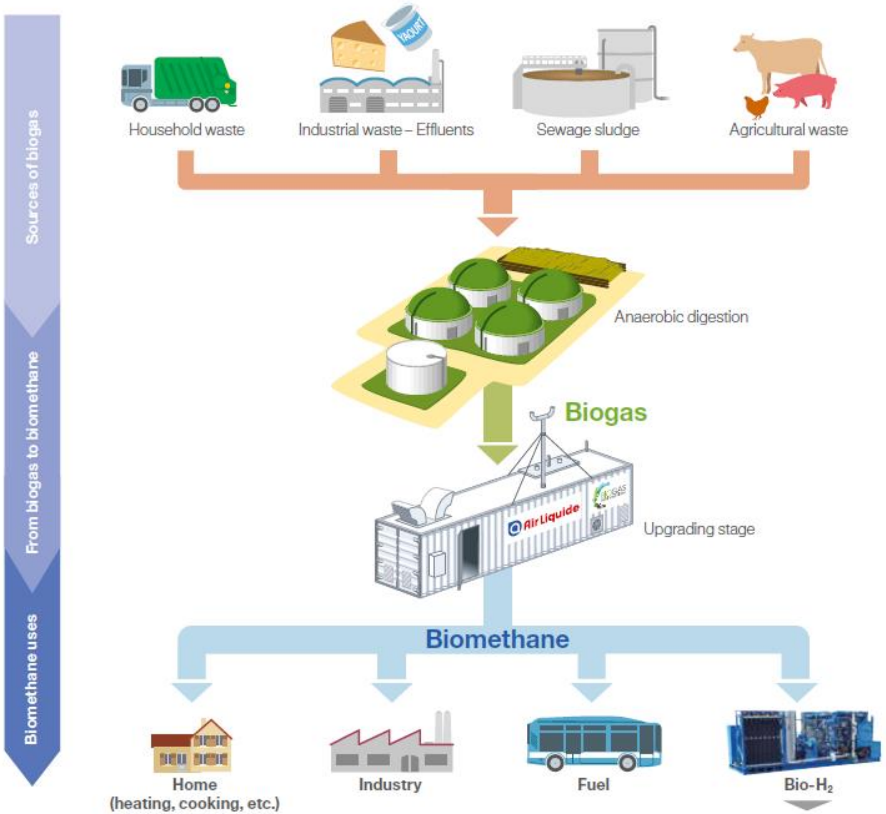
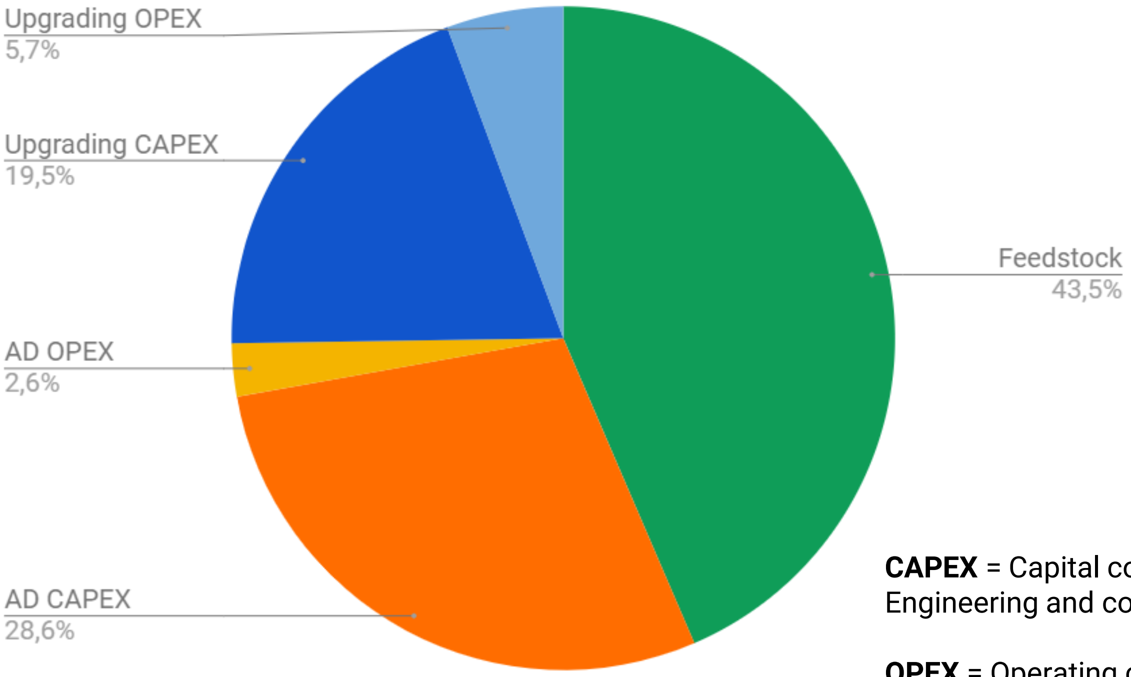
Bio-methane production cost, driven by CAPEX

From biomass to bioenergy



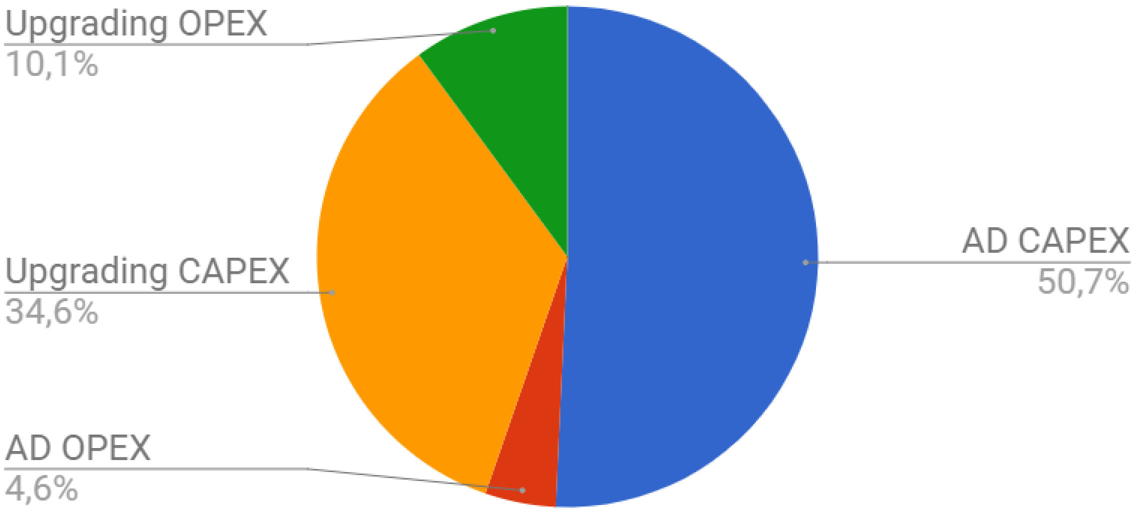
Bio-methane production from anaerobic digestion (AD): cost driven by feedstock cost



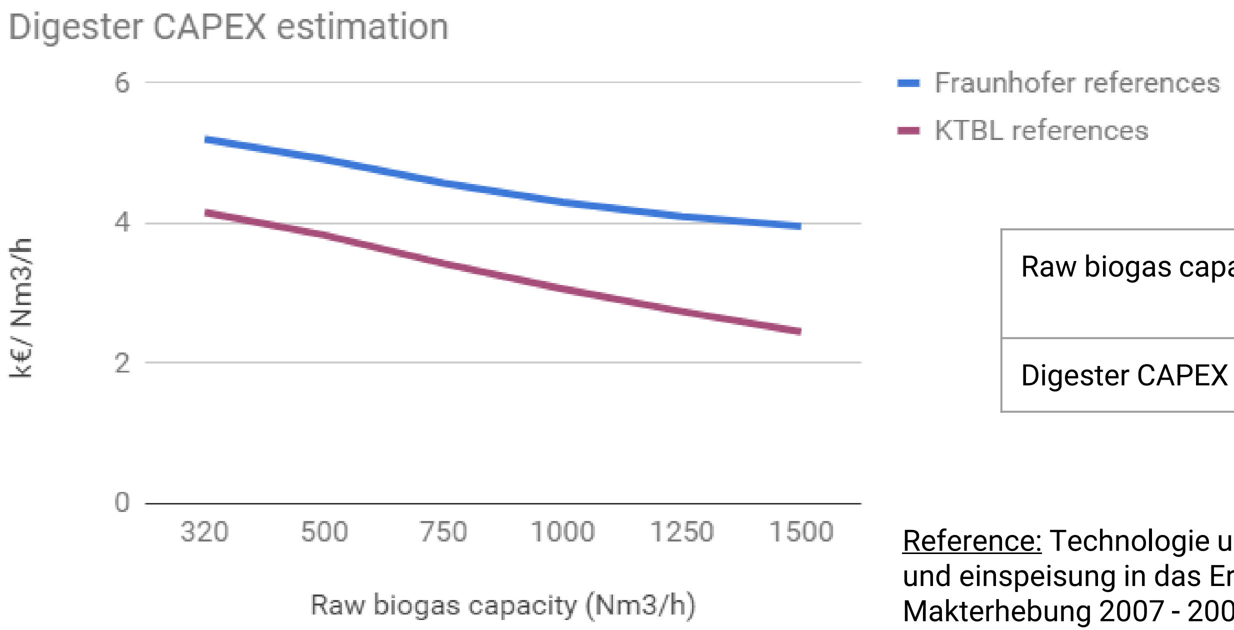
CAPEX = Capital costs = Investment depreciation + Capital cost
Engineering and construction included in investment

OPEX = Operating costs = Power costs

Bio-methane production from anaerobic digestion : cost leads by CAPEX (Except feedstock cost)



Digester CAPEX is not drastically reduced with size



Raw biogas capacity	400 Nm^3/h	1 400 Nm^3/h
Digester CAPEX	2.0 M€	5.6 M€

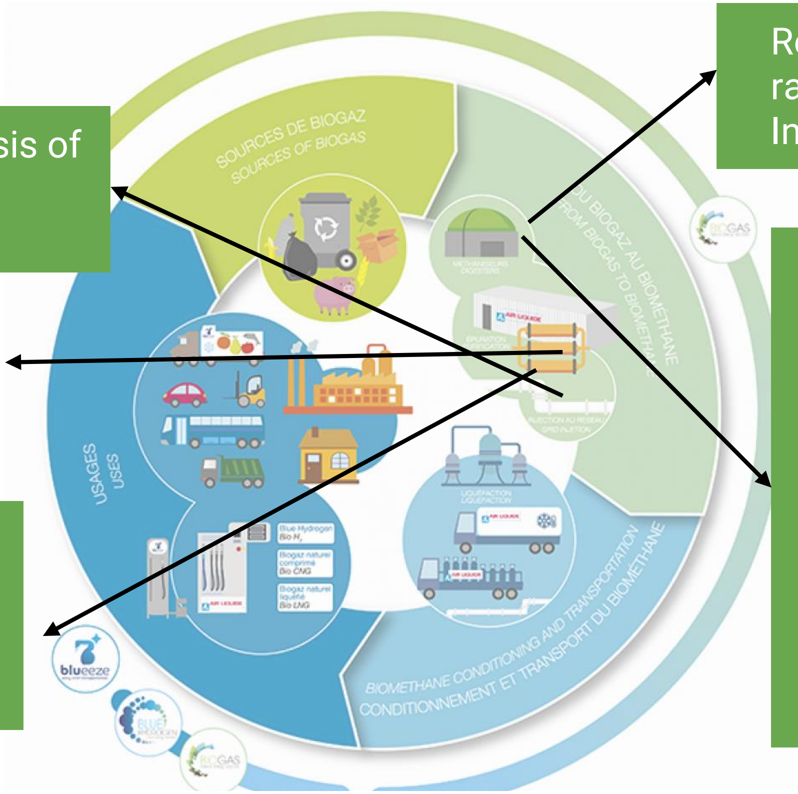
<u>Reference:</u> Technologie und kosten der biogasausbereitung und einspeisung in das Erdgasnet. Ergebnisse der Makterhebung 2007 - 2008, Fraunhofer Umsicht
KTBL database

Main scientific and technological hurdles to reduce CAPEX

Reliable sampling and analysis of impurities in bio-methane
In-line analysis

Technologies to remove impurities

Membrane improvement: new materials, new bundles, new operating conditions, new processes



Reliable sampling and analysis of raw biogas
In-line analysis

Pretreatment of lignocellulosic biomass: **Funghies**
Pretreatment of biomass: **Enzyms**
Innovative digestion technology

⇒ **To reduce bio-methane production cost**

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Biomass pretreatment to reduce digester CAPEX

Air Liquide

Enzyme pretreatment, to enhance hydrolysis
Higher and faster material degradations

Mainly **hydrolases**:

- ★ Carbohydrase
- ★ Lipase
- ★ protease

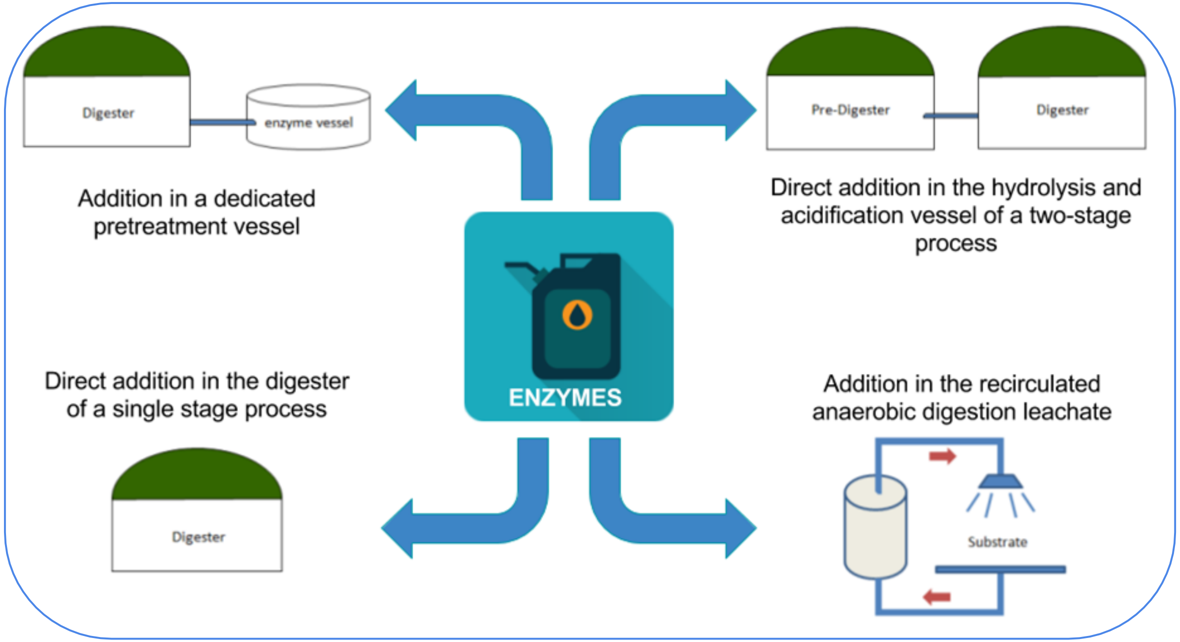
But also **oxidoreductases**:

- ★ Laccase
- ★ Peroxidase

Only interesting for substrate not easily biodegradable:

Lignocellulosic agricultural waste
Lignocellulosic rich OFMSW
Sludge
MSW in Landfill

Possible ways to apply



Biomass pretreatment, to increase productivity

Type of enzyme	Impact on feedstock recalcitrance	Potential impact on biogas yield	Existing commercial product for biogas
Protease	/		No
Lignase	+++		In development
Carbohydrase	+		Yes

Favor accumulation of inhibiting intermediates
degrade some essential enzymes
can attack microorganisms at their surfaces

Increase in methane yield **very promising**, BUT
AD inhibition & need of cofactors/redox med

Easiest to produce, no interference, no cofact/redox
med BUT process optimization requested

- ➔ Enzyme cocktail more efficient
- ➔ Impact on biogas yield depends on: feedstock, quantity/type of enzymes, process environment (T, pH, buffer) → Need tailoring

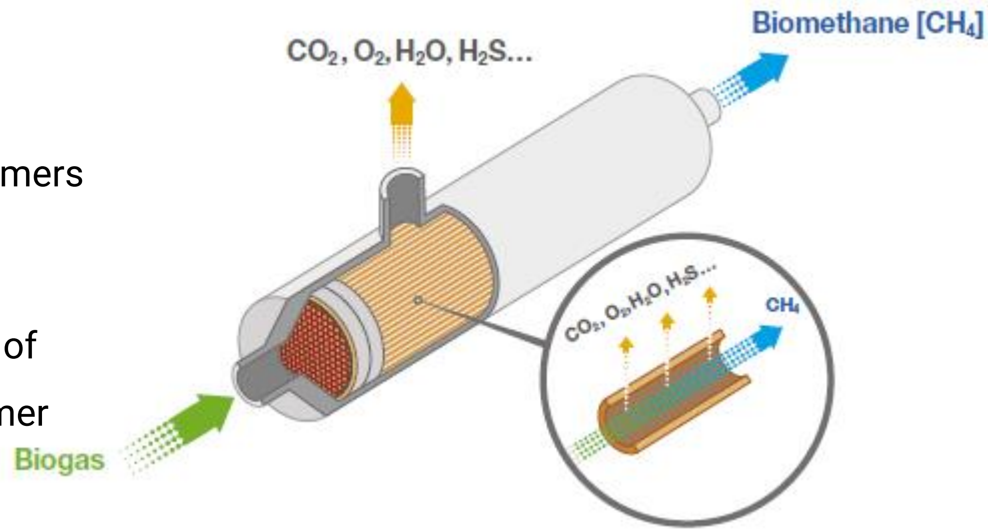
4

Innovative membrane solution to reduce upgrading CAPEX/OPEX

Biogas upgrading through membrane
Principles

- **Permeation by polymeric membrane fibers**
Impact of molecule size and affinity with polymers

- **Key parameters:**
  - **Selectivity:** preferential permeation of certain molecules through the polymer fibers porosity
  - **Permeance:** flux passing through the fibers porosity



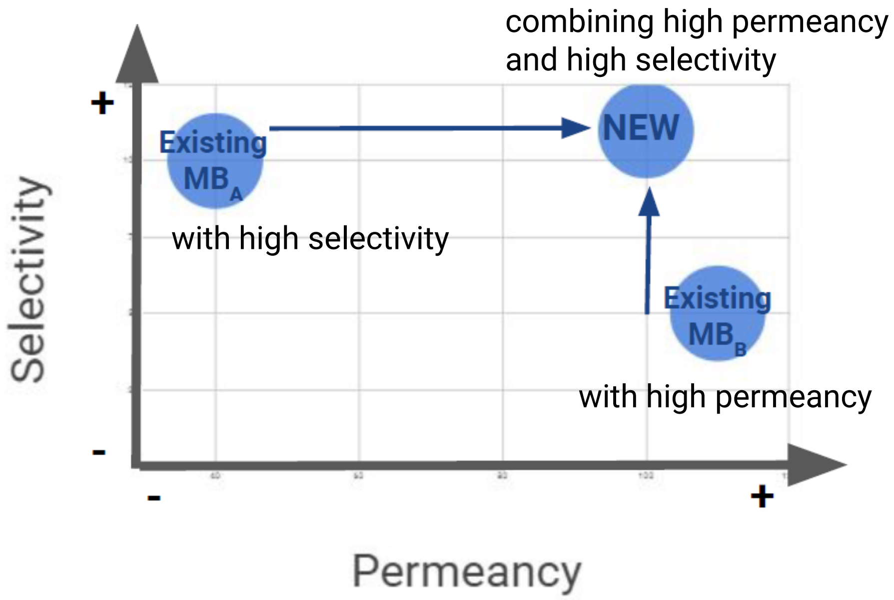
- **R&D for polymer improvement**

Innovative membrane solution developed and commercialized

- **Aim:** increase permeance while maintaining same selectivity

- **Results:**
  - **Permeance:** doubled
  - **Selectivity:** 10% increase

- **Consequence:** new MEDAL membrane commercialized since one year



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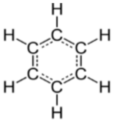
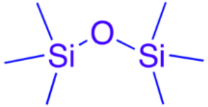
Analytical methods for biogas and bio-methane

Analytical method for the detection of impurities in biogas

Analytical method development on TD/GC/MS



- Volatil Organic Compounds
- Siloxanes
- BTEX



Gas sampling with adsorbent tubes

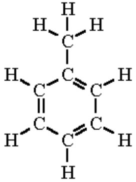
- Adsorbent tube selection vs chemical species
- Breakthrough
- check the performance of the tube on the sample biogas
- Implementation on site

Gas sampling on Tedlar bag

- Species conservation in bags
- Less selective technique

→detects all visible compounds by GC/MS

For both sampling modes standards prepared in biogas with dynamic methods



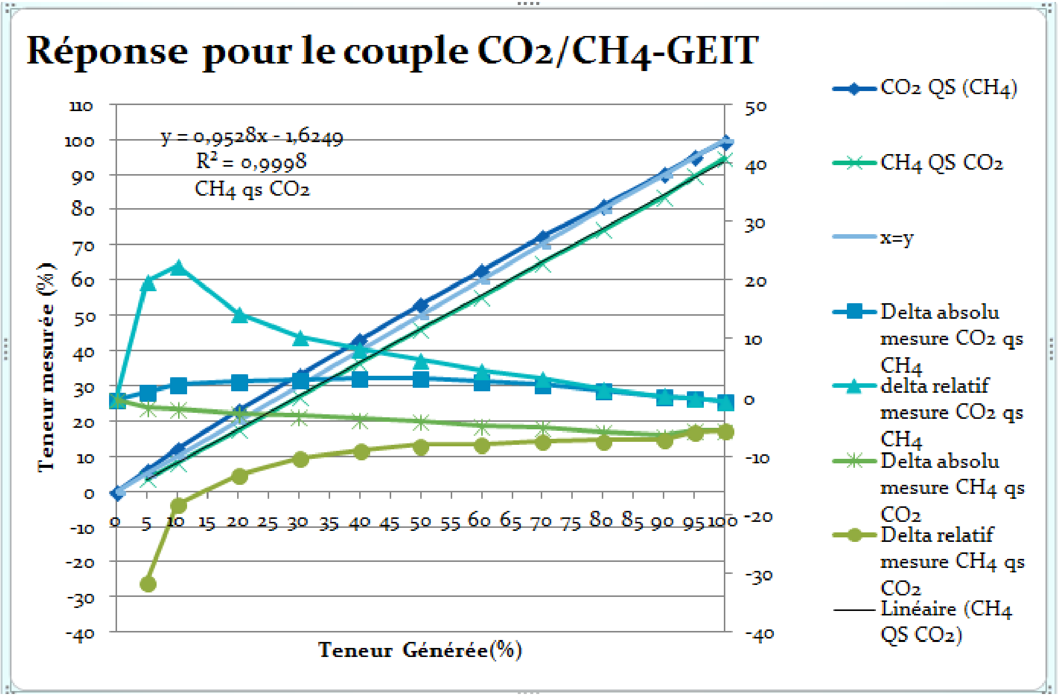
Analytical method for the detection of impurities in biogas

- **Maximum impurities measured in raw biogas :**

Family	Name	Maximal content measured by analysis
Siloxanes	Trimethylsilanol Hexamethyldisiloxane (L2) Hexamethylcyclotrisiloxane (D3) Decamethyltetrasiloxane (L4) Octamethylcyclotetrasiloxane (D4) Decamethylcyclopentasiloxane (D5)	47 000 µg/m^3 33 000 µg/m^3 3 100 µg/m^3 64 000 µg/m^3 2 700 µg/m^3 5 900 µg/m^3
BTEX	Toluene Ethylbenzene Xylene (m, p, o) Alphapinene 4-Ethyltoluene Limonene	110 000 µg/m^3 28 000 µg/m^3 48 000 µg/m^3 81 000 µg/m^3 14 000 µg/m^3 61 000 µg/m^3
Ketones	Acetone 2-Butanone Cyclohexanone	70 000 µg/m^3 97 000 µg/m^3 46 000 µg/m^3
Ethers	Ethyl acetate Tetrahydrofurane n-Butylacetate	40 000 µg/m^3 15 000 µg/m^3 20 000 µg/m^3

biogas composition: portable analyser

- **Evaluation of analysers used on site : example of NDIR**
- Matrix effect due to balance gas (CO_2 and CH_4)
- Systematic error if calibration is done in N_2 balance gas



Off gas sensor

Geotech

- **Context :** Lost of methane on off gas emission (about 2%) leading to:
    - Environmental issue (GWP of CH_4 = 25)
    - Processing and economical issue to estimate yield
- **Current methodology :** Geotech 3000 : expensive maintenance and low precision

- **Specifications :**

CO_2 [95% - 99%]	H_2O [0% - 1%]	T° [10 - 30°C]
CH_4 [0.2 - 5%]	Pressure [100 mbar]	ATEX
Air [0 - 2%]	Flow [20 - 2100 Nm3/h]	Price = 10k€

1. Benchmark on various providers, technologies and analyser
2. Command, installation & formation on each analyser
3. R&D evaluation of each technologies based on specifications
4. Test on industrial site
5. R&D and industrial report

Online bio-methane analysis: CH_4 analysers

- **Evaluation of on line sensors for methane concentration in biomethane**

Ultrasonic Sensor
Range 10 to 100%

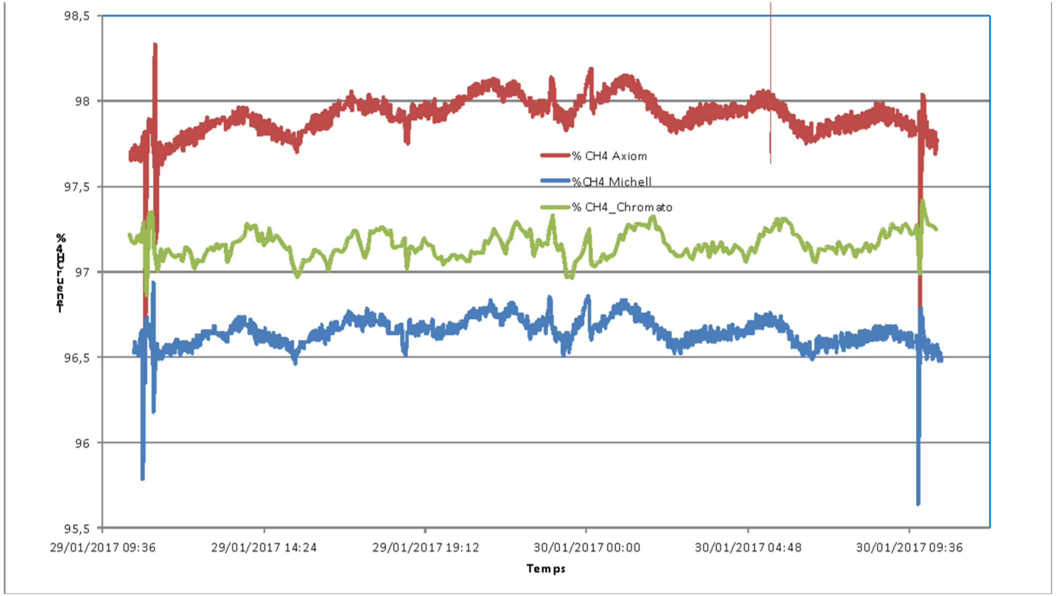
Thermal Conductivity Sensor
Range 0 to 100%

Online bio-methane analysis: CH_4 analysers

- Both sensors follow the same trend (comparable to GC)
- The standard deviation for all analyzers is the same around 0.2%
- Ultrasonic sensor gives a higher methane value and TCS always gives a lower methane value than the GC (<0.5%)
- Calibration of sensors for same matrix is critical for trueness
- Other component in the bio-methane (CO_2 or N_2) may impact the result

Evolution during 24 hours

Red: Ultrasonic sensor ; Green: GC ; blue: TCS



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Conclusion

Improvement of bio-methane production cost

- **Digester CAPEX reduction by enzyme selection**
  - Enzyme pretreatment to enhance hydrolysis
  - Increase of biomethane production from 17 to 41%
- **Upgrading CAPEX reduction by new membrane development**
  - AL innovative membrane: Doubled permeance & selectivity increase of 10%
  - Membrane surface reduction by 35%
- **Analysis development to reduce Upgrading CAPEX**
  - Online analysis of biogas composition
  - Off line analysis of impurities in biogas
  - Online analysis of bio-methane composition

Thank you for your attention

For further information

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