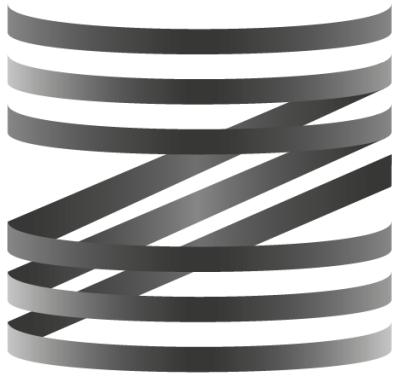

ZEOCAT-3D

This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 814548

Application of ZEOCAT-3D technology in the biogas industry and beyond

Themistoklis D. Sfetsas

BIOENERGIA NIGRITAS S.A.

ZEOCAT-3D

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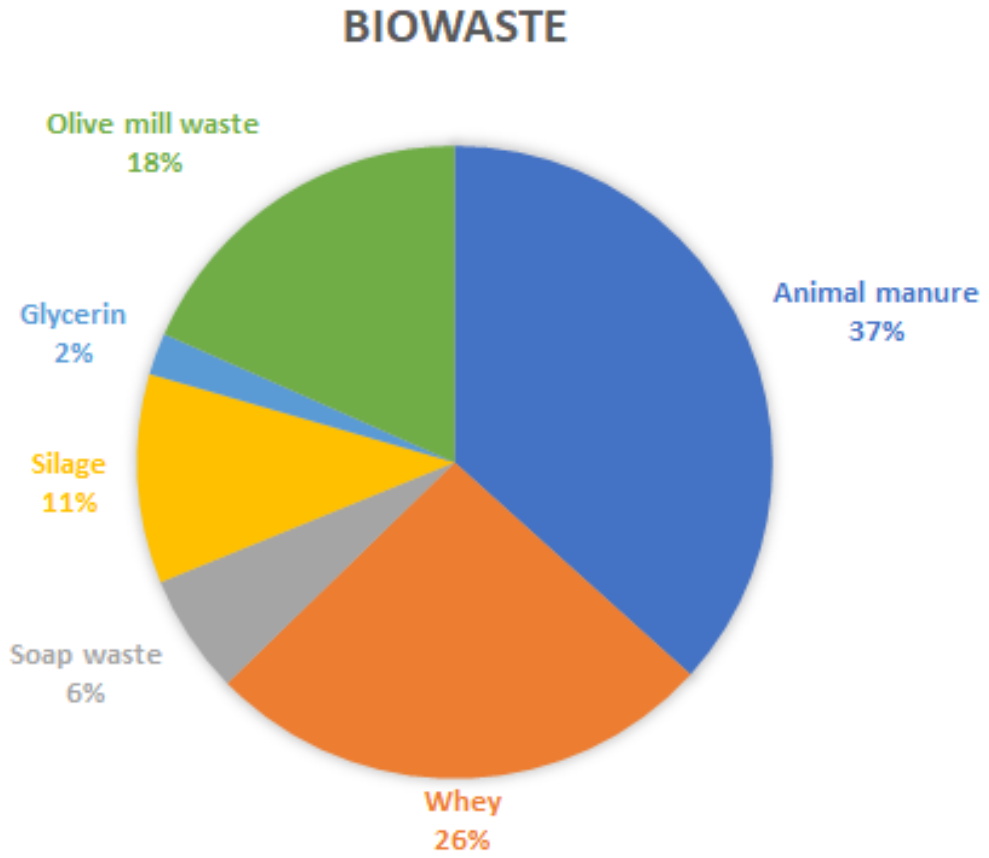
ZEOCAT-3D

Biogas plant

A privately held SME → Biogas production from anaerobic digestion of biowaste constructed in 2016

Situated in Nigrita in Northern Greece



- Waste treatment via anaerobic digestion for biogas production.
- Total waste treated ~32.000 tn/y
- Total capacity **1MW.**
- Power expansion to **3MW** (2021)

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Biogas plant

Mesophilic CSTR Digester

- Capacity 4.200 m³
- HRT 40 days
- 4 submersible mixers

Residue storage tank

- Capacity 8.100 m³
- 180 days
- 3 submersible mixers

Mechanical separator

- Liquid and solid state
- Feeding digestate back in

Pasteurization

- Animal by-products
- 1 hour at 70 ºC

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Biogas plant

- Silage storage 4 x 5.000 m^3
- Underground pretank 150 m^3
- Overground pretank 500 m^3

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Biogas plant

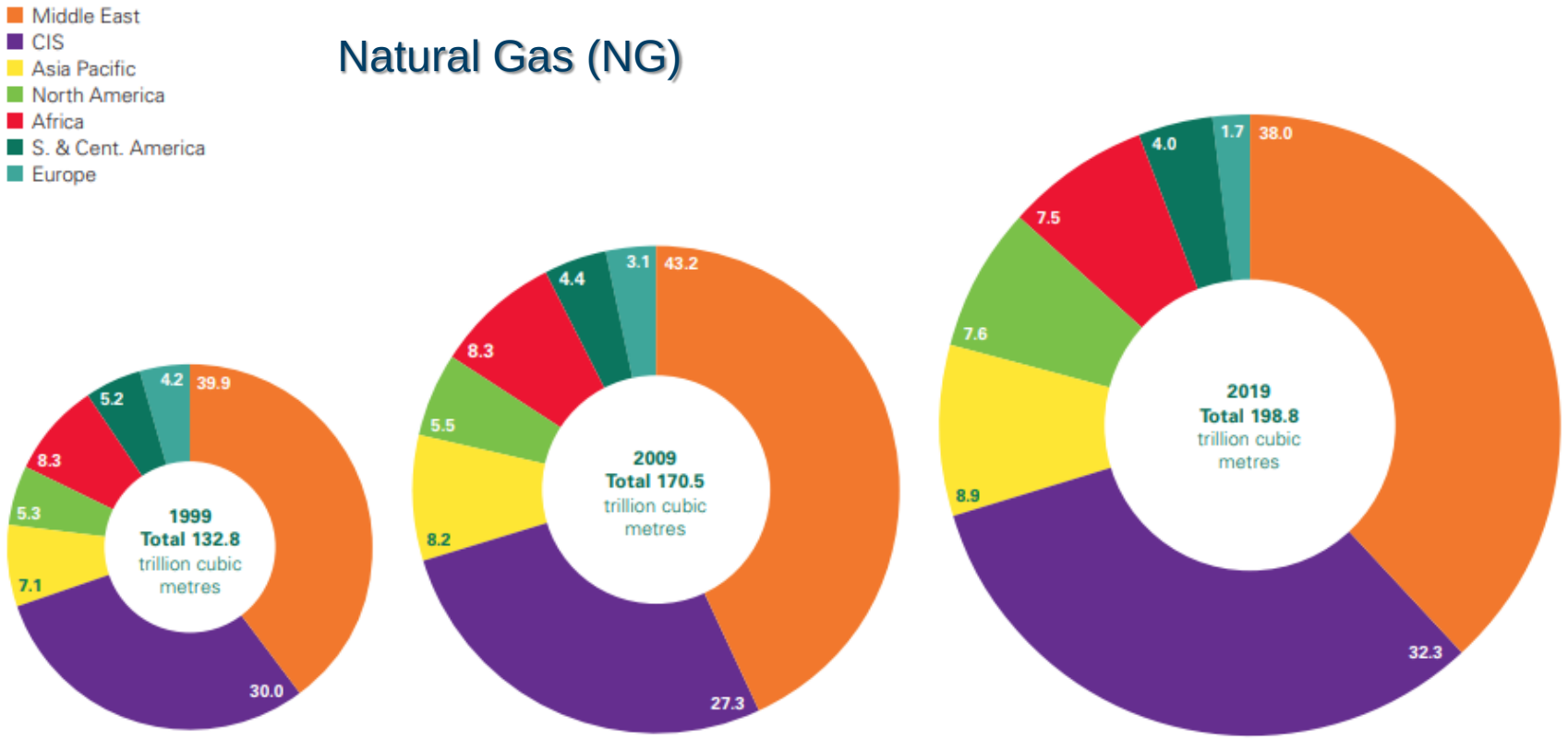
Biogas:

- 11.500 m^3/d.
- 55% ~ 65% CH_4

Treatment & Utilization:

- Condensate circuit
- Gas flare
- Chiller
- Genset - Jenbacher Engine & Stanford Generator
- η = 40,5%

Natural gas



Distribution of natural gas proved reserves in 1999, 2009 and 2019 (percentage)

Source: "bp Statistical Review of World Energy 2020".

- Global NG reserves are increased the past decade since the rate of new deposits discovery is greater than the consumption rate. Purification steps are required to obtain pure CH_4
- Part of global natural gas resources remain stranded or isolated in remote locations
- Liquid energy carriers can be transported much more compactly and easily

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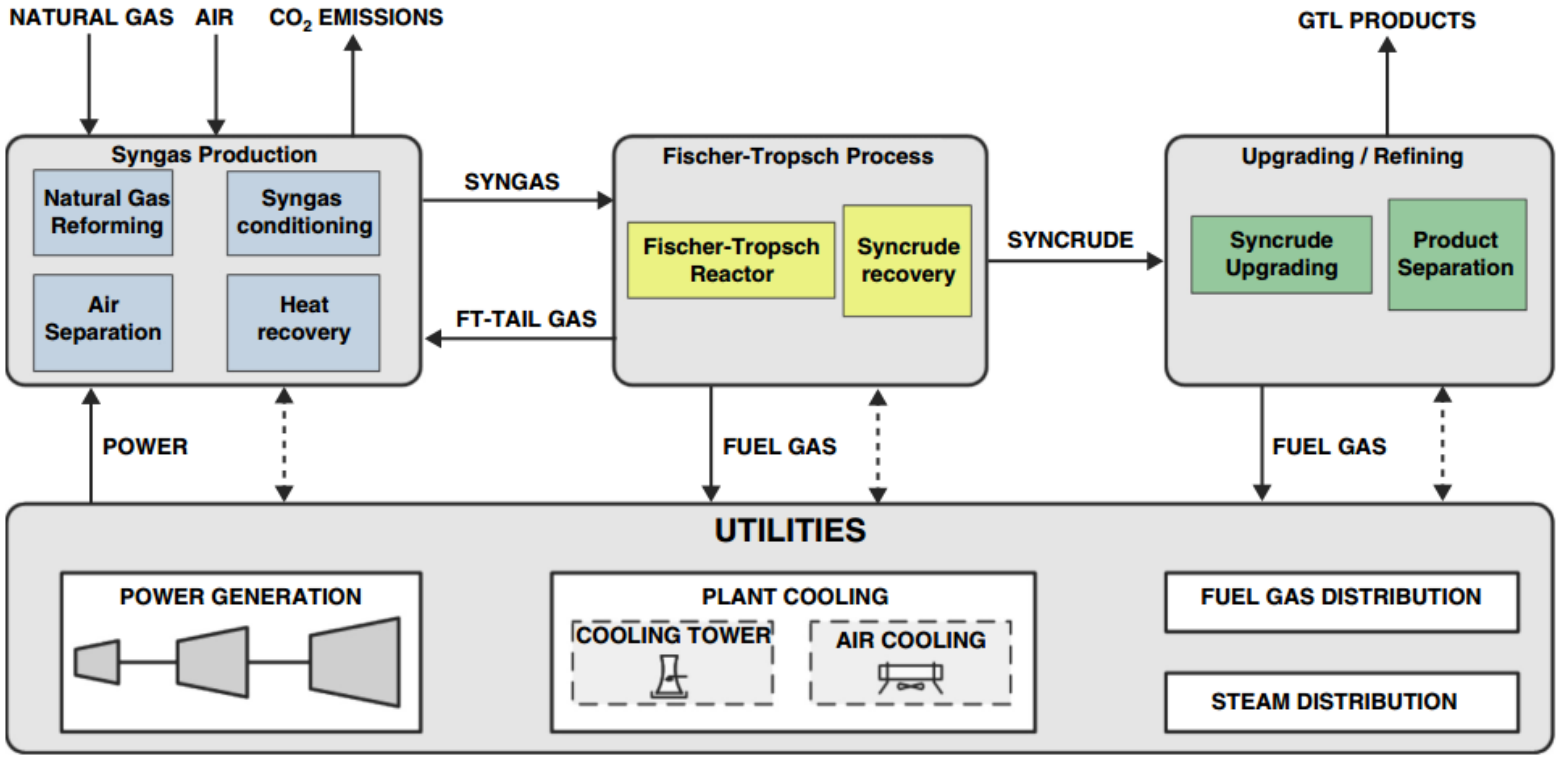
Gas to Liquid (GTL) technology

Air Separation (O_2, N_2)

Production of pure O_2 and pure N_2

The GTL process can be divided into three distinct processing sections:

- Syngas production (includes cleaning and conditioning)
- FT syngas conversion and
- FT syncrude upgrading and/or refining



Flow diagram of GTL process

Source: Current Opinion in Chemical Engineering 2014, 5:49–54, https://doi.org/10.1016/j.coche.2014.05.001

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Gas to Liquid (GTL) technology

Reforming

Steam reforming $CH_4 + H_2O \longrightarrow CO + 3H_2$

Partial oxidation $CH_4 + 1/2O_2 \longrightarrow CO + 2H_2$

Auto Thermal Reforming

Carbon dioxide reforming $CH_4 + CO_2 \longrightarrow 2CO + 2H_2$

Water gas shift reaction $CO + H_2O \longrightarrow CO_2 + H_2$

Fischer-Tropsch synthesis

$nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$

$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$

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Gas to Liquid (GTL) technology

Hydrotreating / Cracking

Fischer Tropsch products are hydrotreated and cracked in order to receive a variety of other products like

- Naphtha
- Aviation fuel
- Diesel
- Lubricants
- Paraffin wax
- etc

Hydrogen Production

Hydrogen sent to the Reforming and Hydro Treating/Cracking unit

GTL plant examples

Oryx GTL plant in Qatar
https://oryxgtl.com.qa/

Pearl GTL plant in Qatar
https://www.shell.com.qa/

Altalto in Immingham, UK
https://www.velocys.com/

Bayou Fuels
in Natchez, Mississippi, USA
https://www.velocys.com/

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Methane Dehydroaromatization

Methane Dehydroaromatization (MDA) is the conversion of methane to aromatics

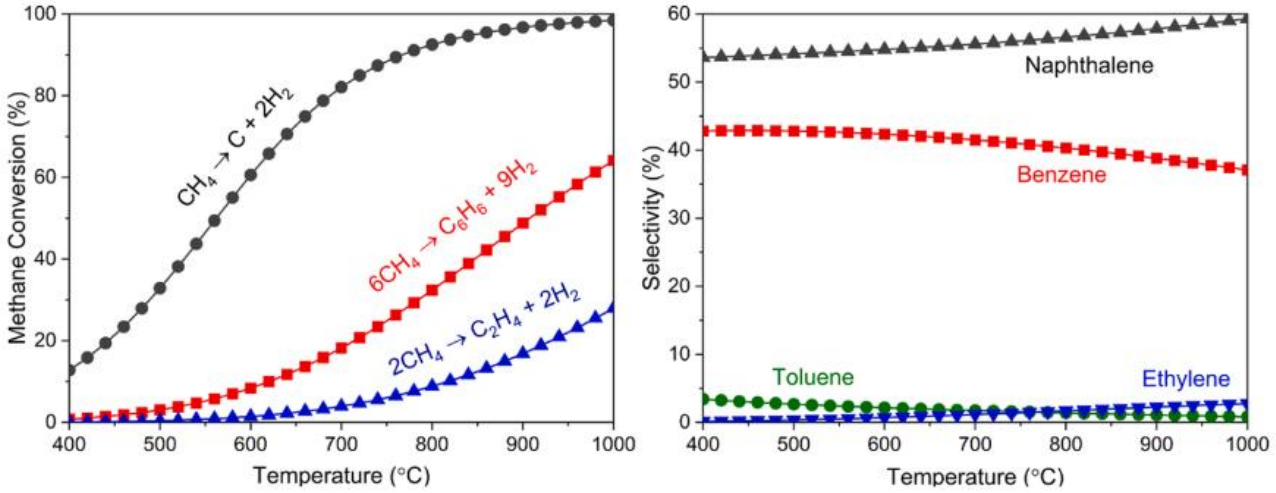
$$6CH_4 \longrightarrow 9H_2 + C_6H_6$$

Pros

- Non oxidative reaction
- One step reaction
- Modular process design

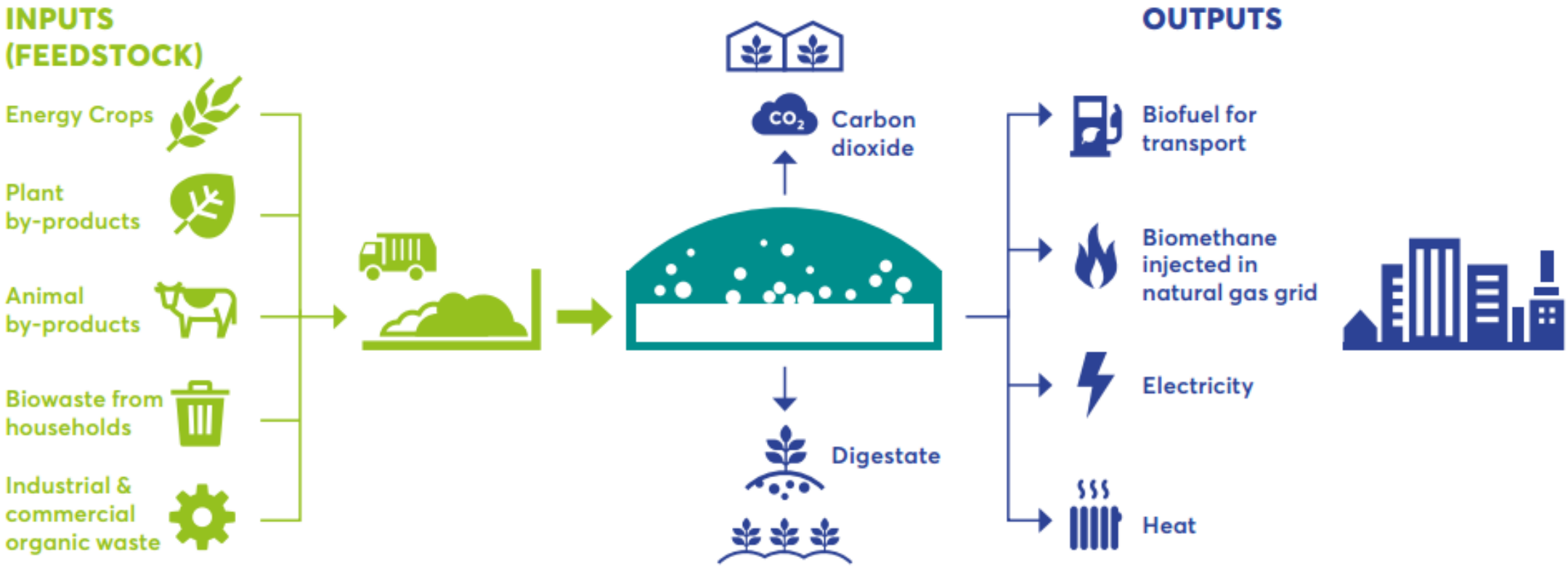
Cons

- Reaction Thermodynamic limitation 12%
- High reaction temperature ~700 oC
- Benzene selectivity 50-60%



Source: U. Menon et al., Applied Catalysis A, General 608 (2020) 117870, https://doi.org/10.1016/j.apcata.2020.117870

Biogas plant



Inputs and outputs of the anaerobic digestion (AD) process

Source: EBA 2020. "Statistical Report of the European Biogas Association 2020."

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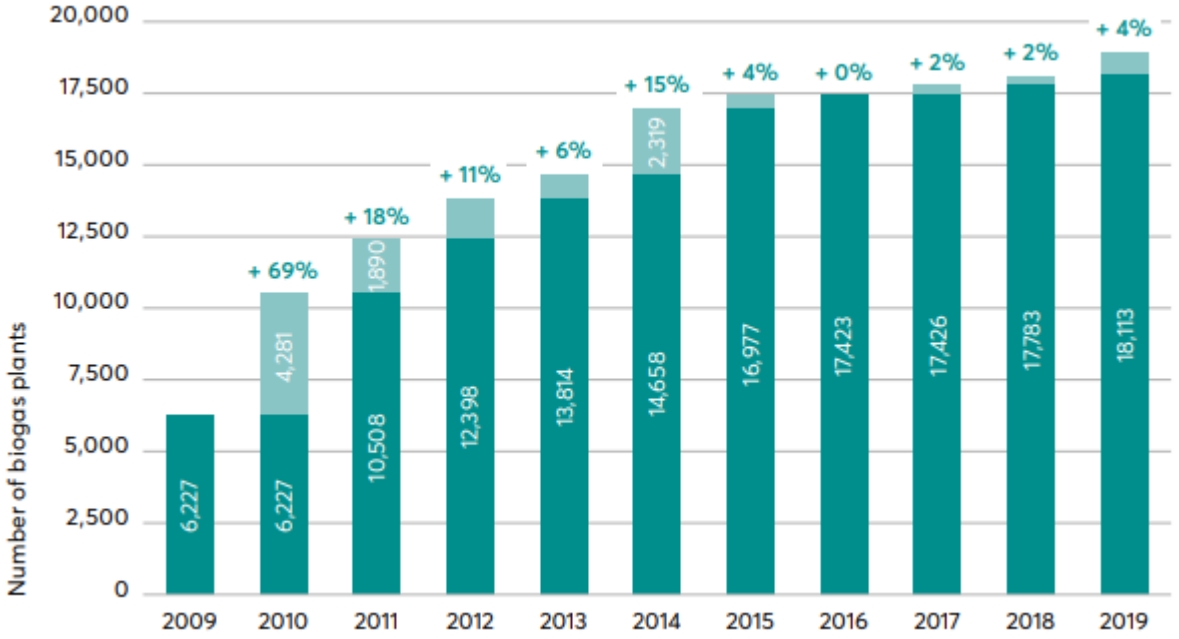
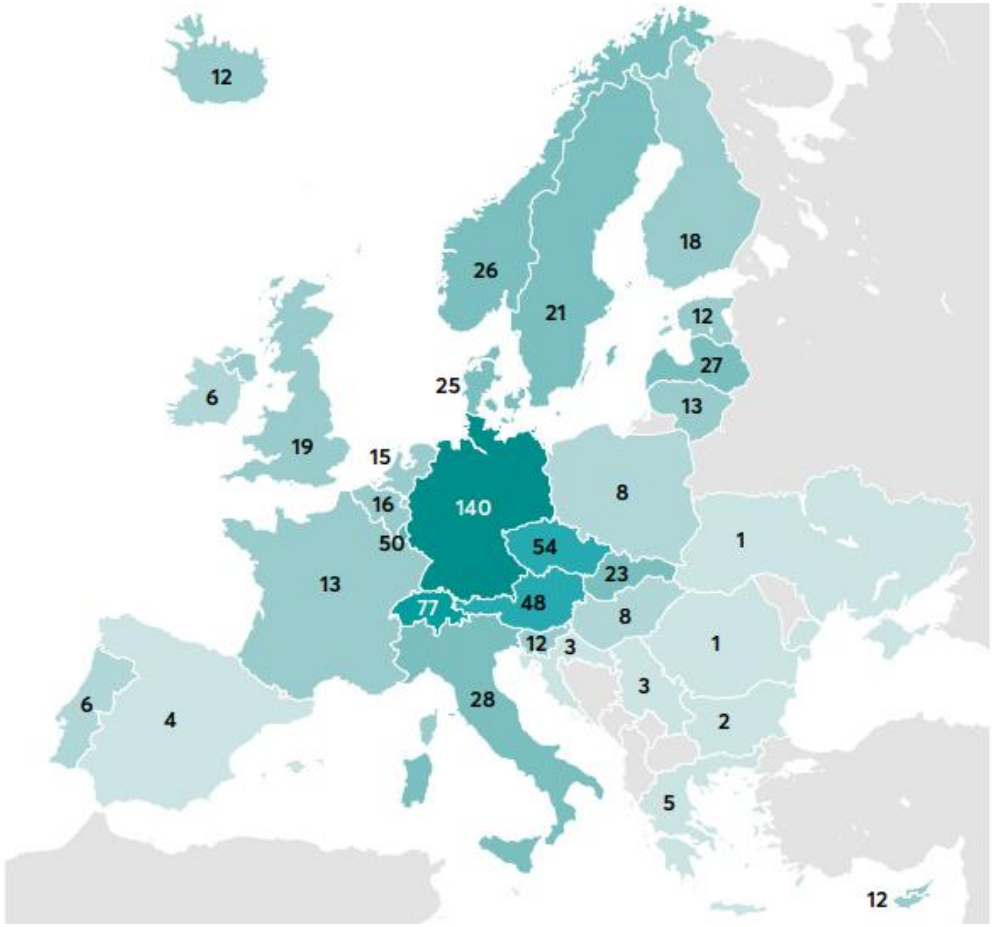
Biogas sector



Number of biogas plants in Europe



Number of biogas plants per 1 Mio capita, per country, in 2019

Source: EBA 2020. "Statistical Report of the European Biogas Association 2020."

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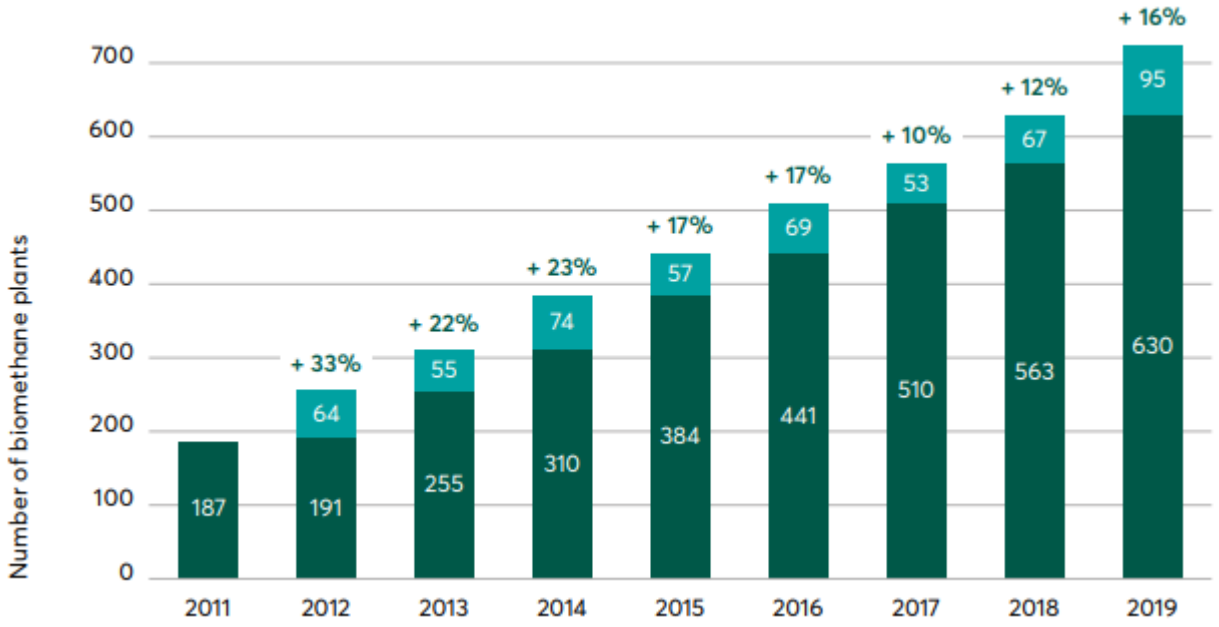
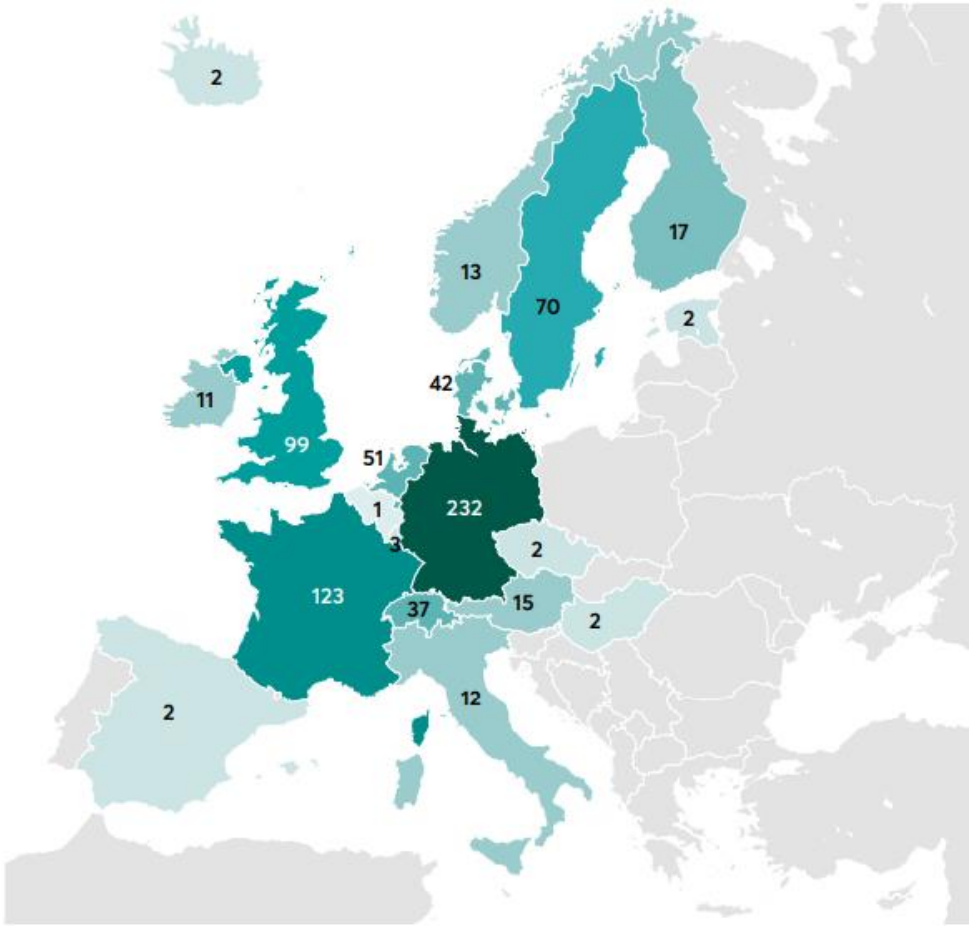
Biomethane sector



Number of biomethane plants in Europe

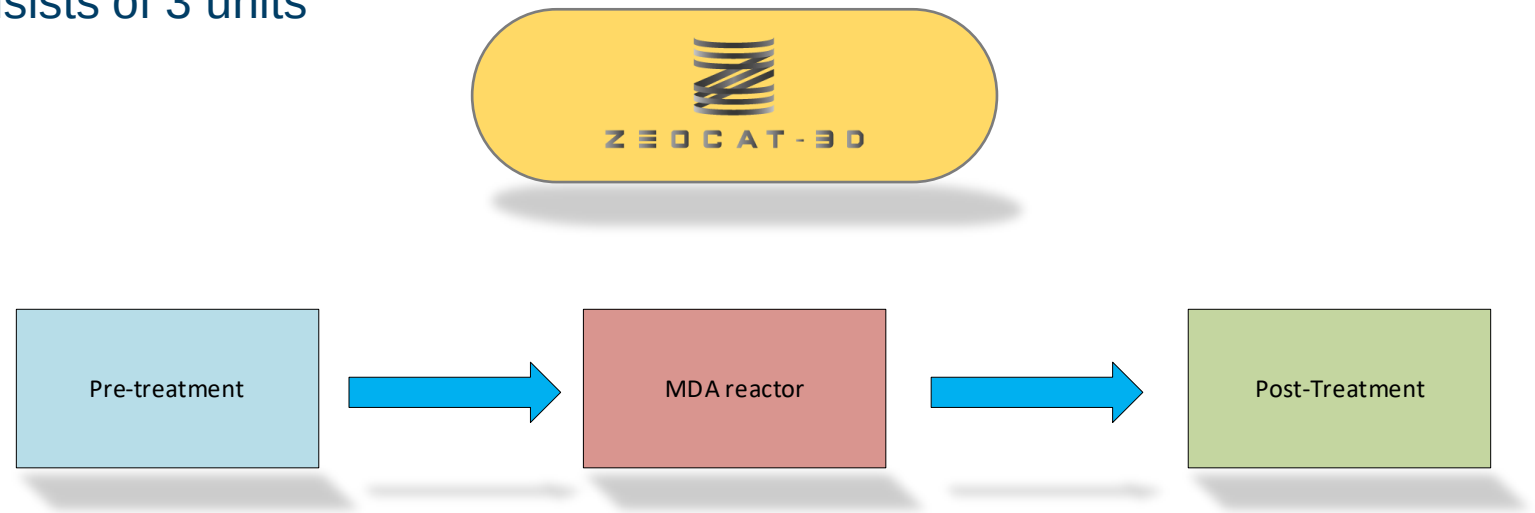


Number of biomethane plants per 1 Mio capita, per country, in 2019

Source: EBA 2020. "Statistical Report of the European Biogas Association 2020."

Zeocat-3D technology

The prototype consists of 3 units



- A purification system of the biogas feed
  - ✓ H_2S removal and impurities
  - ✓ CO_2 separation
- Methane DehydroAromatization reactor (MDA)
- H_2 selective membrane

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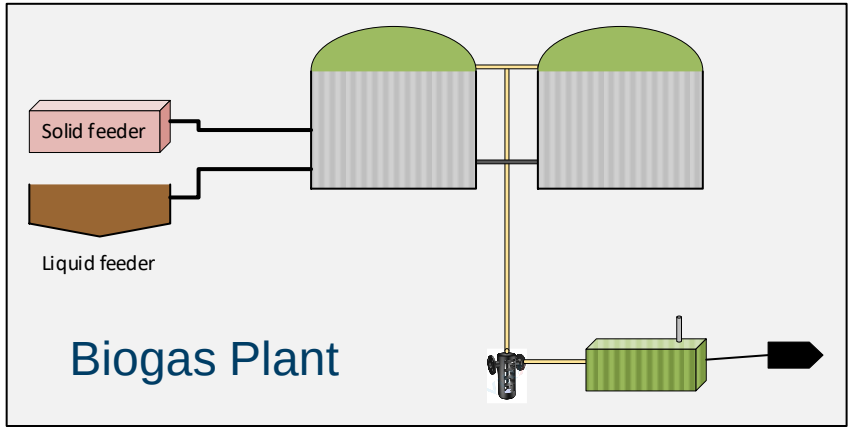
Zeocat-3D technology

Pre-treatment

- Activated carbon or Iron Oxide filters
- Cu/Zn mixed oxide NanoParticles
- Gas-Liquid Membrane Absorption



Methane recovery >98%

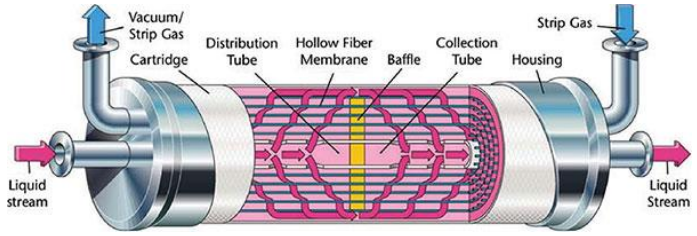
CH4: 60%
CO2: 40%

Gas to MDA

Feed gas

CO2 recovery >99%

Methane purity >95%



CO_2 in liquid stream

Image by 3M

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Zeocat-3D technology

MDA reactor

- Methane Dehydroaromatization MDA process $6CH_4 \longrightarrow 9H_2 + C_6H_6$

GAS

- CH_4 conversion to aromatics

  Thermodynamic limitation 12%
  After recirculation >98%

LIQUID

- Liquid Hydrocarbons

  Benzene selectivity (60%)

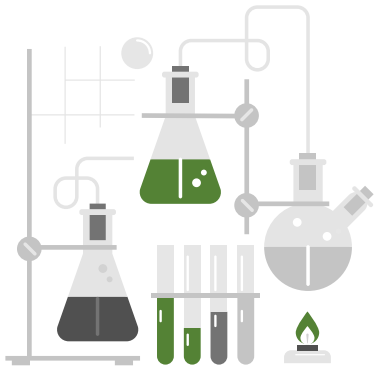
  Toluene

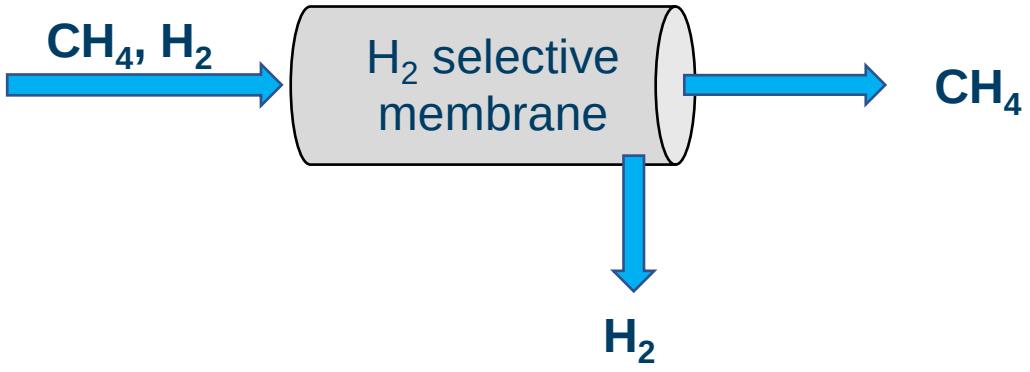
  Naphthalene

Zeocat-3D technology

Post-Treatment

- Gas Separation
- Hydrogen selective membranes





H_2 selectivity >98%

Application in biogas plant

Hydrolysis

↓

Acidogenesis

↓

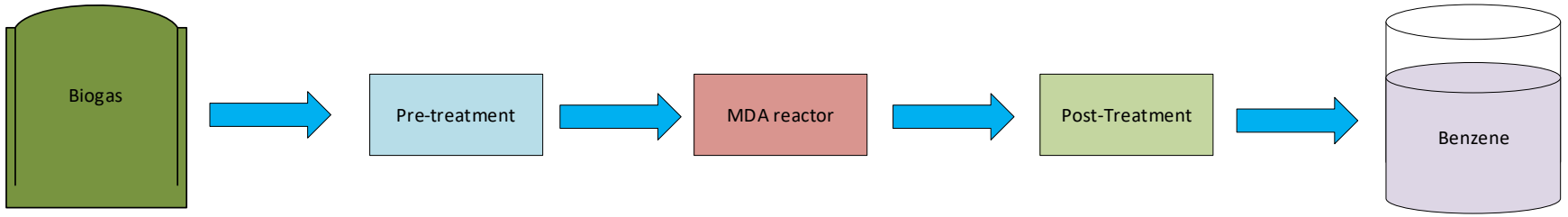
Acetogenesis

↓

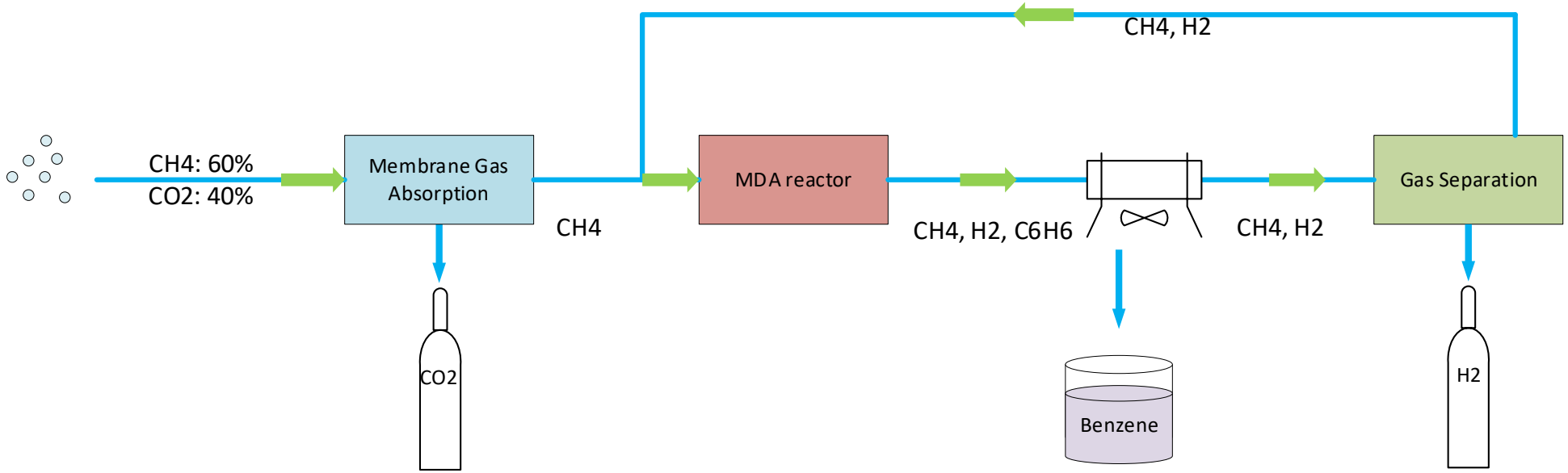
Methanogenesis

Zeocat-3D main goal is the production of aromatics with a stable and sustainable matter

Anaerobic digestion is a sequence of processes by which microorganisms break down biodegradable material in the absence of oxygen.
The process is used for industrial or domestic purposes to manage waste or to produce fuels



Application in biogas plant



- The produced biogas (CH_4: 60 % and CO_2: 40 %) is purified
- Next is separated in 2 “pure” gaseous streams CH_4 and CO_2
- Following comes the MDA reactor producing C_6H_6 and H_2
- Afterwards the vapours of aromatics are condensed forming a liquid phase
- Subsequently gaseous stream is separated so that pure H2 is obtained
- Finally, excess CH4 and H2 are recirculated to the MDA reactor

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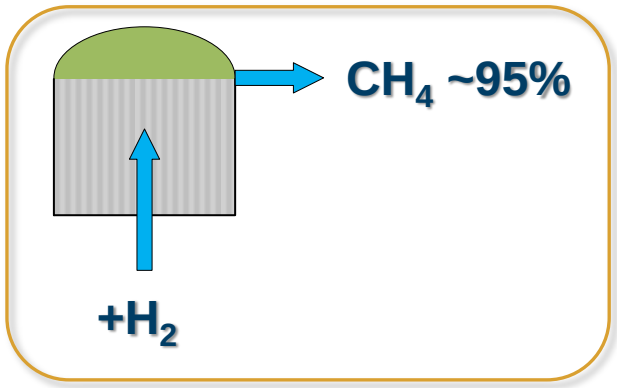
Biogas upgrading to biomethane

Surplus electricity from Renewable Energy Sources can be stored in the form of H_2 produced by the electrolysis of water

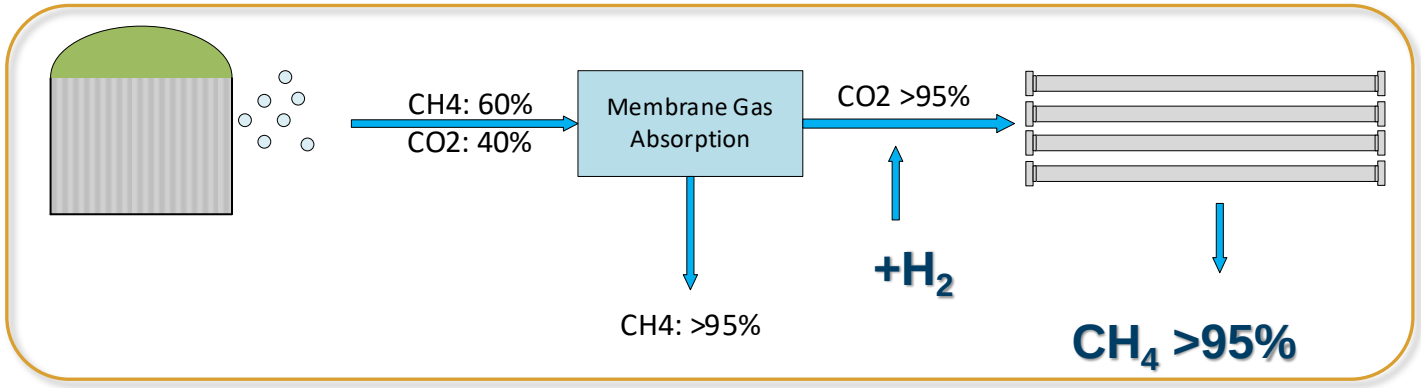
In biological conversion of carbon dioxide to biomethane Hydrogenotrophic methanogenic archaea produce biomethane by carbon dioxide and hydrogen

$$4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O$$

in situ



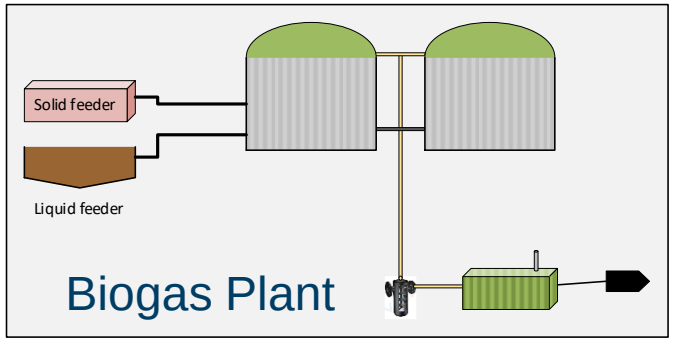
ex situ

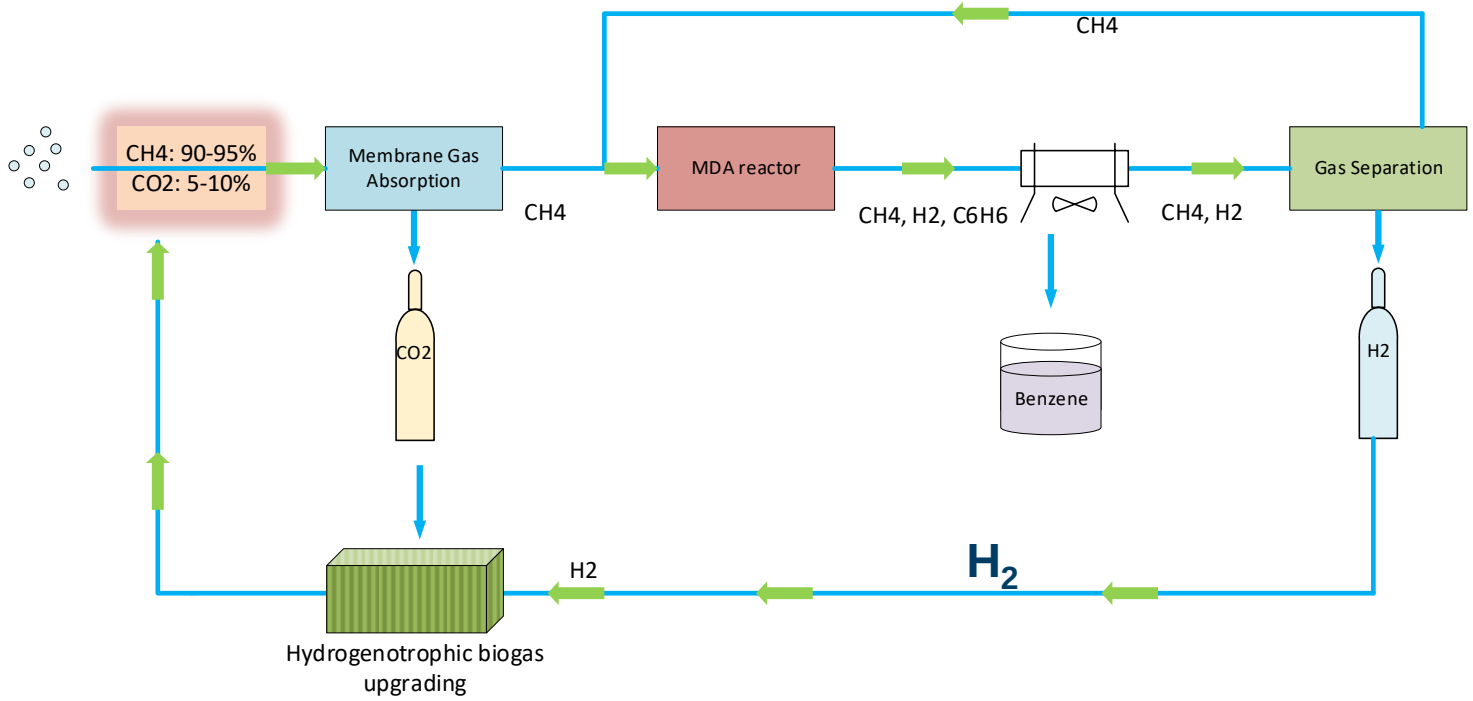


In an in-situ methanation system organic substrate and additional hydrogen is added to the digester where the biogas is produced

In an ex-situ system carbon dioxide hydrogen, essential nutrients and hydrogenotrophic methanogens are required

Zeocat-3D coupled to biogas upgrading

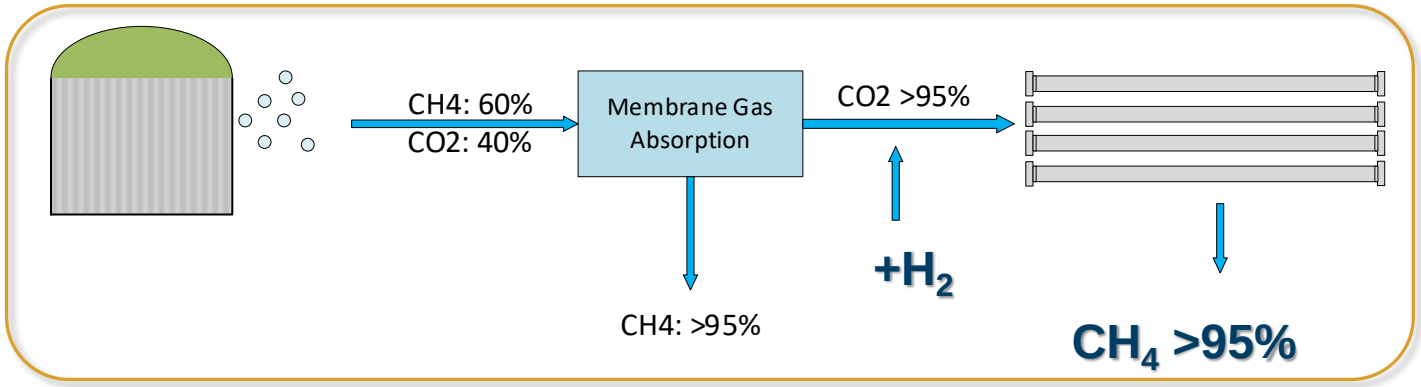




Ex situ biological biogas upgrading could be another path exploiting the hydrogen side stream produced by the MDA reaction, resulting in extra biomethane production per digested biomass and stressing less the separation and purification systems

Biogas and Beyond

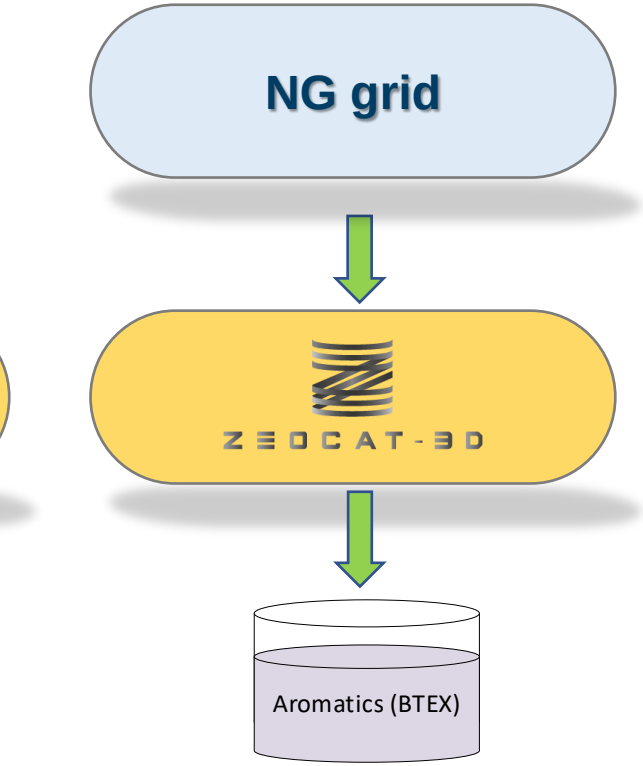
Delocalized liquid energy carriers production



- Building blocks for synthetical pathways
- Storage of excess energy in liquid media
- Easier transportation of chemicals
- In situ production of chemicals

Access to NG or BM ensures aromatics supply!!!

Within NG pipeline grid access



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Biogas and Beyond

Markets under construction…

Standardization and Modularization is possible

Plug and Produce modular design

Scale up capacity option

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Thank you

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Any questions?

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