BOKU

IFA
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Trickle bed reactors for biomethanation

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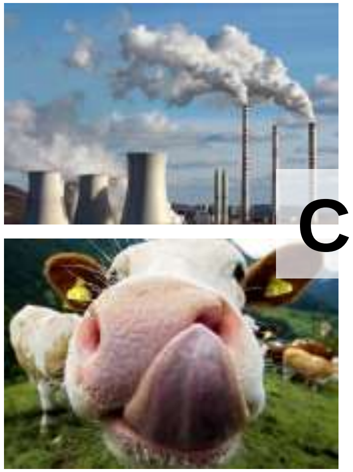
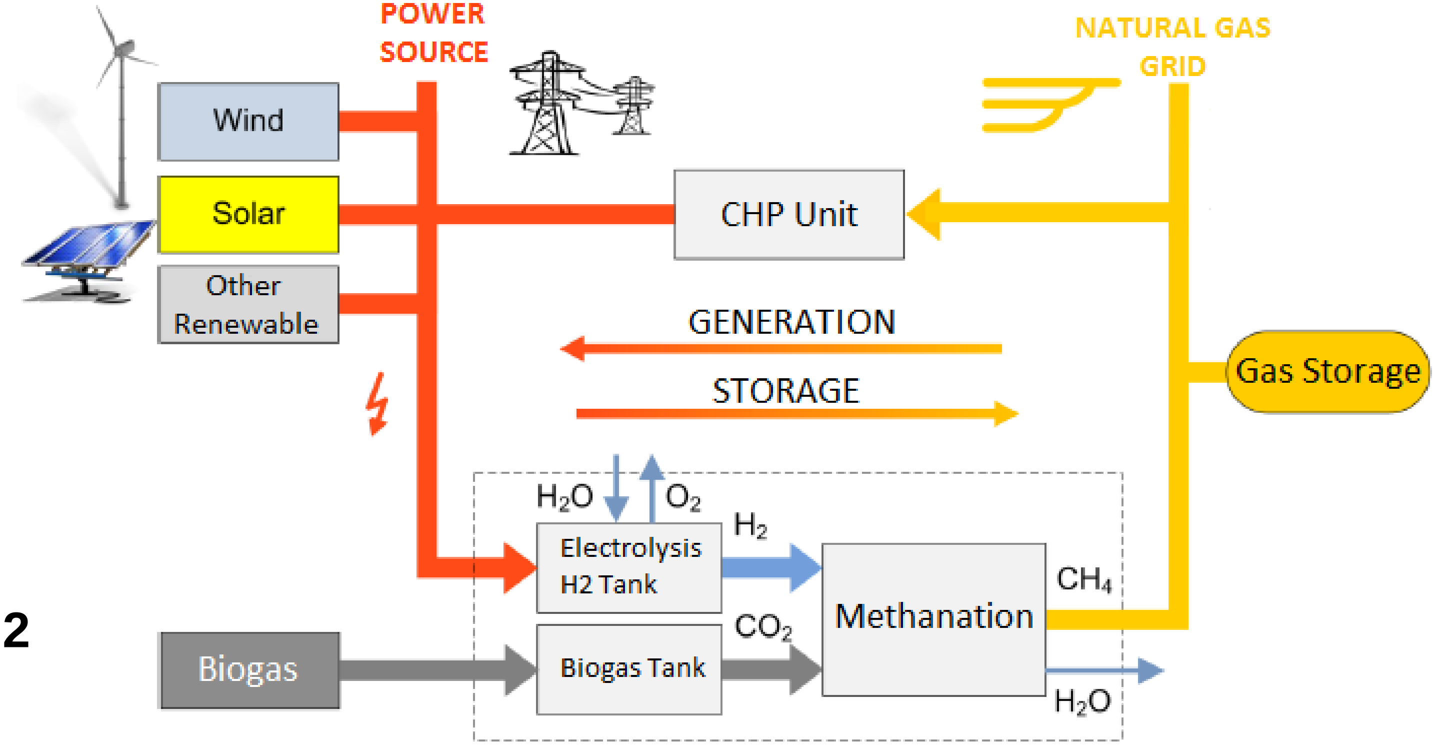
bioenergy2020+

Power-to-Gas concept

H_2



CO_2



POWER SOURCE

Wind

Solar

Other Renewable

CHP Unit

NATURAL GAS GRID

GENERATION

STORAGE

Gas Storage

H_2O

O_2

Electrolysis H2 Tank

H_2

Methanation

CH_4

Biogas

Biogas Tank

CO_2

H_2O

Power-to-Gas Plant

Source: Own elaboration based on data from Sterner, 2009 & Specht et al., 2010

Biological vs. Chemical methanation

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$$

Biological conversion

- Methanogenesis by hydrogenotrophic Archaea
- Mild conditions
  - Ambient pressure
  - Moderate temperature range
  - → Easy handling
- No cost intensive catalysts

Chemical conversion

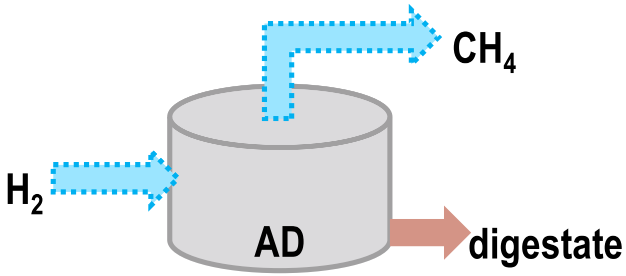
- Sabbatier process
- Process parameters
  - 300-600°C
  - High pressure (~ 10 atm)
- Ni as catalysts

Hydrogen utilisation for biogas upgrading

- In situ approach

→ Classic methane production with integrated methane enrichment

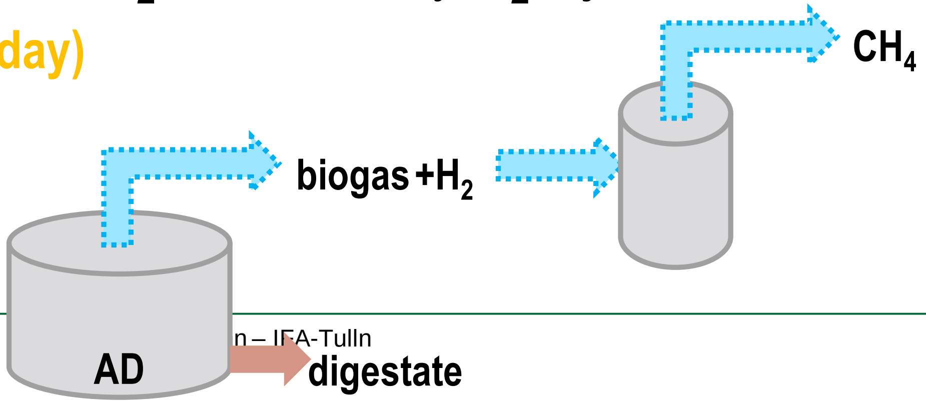
$0{,}5\ m^3CH_4/(m^3_{bed\ V}\cdot day)$



- External methane enrichment

→ Separate bio-reactor for CO_2 reduction by H_2 injection

$1{,}2 – 1{,}6\ m^3CH_4/(m^3_{bed\ V}\cdot day)$



Critical factors

- Crucial parameters for industrial application:
  - Volumetric methane production rate (methane evolution rate, MER)
    - effect on reactor size
    - optimize cost-efficiency

→ **CSTR**

  - CH_4 concentration in product gas
    - depending on applications (88-98 Vol%)
    - high concentrations required to minimize costs for gas clean-up

→ **Trickle-bed**

Seifert et al. (2014)

Gas/liquid mass transfer

- Gas transfer rate dependent on
  - Concentration gradient between equilibrium and dissolved gas concentration as driving force
    - Partial pressure of gas
  - Volumetric mass transfer koefficient *kLa*
    - Stirrer speed, gassing rate
    - Directly related to effective exchange area (m^2/m^3)

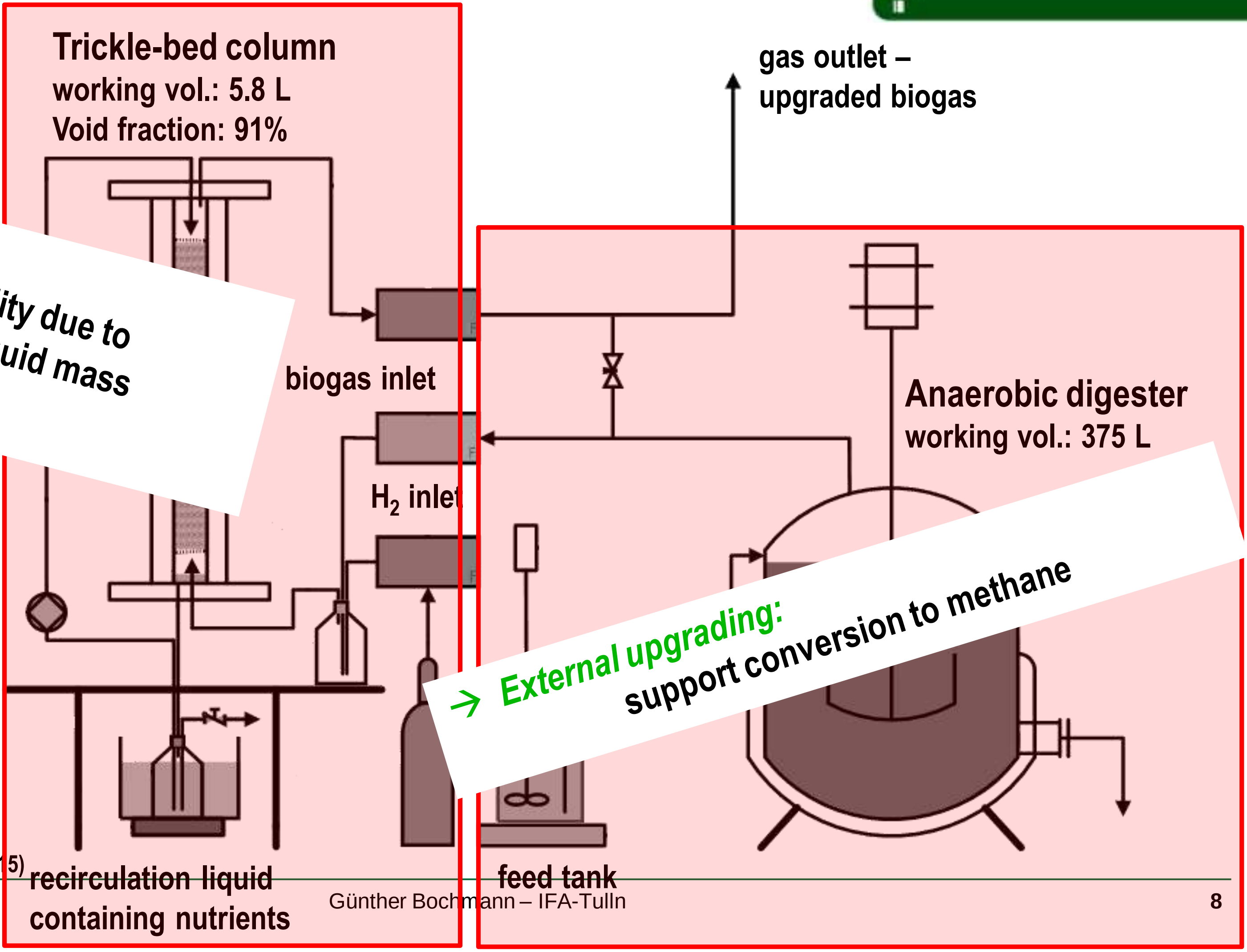
➢ In continuously operated **trickle-bed** reactor the **gas flow rate** can be set **low** to achieve high conversion rates **without substantial loss in *kLa***

Methane evolution rate (MER)

- CSTRs:
  - 2.4 - 4.1 m^3 CH$_4$/m^3*day
- Packed beds:
  - 1.17 - 1.34 m^3 CH$_4$/m^3*day
- Hollow fibre biofilm membrane bioreactor:
  - 4.6 m^3 CH$_4$/m^3*day
- Trickle-beds:
  - 1.49-6.35 m^3 CH$_4$/m^3*day

Rittmann et al. (2015) and Muñoz et al. (2015)

Experimental set-up

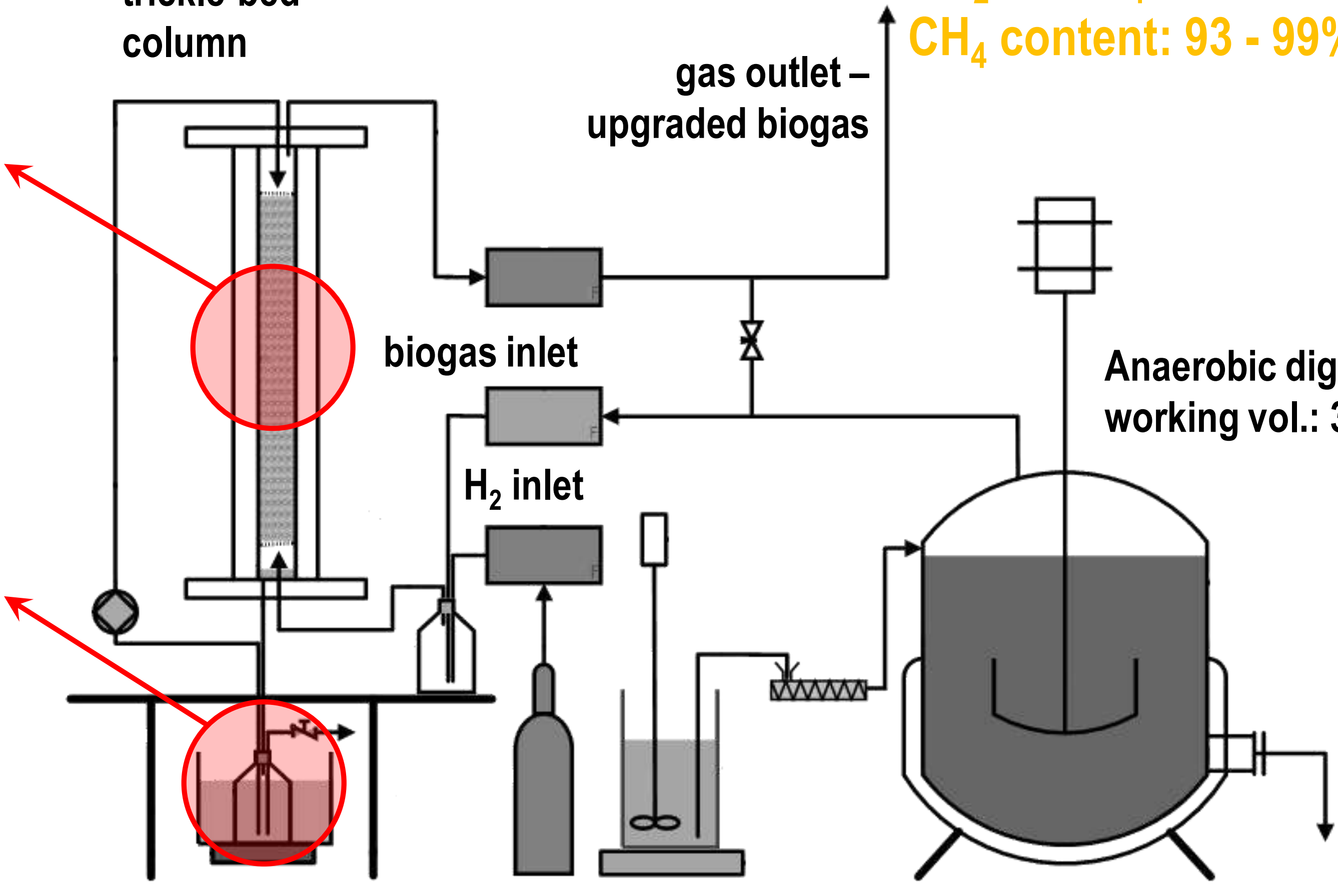


→ *Trickle-bed reactor:*
better H_2 solubility due to increased gas/liquid mass transfer

→ *External upgrading:*
support conversion to methane

Burkhard et al. (2015), and Alitalo et al. (2015)

Experimental set-up



$CO_2 \rightarrow CH_4$ ~ 95%

CH_4 content: 93 - 99%

trickle-bed column

gas outlet – upgraded biogas

Sampling point 2:
Adapted biofilm inside the reactor

biogas inlet

Anaerobic digester working vol.: 375 L

H_2 inlet

Sampling point 1:
washed off material during start-up

recirculation liquid containing nutrients

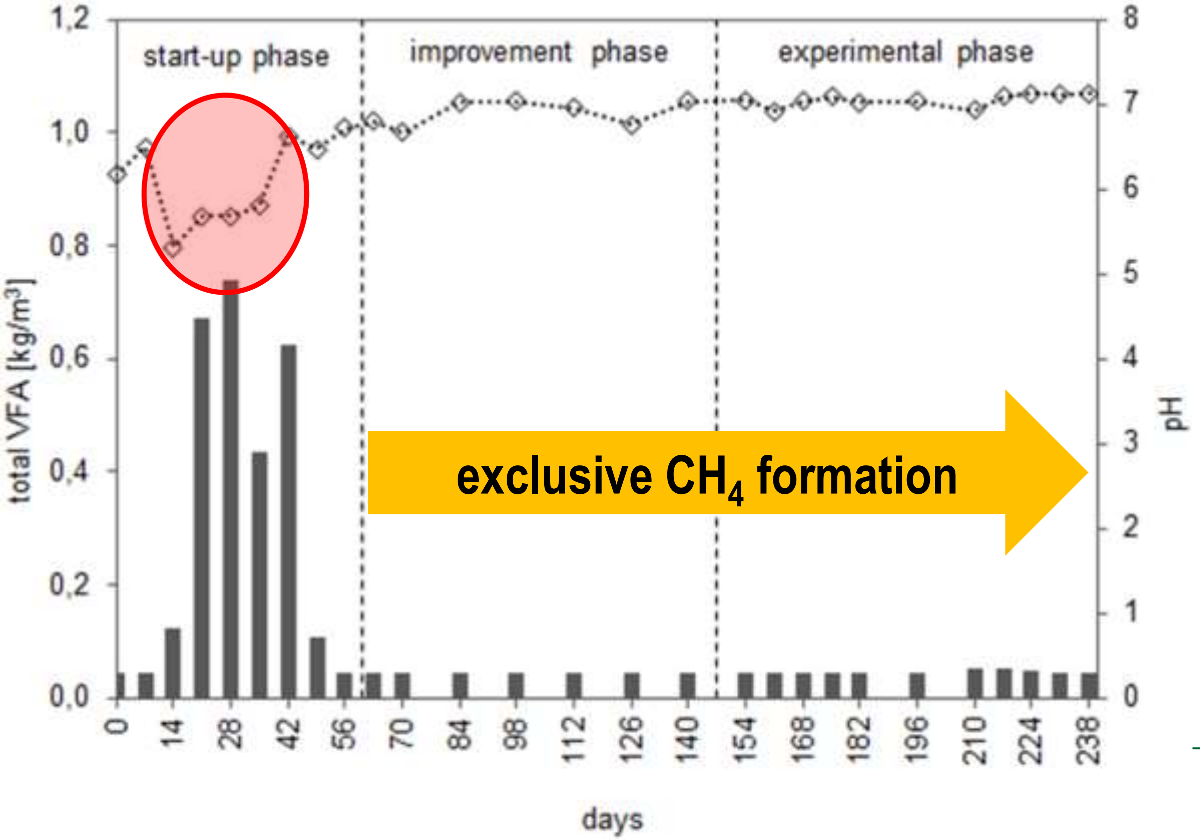
feed tank

Reactor performance

(I) Volatile fatty acid accumulation during reactor start-up

(II) Conversion rates in the range of 75 – 96 % CH_4

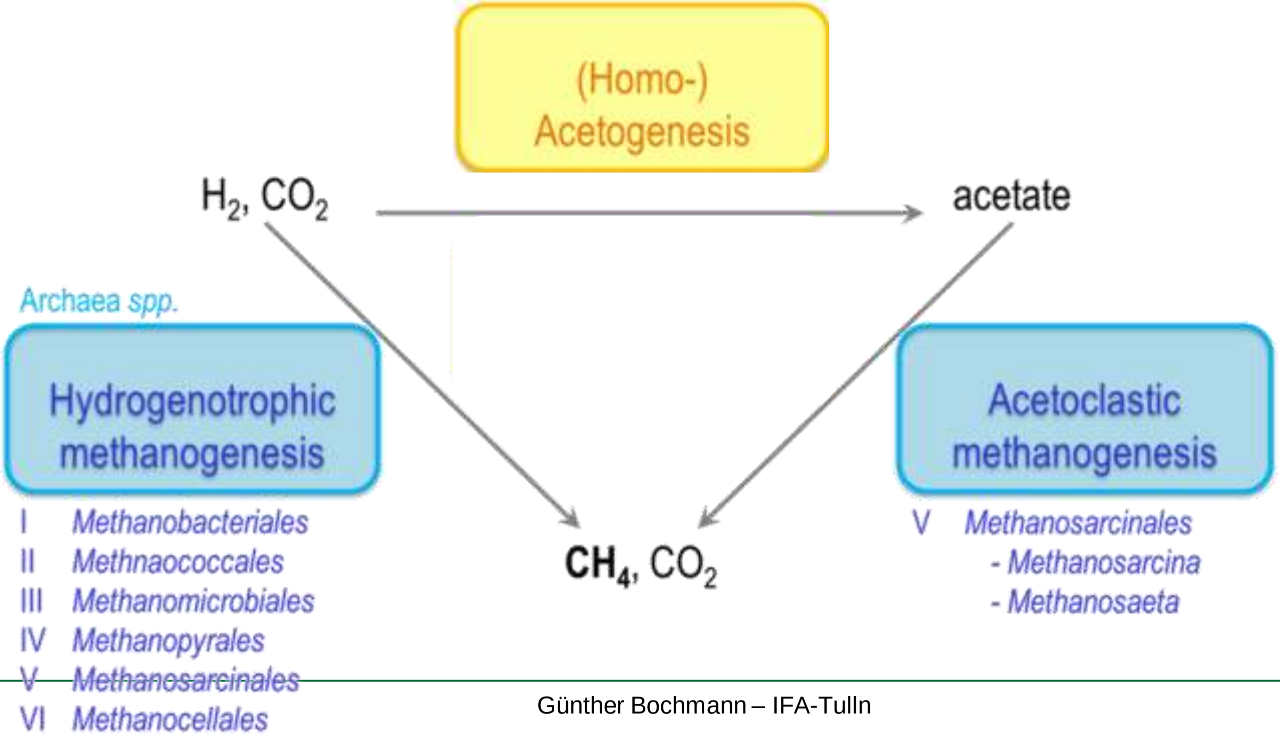
(III) Max. CH_4 content: 98% with < 0,1% residual H_2 under optimized conditions



Consortium analysis - liquid

16 S rRNA gene sequencing of adapted hydrogenotrophic consortium

- Proved a balanced mix of hydrogenotrophic methanogens (*Methanobacteriales*) and acetogenic bacteria



(Homo-) Acetogenesis

H_2, CO_2

acetate

Archaea *spp.*

Hydrogenotrophic methanogenesis

I *Methanobacteriales*
II *Methnaococcales*
III *Methanomicrobiales*
IV *Methanopyrales*
V *Methanosarcinales*
VI *Methanocellales*

CH_4, CO_2

Acetoclastic methanogenesis

V *Methanosarcinales*
- *Methanosarcina*
- *Methanosaeta*

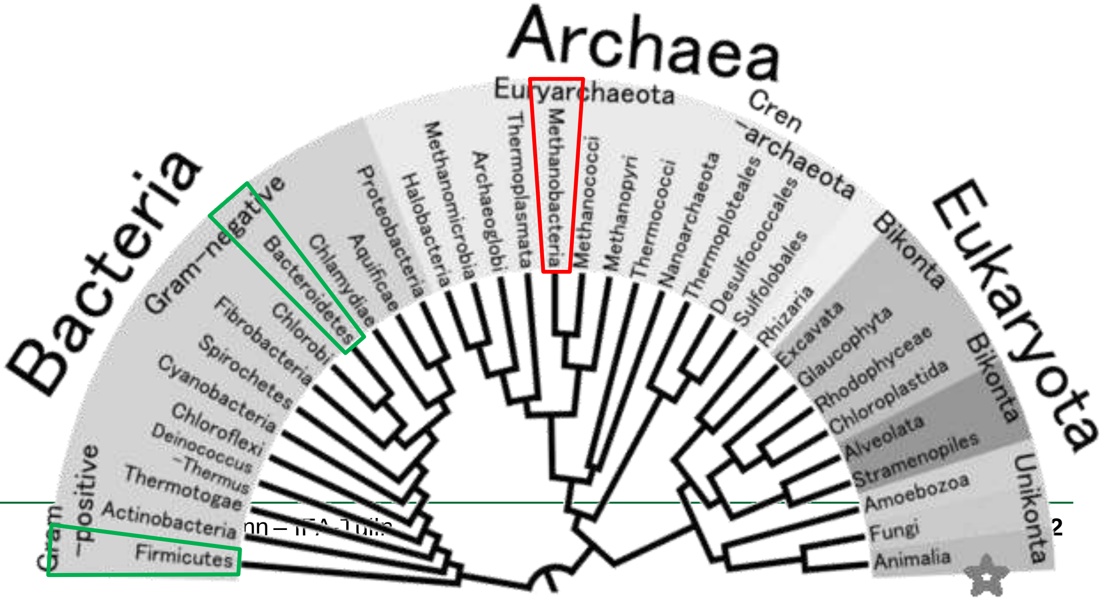
Consortium analysis

16 SrDNA analysis of adapted hydrogenotrophic consortium

- Proved a balanced mix of methanogenic Archaea species and acetogenic bacteria

- Acetogenic Bacteria (Bacetiodetes and Firmicutes):
    - Bacteroidales 23%
    - Clostridiales 17%

- Methanogenic Archaea:
    - Methanobacteriales 49%



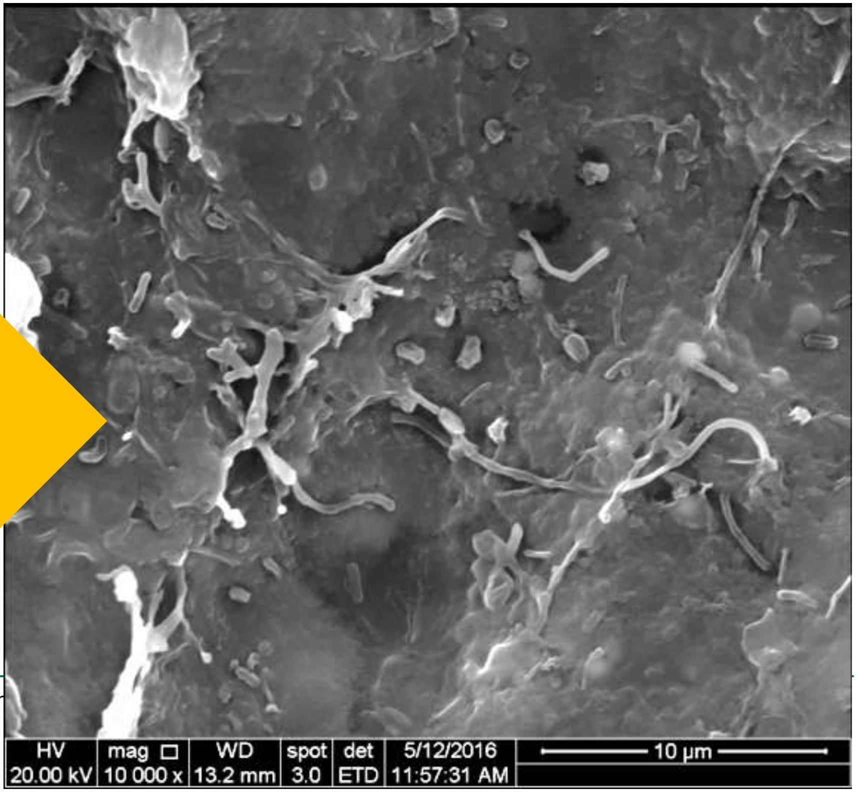
Consortium analysis 2 – carrier material

16 S rRNA gene sequencing of immobilized consortium (biofilm in trickle-bed column)

- Proved > 80% of Methanobacterium species

➢ Known hydrogentrophs

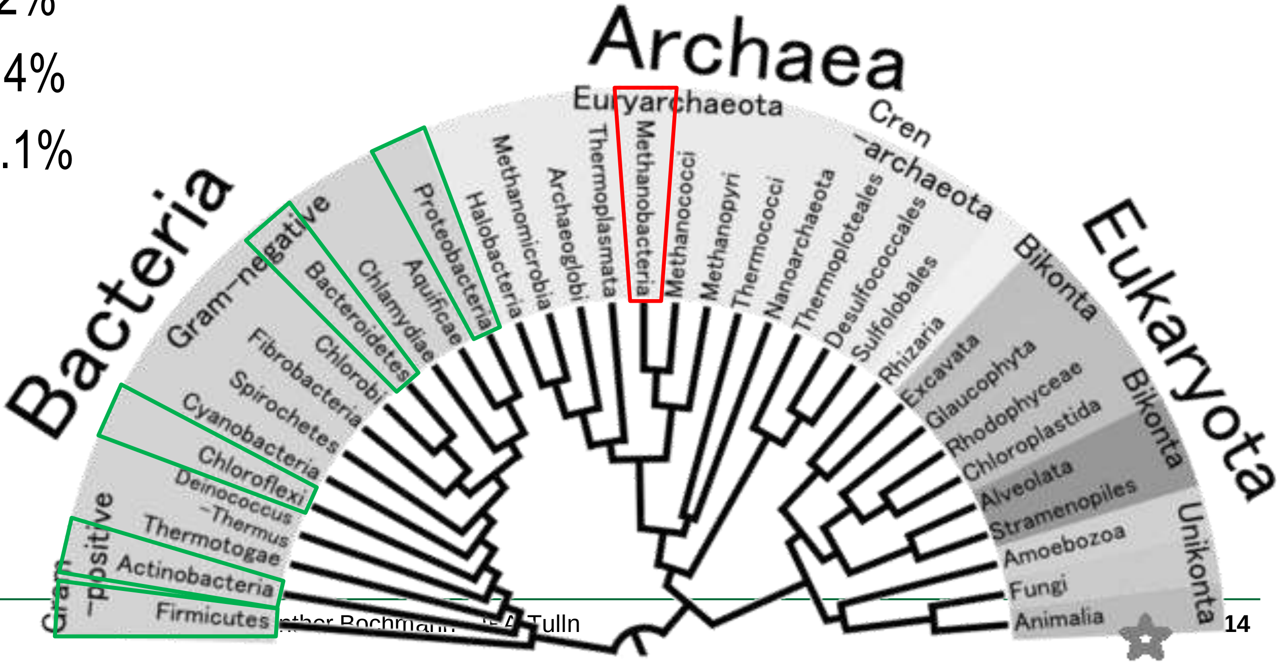
SEM of mixed culture immobilized



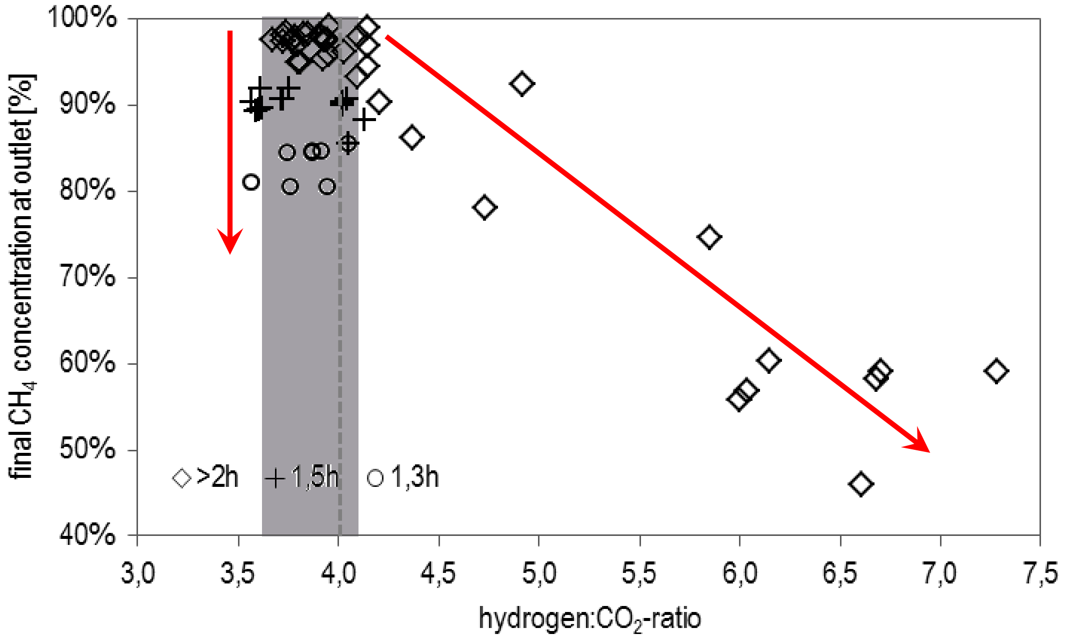
Consortium analysis

16 S rDNA analysis of immobilized consortium (in trickle-bed column)

- Proved over 80% of a Methanobacterium strain
- Rest mostly acetogenic bacteria:
  - Firmicutes 11.7%
  - Bacteroidetes 3.2%
  - Actinobacteria 1.4%
  - Proteobacteria 1.1%
  - Chloroflexi 0.1%



Results I



Final CH_4 concentrations…

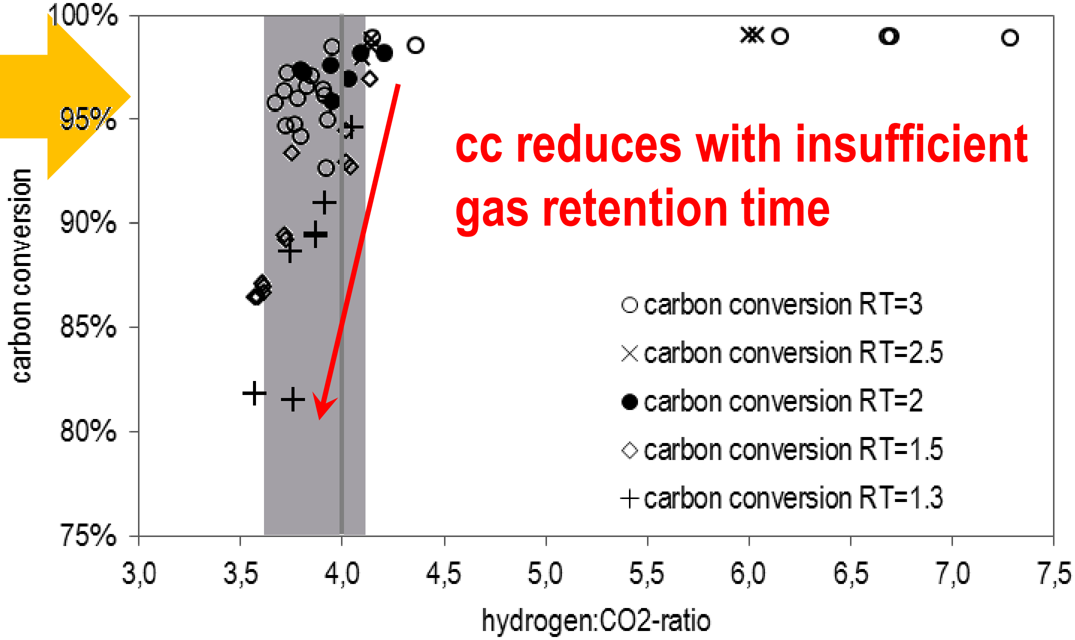
- Decrease with increasing H_2:CO_2 ratio
- Decrease at reduced retention times below 2 h
- Good upgrading quality even below stoichiometric H_2:CO_2 ratio of 4

Final methane concentrations 98% at optimized H_2:CO_2 ratio and gas retention time

Results II

Carbon conversion…

at RT>2h



cc reduces with insufficient gas retention time

- Max. MER of 2.52 m^3 CH_4/m^{3}*d
- Under optimized conditions: residual CO_2 in outlet gas in the range of 1-4%, 100% H_2 utilization

Results III

Upgrading capacity:

- At a retention time of 2 h
  - Upgrading capacity of 6.9 m^3 biogas/m^3*day
  - MER of 1.9 m^3 CH_4/m^3*day
  - ➢ Decreased pH_2 as a result of conversion to CH_4, thus lower MER

  - Stable conversion at gas inlet ratio even below stoichiometry
  - Methane concentrations suitable for grid injection

4.4 m^3 biogas/m^3 upgraded
1.4 m^3 biogas/m^3 produced

~ 1/4 the size of digester

Conclusions

- Efficient biological biogas upgrading…
  - Was established in a **trickle-bed reactor**
  - **Without gas recirculation**
  - **Minimal** amounts of **mineral media**

- External hydrogenotrophic methanogenesis…
  - Suitable with adapted enrichment culture
  - **Stable conversion at high final CH_4** concentrations
  - Residual **H_2** at outlet **below 0.1%**
  - Residual **CO_2** at outlet **0 – 4%**

Challenges for the future

- Upscaling of the trickle bed reactor
- Relevant size of the reactor
- Production of hydrogen
    - Costs of the hydrogen production

Question?

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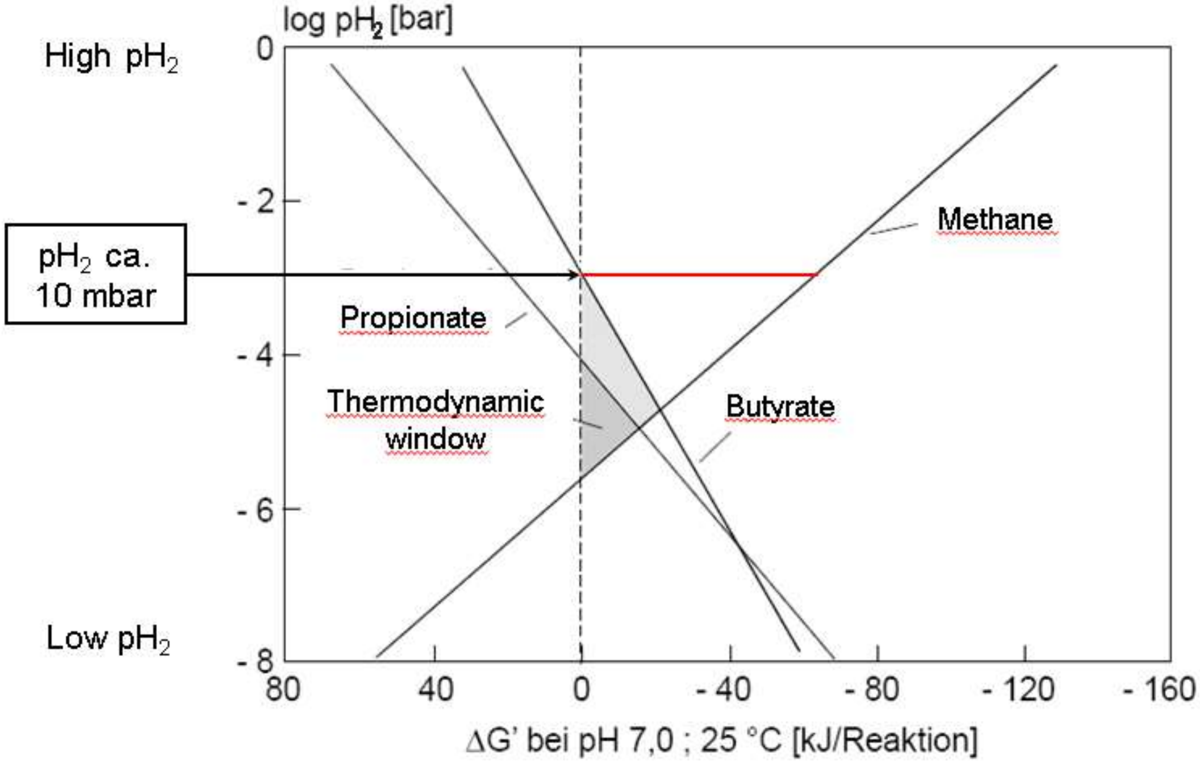
Influence H_2-partial pressure

Influence of H_2-partial pressure (pH_2) on Gibbs free energy ($\Delta G°'$)



Anaerobic digestion:

pH_2 needs to be kept within thermodynamic window

→ syntrophic growth of acetogenic bacteria and methanogenic archaea

External biogas upgrading:

Higher pH_2 supports CO_2 conversion to methane

Methane evolution rate

- MER for **thermophilic** archaea significantly higher (up to 6.89 CH_4/m^3*day)

- Drawbacks…
  - Synthetic gas mixtures
  - Low operational period with extremely dense packing
  - Low CH_4 concentrations (~50 – 60%) at max. MER

Burkhard et al. (2015), and Alitalo et al. (2015)