STATE OF THE ART AND DYNAMICAL MODELLING OF BIOLOGICAL METHANATION

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NEO CARBON ENERGY

NEO-CARBON ENERGY 6th RESEARCHERS' SEMINAR

30.8.2016

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- Biological vs. catalytical methanation
- Modelling of CSTR biomethanation reactor
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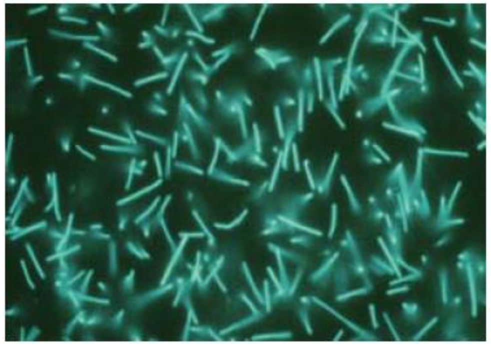
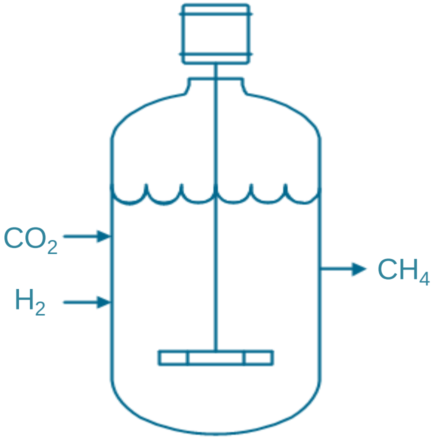
Biological methanation

- Methanation by microorgamisms, which obtain the energy for growth by anaerobically metabolising H_2 and CO_2 and produce CH_4
- Methanogenes typically found in
  - Oxygen free sediments, ricefields, swamps
  - Digestive system of animals
  - Geothermal and deep see wells
- Methanation takes place within aquaeous solution of microorganisms
- Hydrogen is poorly soluble to water and supplying gaseous hydrogen to microorganisms is main challenge in BM





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BM state of the art

- Experience from BM currently only in laboratory/pilot scale
- First pilot plants mainly in conjunction with biogas plants for biogas upgrading (other carbon sources possible)
- PFI’s P2G plant in Pirmasens-Winzeln Energy Park in Germany
  - 2 x 40 m^3 biological methanation reactors
  - 2.5 MW electrolysis
  - Goal to produce up to 440,000 m^3 of biomethane from wind and solar power annually into the natural gas grid.
- BioCatProject in Denmark
  - 5 m^3 biological methanation reactors
  - 1 MW electrolysis, upgrading of biogas from wastewater treatment plant

THE FIRST METHANE HAS BEEN PRODUCED IN THE BIOCAT PROJECT

April 19th 2016

http://biocat-project.com/news/the-first-methane-has-been-produced-in-the-biocat-project/

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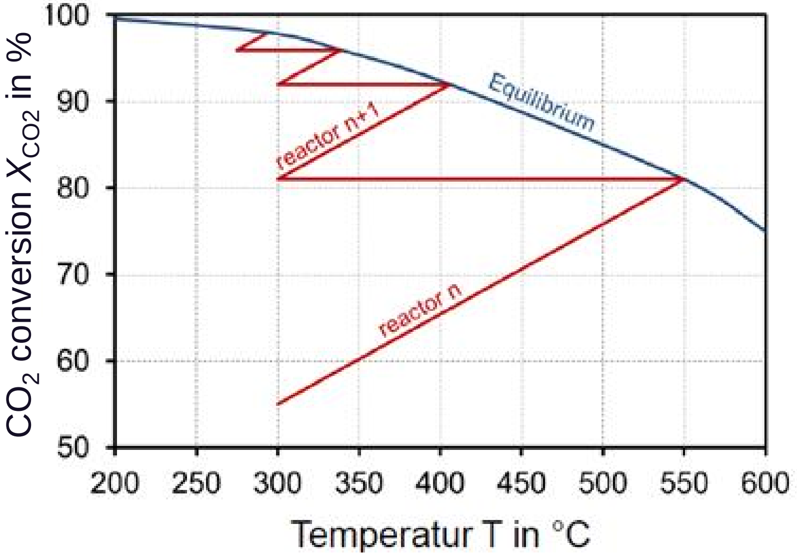
Biological vs. catalytical methanation

- Biological methanation
  - Suitable for smaller units
  - High tolerance against typical catalyst poisons (S-Compounds, O_2, C_xH_y)
  - Low temperature process
    - \+ High equilibrium conversion
    - \+ Flexible operation
    - \- Utilization of reaction heat is difficult
- Catalytic methanation
  - High reaction rate -> smaller reactor size
  - Commercially available in large scale
  - High temperature process
    - \+ Utilization of reaction heat is possible
    - \- Maximum conversion limited by equilibrium
    - \- Cold start slow → Limitation for flexibility



In catalytical methanation several reactors in series with intercooling and condensation are needed to reach high CO_2 conversion. Low temperature BM is not limited by thermodynamic equilibrium.

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Biological vs. catalytical methanation

Reactor type	**BM (ex-situ)**	**Fixed bed CM**
Catalyst	Nutrient + micro-organism solution	Ni-based
GHSV in 1/h $F_{V,\text{gas in}}/V_R$	10 – 100	2 000 – 5 000
T in °C	20 - 70	300 – 550
p in bar	1 - 4	> 5 – 10
Stage of development	Lab scale/pilot	Commercial
H_2-conversion %	99	> 90
Electricity demand in kWh/m^3 SNG (16 bar)	0.4 – 0.8	< 0.4
Tolerance of impurities	High	Low
Minimum load %	~0	~40
Tolerance for load changes	High	Low

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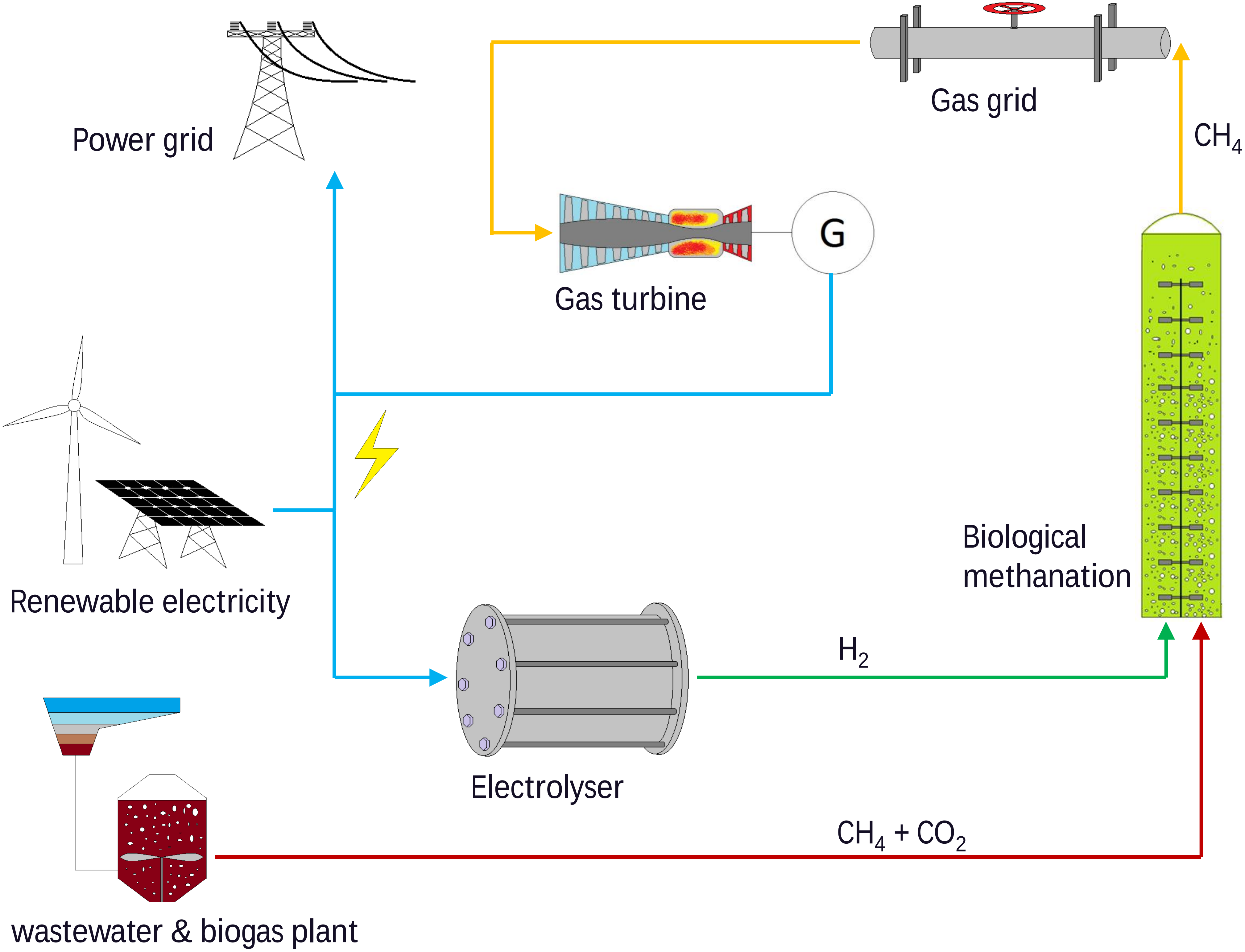
$$GHSV = \frac{\text{Volume flow of gases in to the reactor}\,[\mathrm{m}^3/\mathrm{h}]}{\text{Reactor volume}\,[\mathrm{m}^3]}$$


Gas grid
Power grid
CH4
G
Gas turbine
Biological
methanation
Renewable electricity
H2
Electrolyser
CH4 + CO2
wastewater & biogas plant

Modelling

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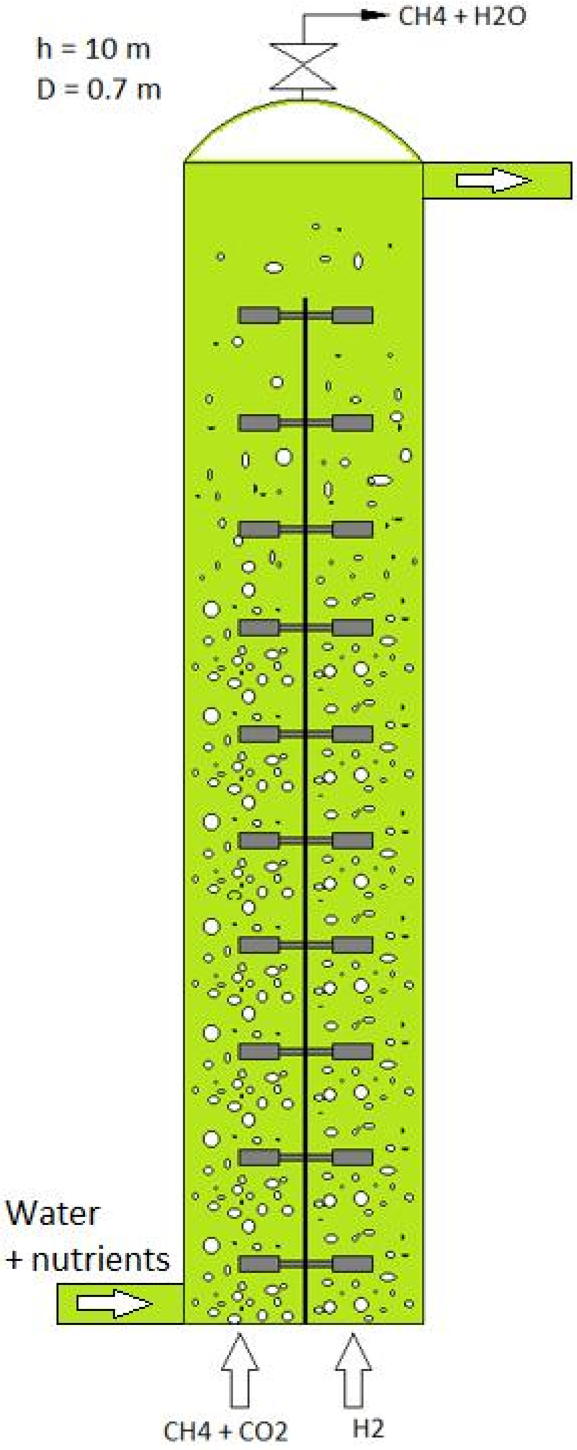


Electrochaea

- 10 stirrers on one axis
- Diameter 0.7 m, height 11.0 m
- Capacity for 1 MW electrolyser, H_2:
  - 19 kg/h
  - 245 m^3/h
  - 5 g/s

Model

- Implemented in Matlab
- Based on two journal articles
    1. Schill et al. 1996. Continuous cultures limited by a gaseous substrate: development of a simple, unstructured mathematical model and experimental verification with Methanobacterium thermoautotrophicum
    2. Garcia-Ochoa & Gomez. 2004. Theoretical prediction of gas-liquid mass transfer coefficient, specific area and hold-up in sparged stirred tanks
- Model for reactions needs to be improved for high tank with multiple stirrers (i.e. 0D → 1D)
- 1st model by literature → calibration & validation by measurements

Reaction & mass transfer

- H_2 concentration: $\frac{dc_D}{dt} = \overbrace{k_L a \cdot (c_D^* - c_D)}^{H_2 \text{ mass transfer}} - \overbrace{q_D^{max} \cdot \frac{c_D}{c_D + k_D} \cdot X}^{H_2 \text{ consumption}}$
- k_L describes mass transfer in the continuous phase around bubbles

  → function of dissipated energy (stirring power) and physical properties
- *a* is the interfacial area

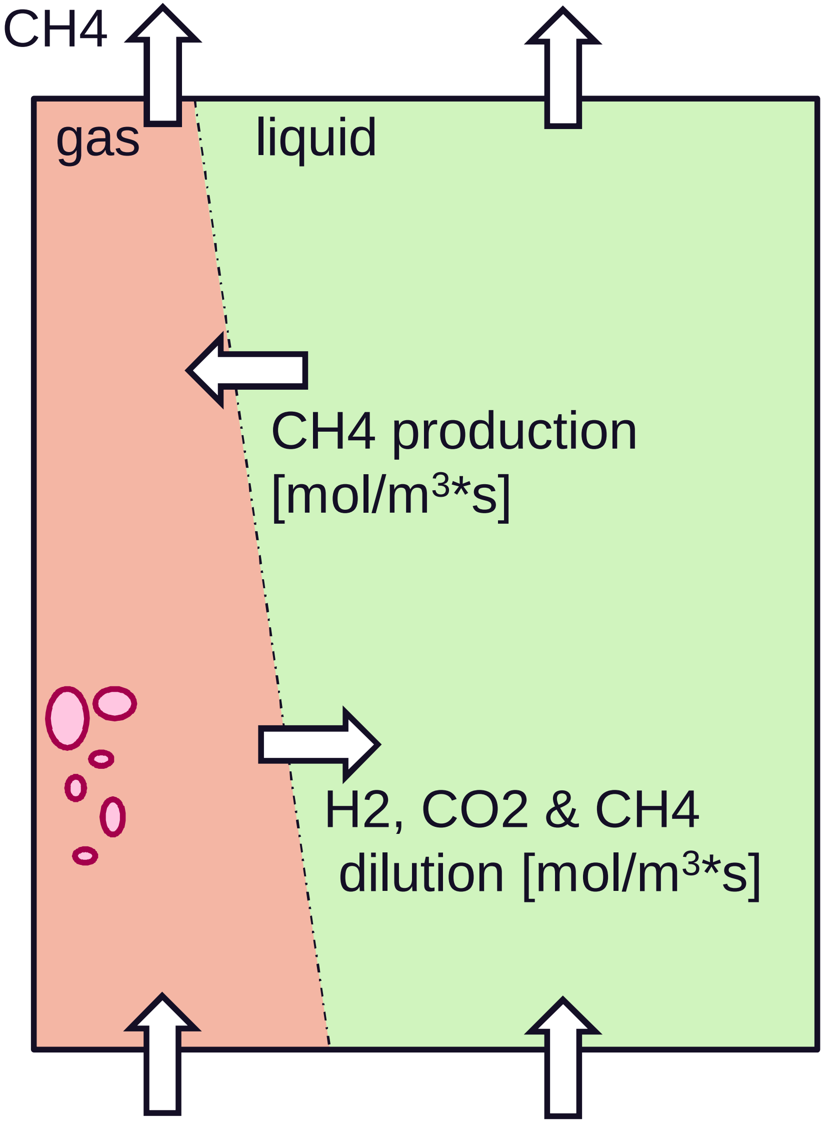
  → function of gas hold-up (gas flow and stirring power), bubble size (stirring power) and physical properties
- *c** is the saturation concentration of H_2 in liquid

  → increases by increasing pressure (Henry’s law)

Control volume

Outflow [m^3/s]
- H_2
- CO_2
- CH_4

Outflow [m^3/s]
- Water, nutrients, diluted gases



gas

liquid

CH_4 production [mol/m^3*s]

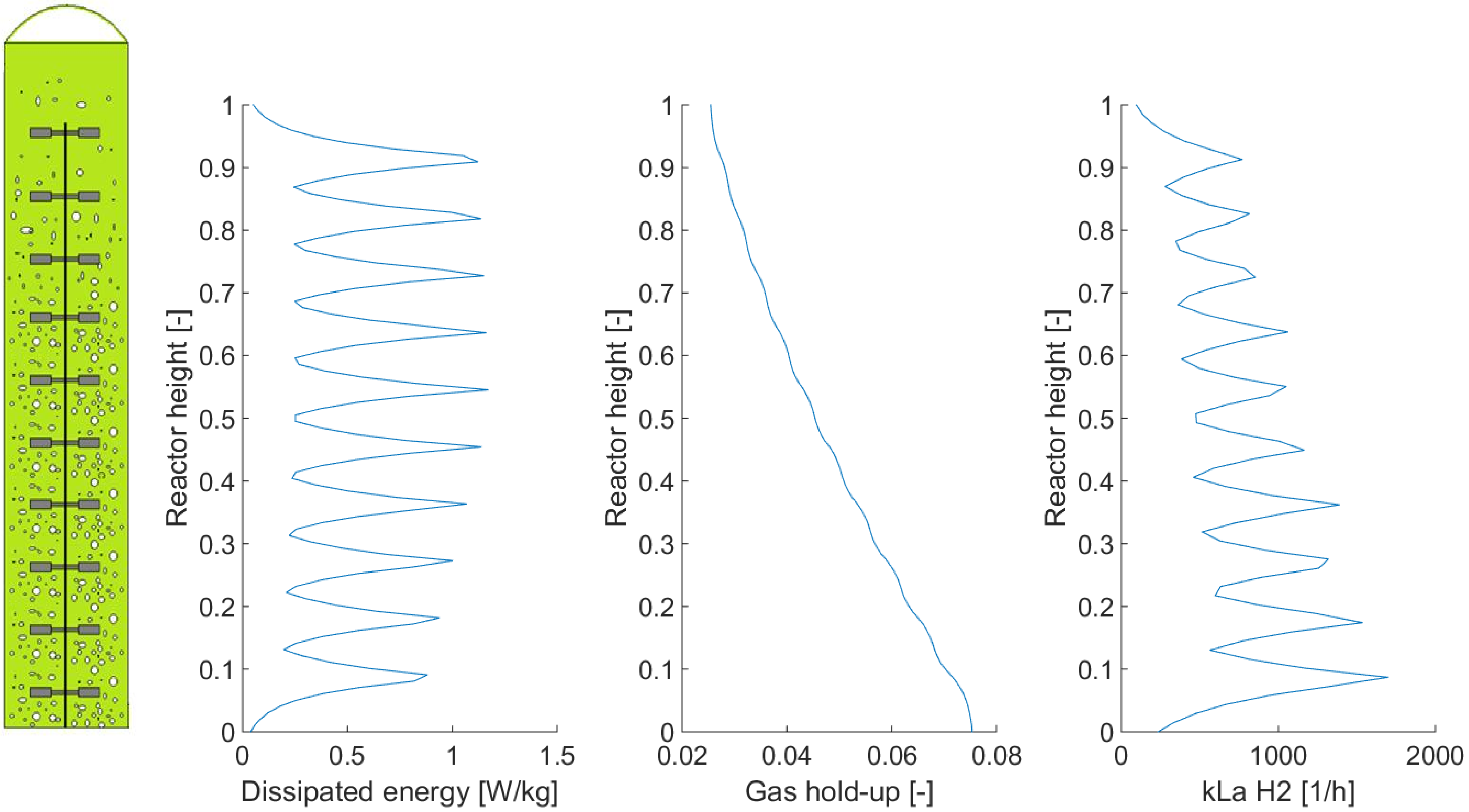
H_2, CO_2 & CH_4 dilution [mol/m^3*s]

Stirring properties
- Bubble rise velocity
- Gas hold-up
- Stirring power
- …

Inflow [m^3/s]
- H_2
- CO_2
- CH_4

Inflow [m^3/s]
- Water, nutrients

Initial results



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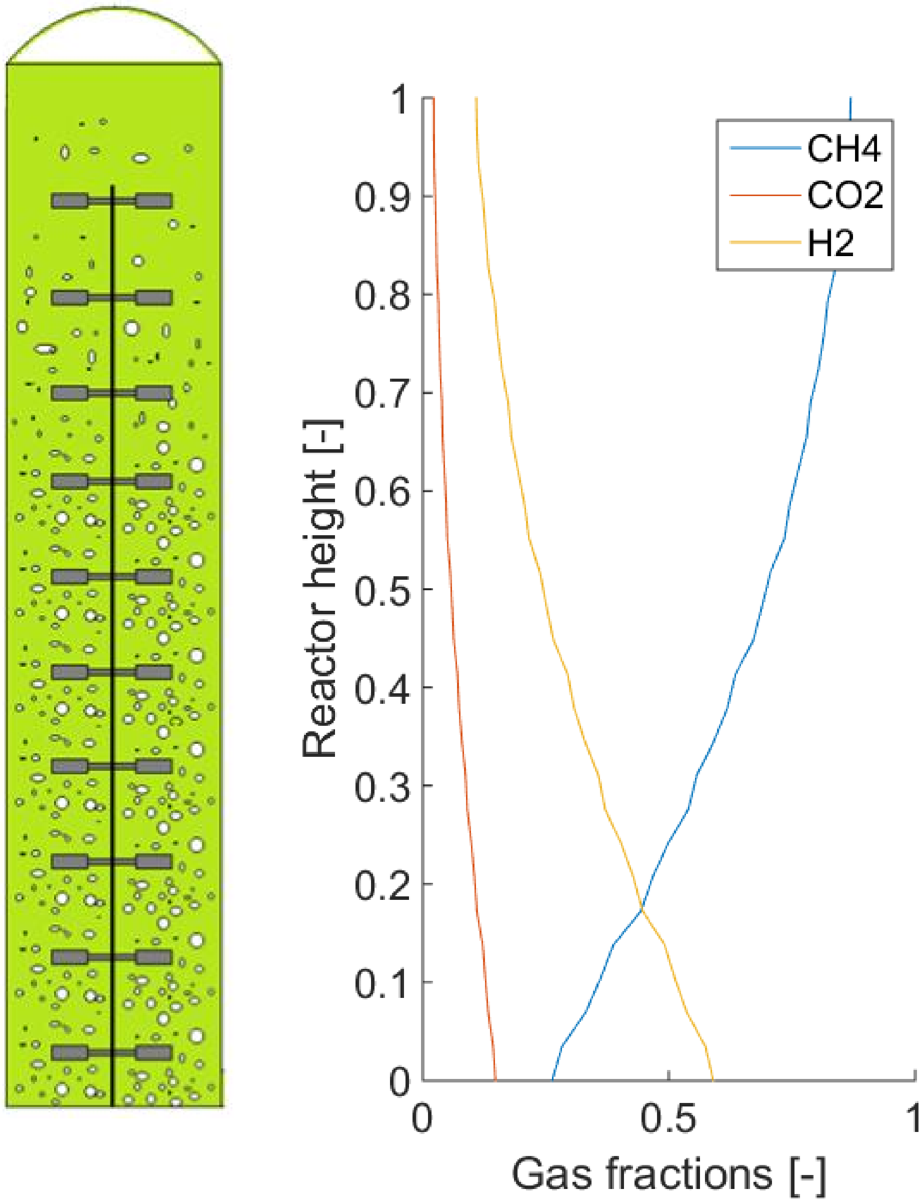

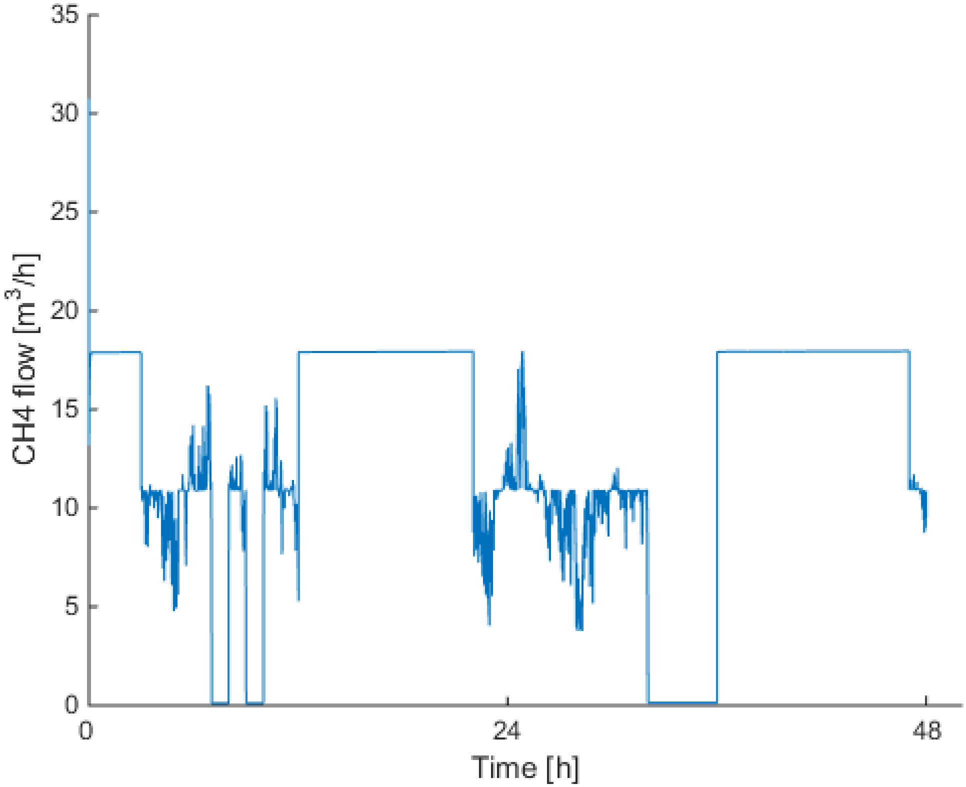

Initial results

- Biogas composition:

  CH4: 63 %

  CO2: 37 %

Inflow (GHSV)	12	30	60	1/h
Conversion efficiency	91.9	82.5	70.6	%
Product gas CH4 content	86.9	74.5	62.1	%
Stirring power	110	100	90	kW

GHSV: Total gas inflow per reactor volume during one hour

Conclusions

- Biological methanation is simple and flexible, but limited in capacity
- Problem is to have good mass transfer with low stirring power
- Validated model can be used for R&D of large scale reactors

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NEO-CARBON Energy project is one of the Tekes strategic research openings and the project is carried out in cooperation with Technical Research Centre of Finland VTT Ltd, Lappeenranta University of Technology LUT and University of Turku, Finland Futures Research Centre FFRC.