

## CHANIA 2023

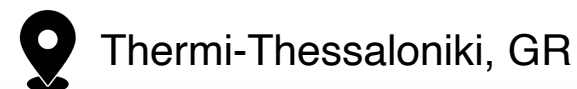
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# Comparative assessment of different packing materials in biological methanation

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- Carbon dioxide released into the atmosphere → Global warming

## Main contributors for the CO<sub>2</sub> emissions:

- Fossil fuel combustion
- Deforestation



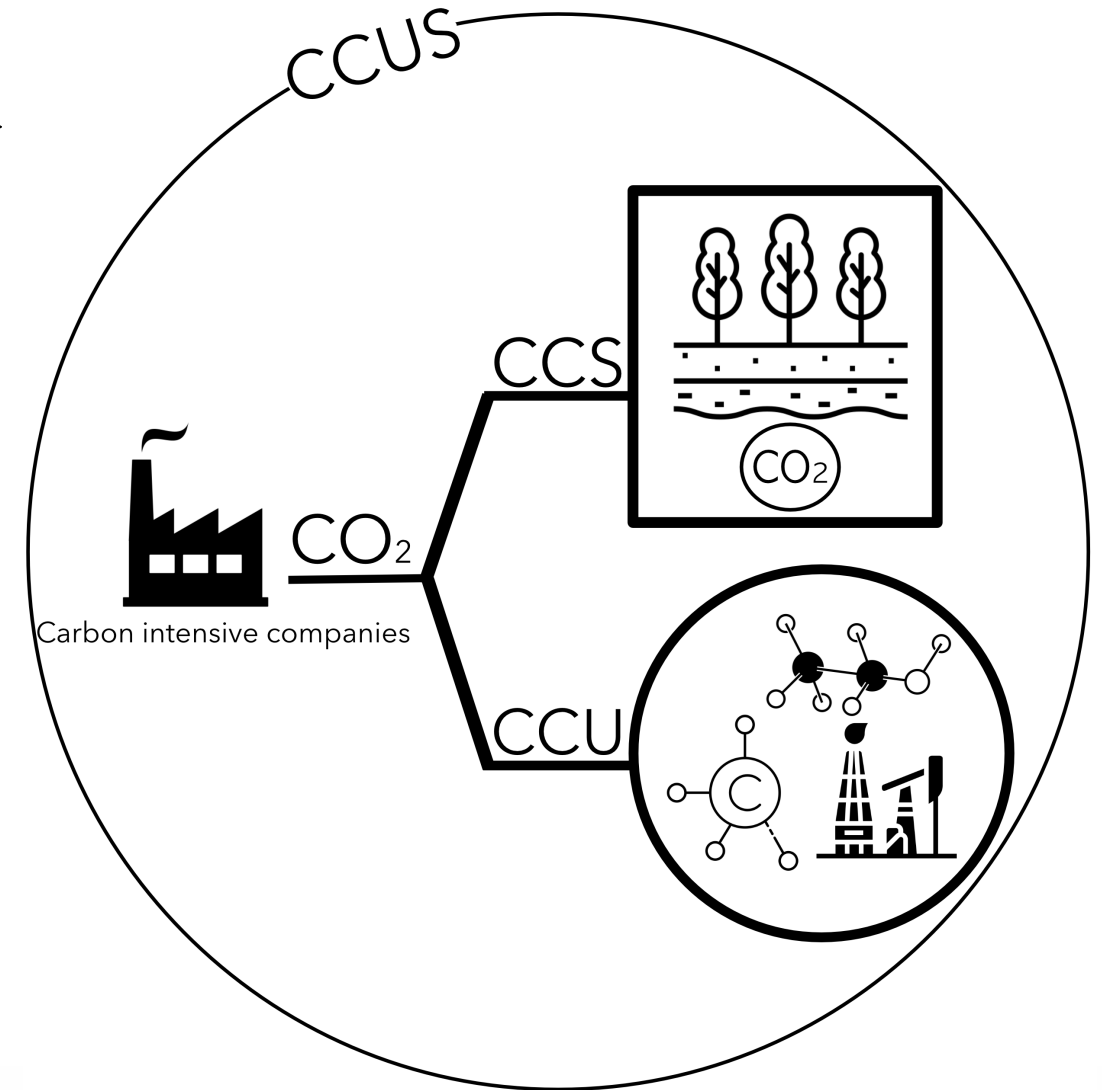
The trend of atmospheric CO<sub>2</sub> emissions is on the rise

## Main mitigation strategies:

- Carbon Capture and Storage (CCS)
- Carbon Capture and Utilization (CCU)



# CCUS



## Part of **Power to Gas** technology

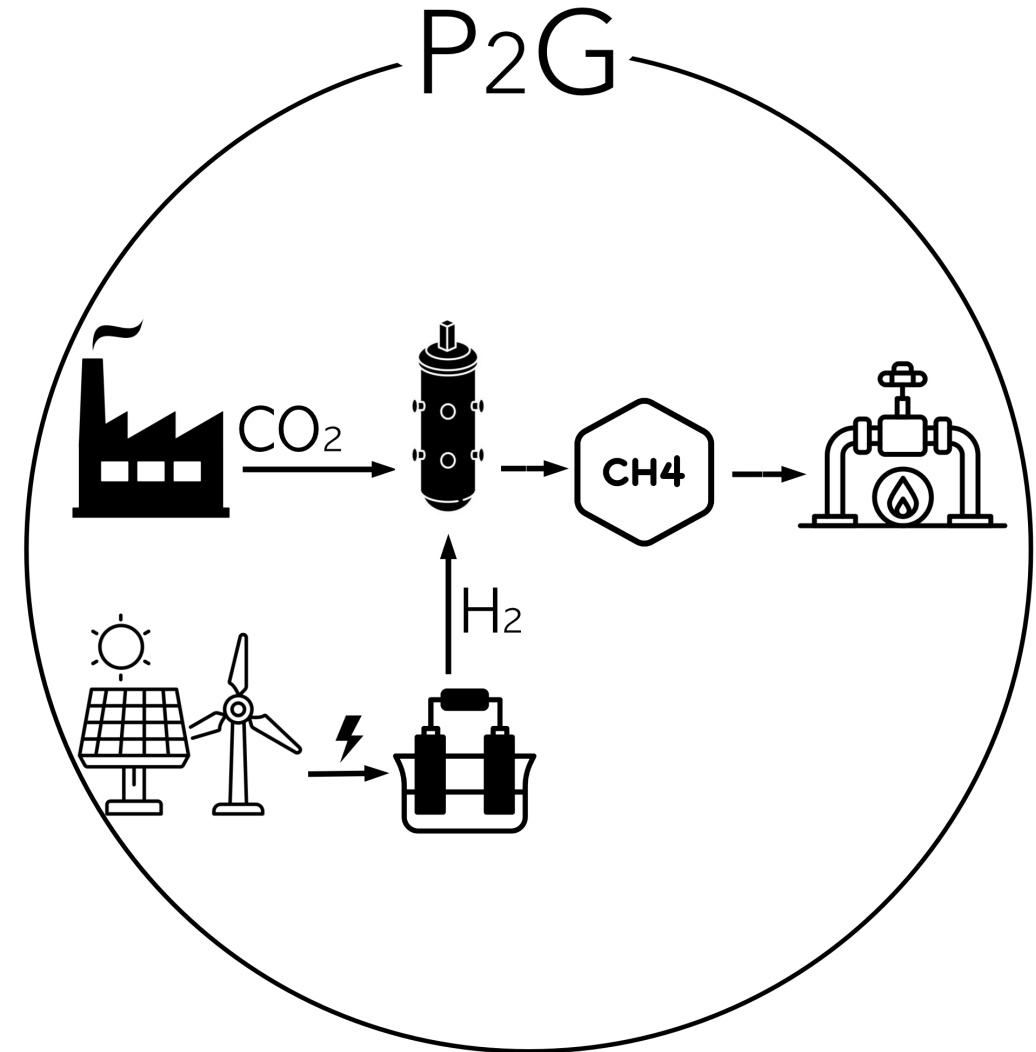
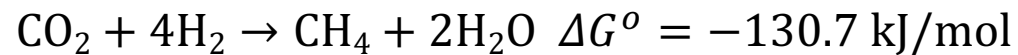
Power-to-Gas (P2G) combines:

- Hydrogen production through PEM electrolysis exploiting the surplus renewable energy (e.g., wind, solar energy etc.)
- Methanation, where the produced  $H_2$  reacts with  $CO_2$  to yield  $CH_4$

Methanation can be accomplished:

- Thermo-catalytically (Sabatier process)
- Biologically

Both processes share the same reaction:



# Biological Methanation

Carried out by **Hydrogenotrophic Methanogens**:

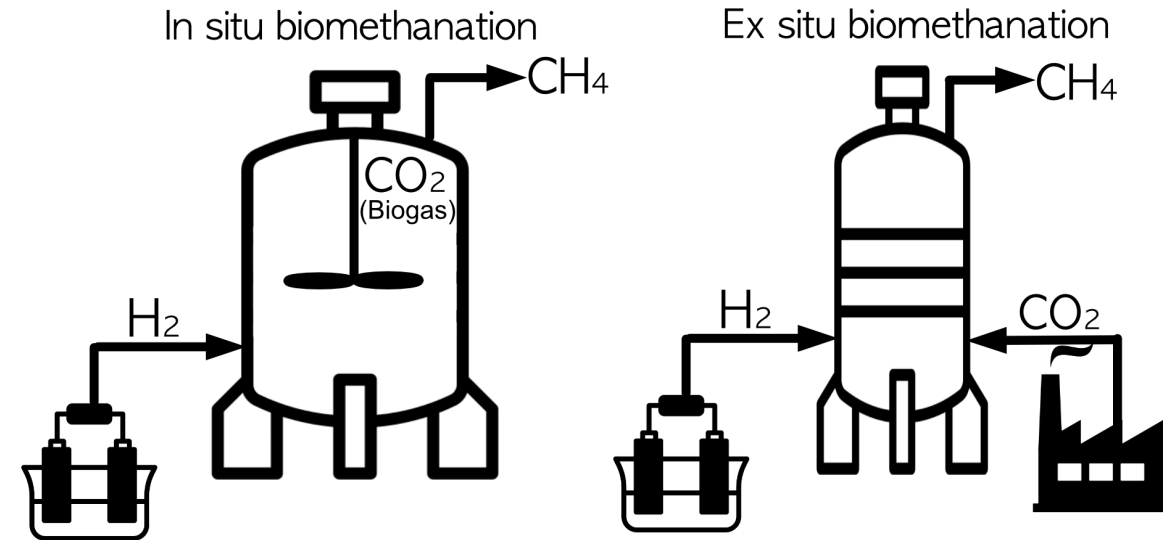
- Utilize  $H_2$  as an electron donor
- Reduce  $CO_2$  to  $CH_4$

**Influenced by several operating factors:**

- **Temperature:**  
Thermophilic systems exhibit higher production rates
- **pH:**  
7-8 (optimum range)
- **Mass transfer of  $H_2$ :**  
The main obstacle to be tackled

**Can be accomplished:**

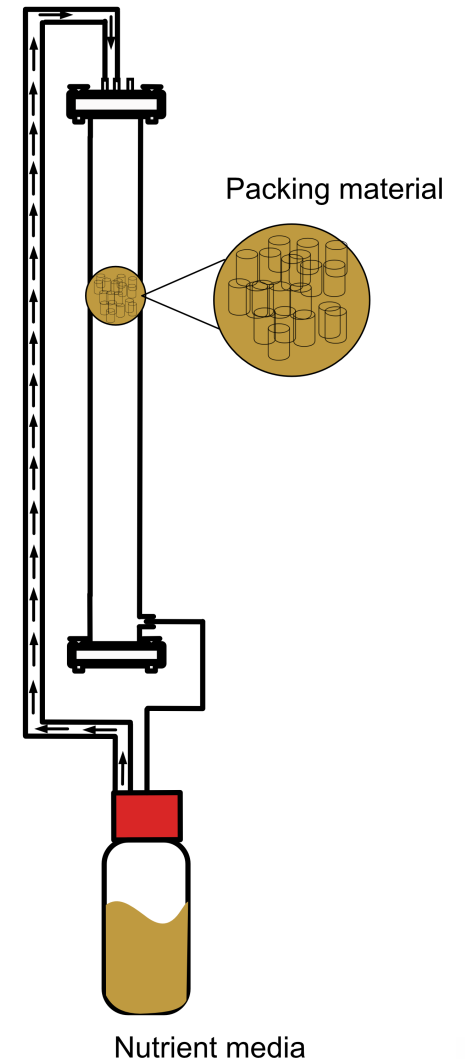
- *In-situ* or
- *Ex-situ*



- **Low  $H_2$  mass transfer** → limited  $H_2$  conversion resulting in the accumulation of Volatile Fatty Acids
- **Trickle bed reactor (TBR)** the most promising technology for biomethanation, where hydrogenotrophic methanogens are immobilized onto a packing material
- By immobilizing the microbial cells, it is possible to increase the efficiency of substrate conversion and to shorten the necessary retention times

## Optimal characteristics :

1. High surface area
2. Non-toxic
3. Reusable and cheap



# Aim & Objectives

The selection of appropriate packing material for the immobilization of biofilm – comparison among three different packing materials:

- Raschig rings (0.01 m<sup>2</sup>/g)
- Activated carbon (20 m<sup>2</sup>/g)
- Biochar (10.5 m<sup>2</sup>/g)

Comparative evaluation of the three packing materials, in terms of:

- Process efficiency:
  - output gas composition
  - average H<sub>2</sub>/CO<sub>2</sub> utilization
- pH
- Volatile Fatty Acids (VFA)





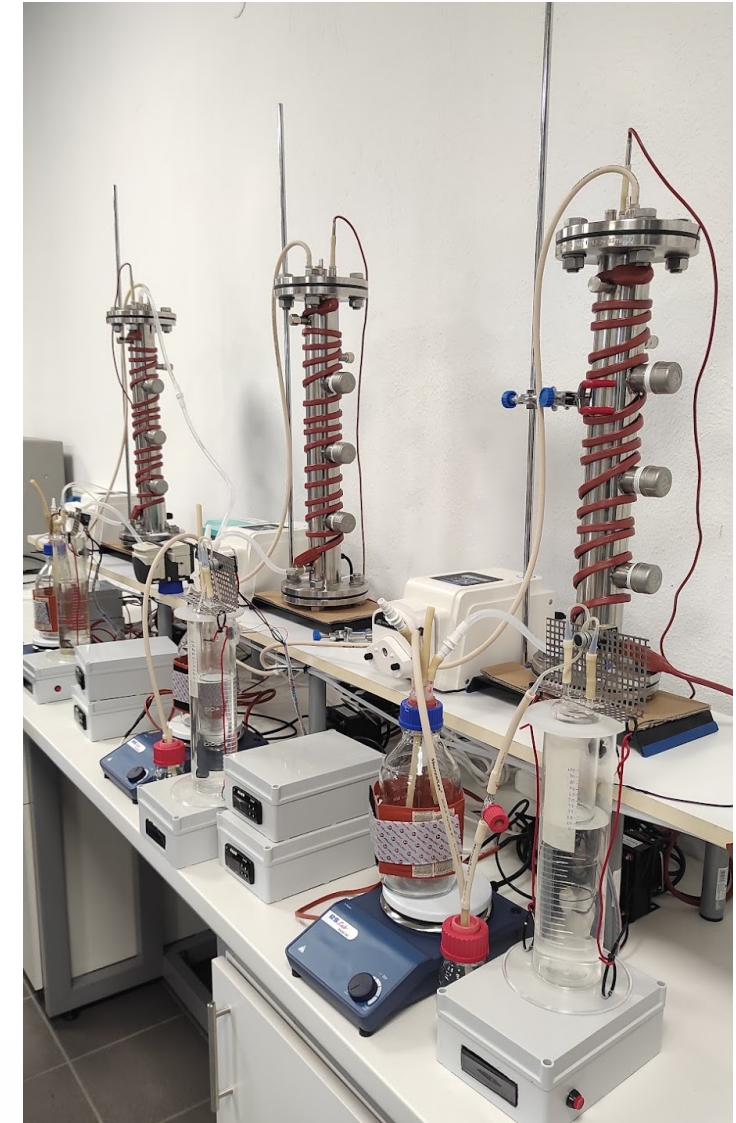
## Experimental procedure

**Three custom-made TBRs, made of stainless steel were installed, with:**

- 1-liter working volume
- 10:1 Height: Diameter ratio

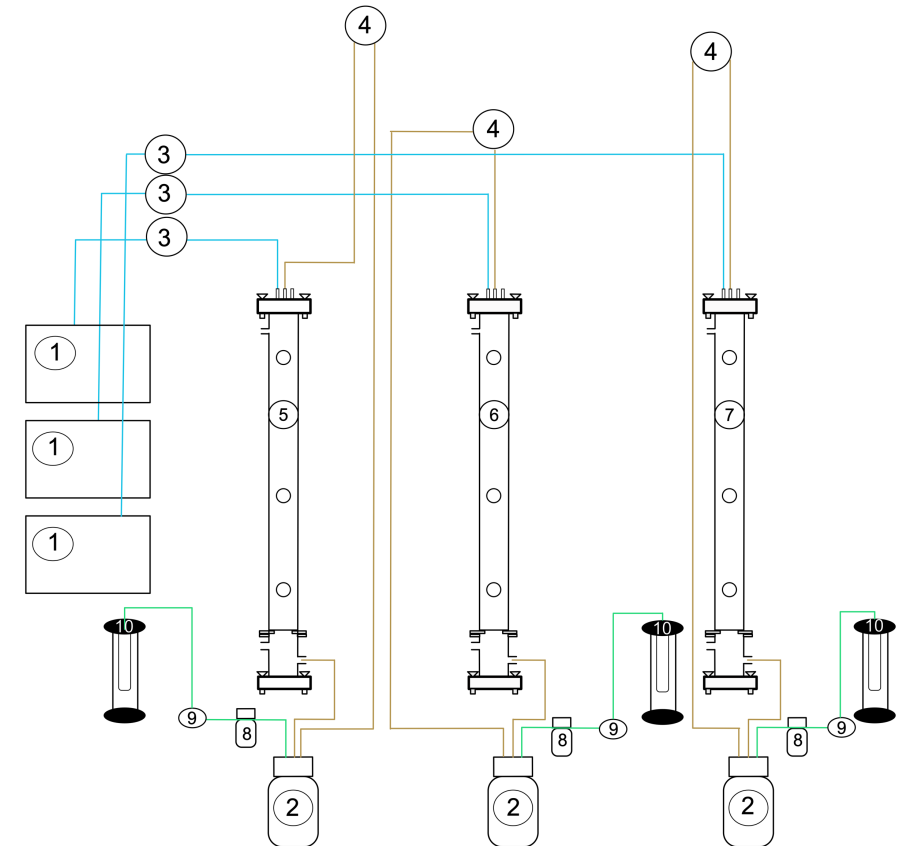
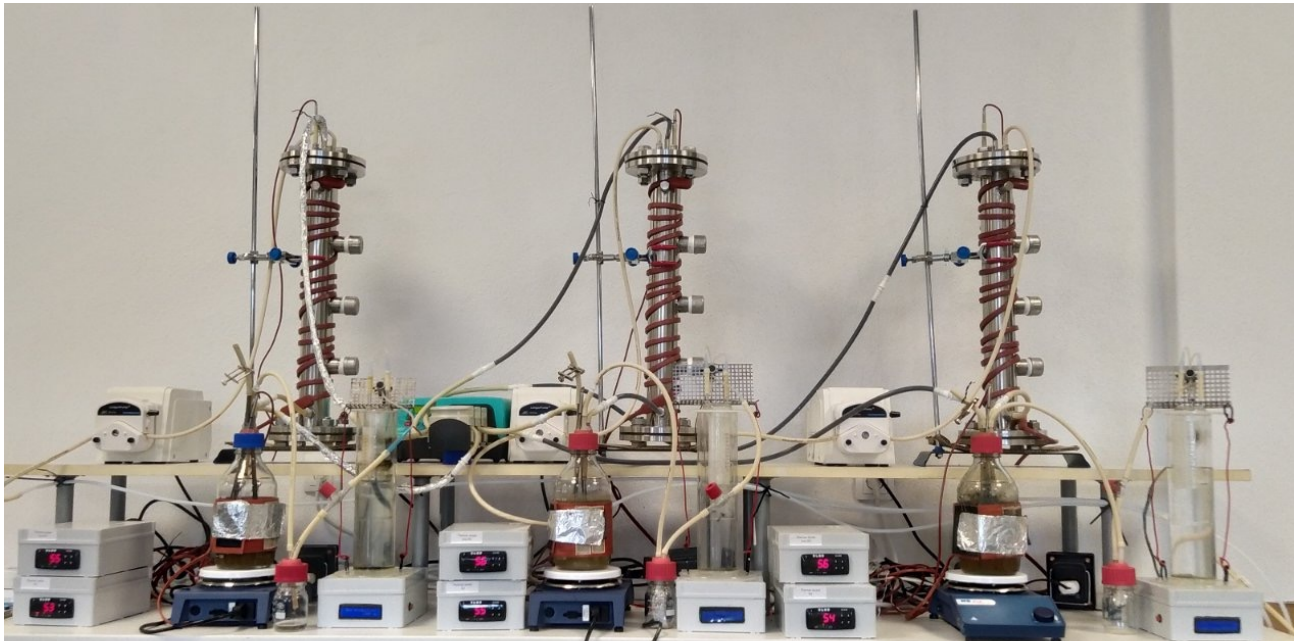
TBRs were tested in five different Gas Retention Times: 4 h, 3 h, 2 h, 1 h, and 45 min in terms of:

- Output gas composition determination (% CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>)
- VFA concentration determination (VFA, mg/L)
- pH measurement
- Produced output gas quantitative evaluation (mL)



# Materials and Methods

## Experimental setup



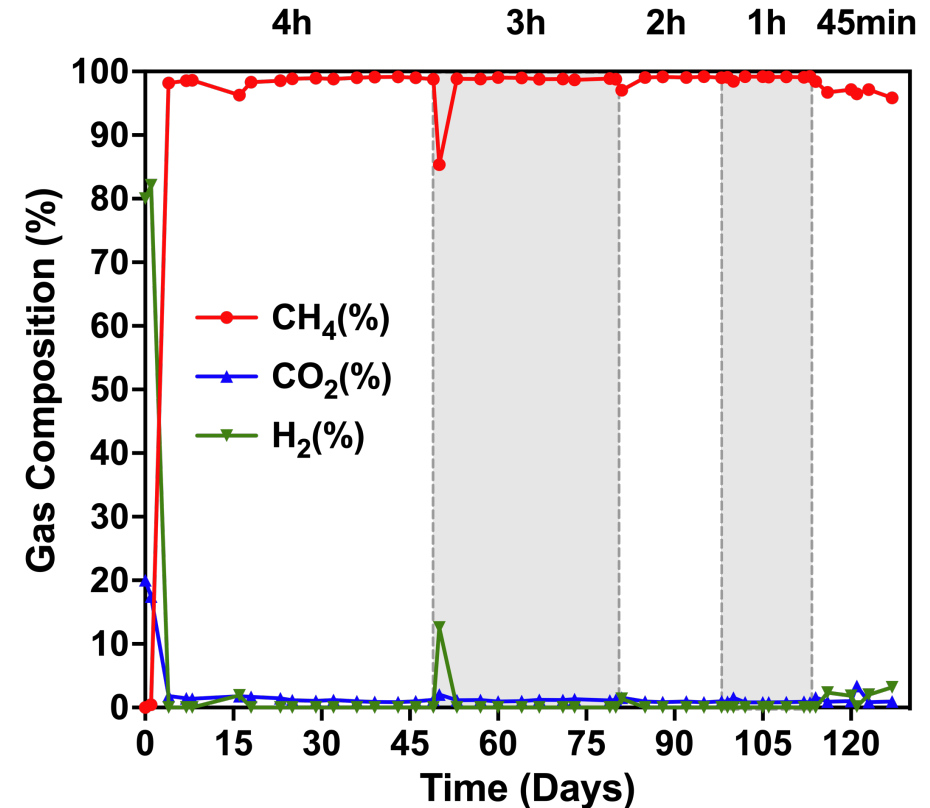
- 1. Gas bags
- 2. Nutrients solutions
- 3. Gas pumps (1 for each reactor)
- 4. Nutrients solution pump
- 5. Reactor R1
- 6. Reactor R2
- 7. Reactor R3
- 8. Water vapor traps
- 9. Gas sampling port
- 10. Gas counters



# Results and Discussion

## Output gas composition of TBR1 (Raschig rings)

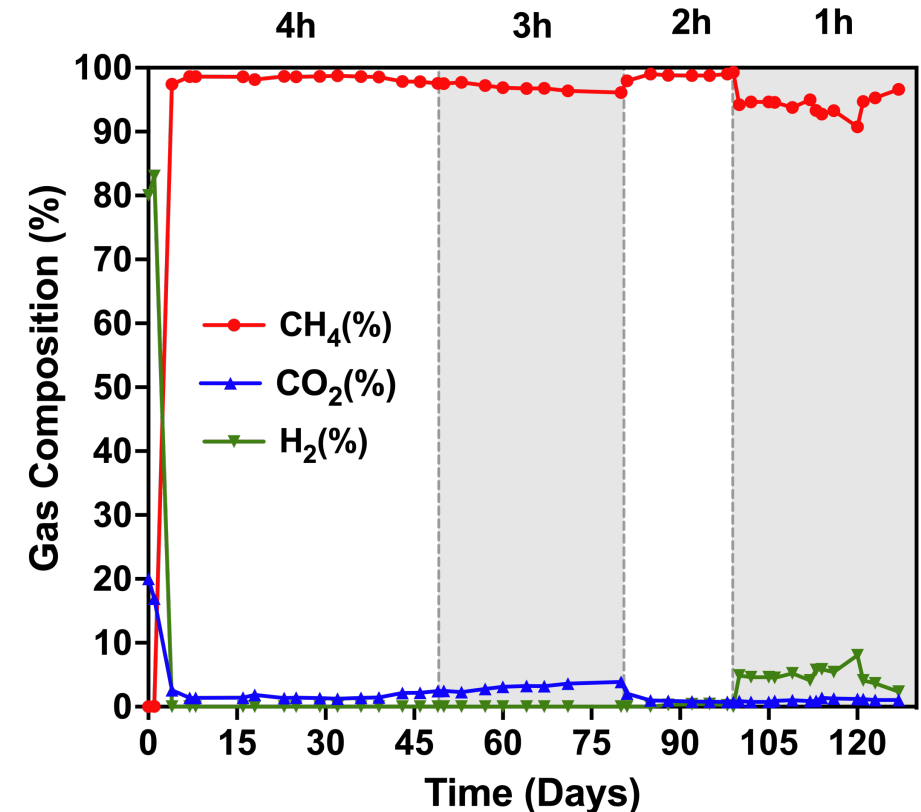
- **Quick adaptation** (4 days) for the microbial community applying 4 h GRT
- A drop during the 1<sup>st</sup> day of 3 h GRT, **consistent with other similar research**
- Stable  $\text{CH}_4$  production for all GRTs examined
- $\text{CH}_4$  composition higher than 98% in 4, 3, 2, 1 h GRT
- $\text{CH}_4$  composition higher than 95% in 45 min GRT



# Results and Discussion

## Output gas composition of TBR2 (Activated carbon)

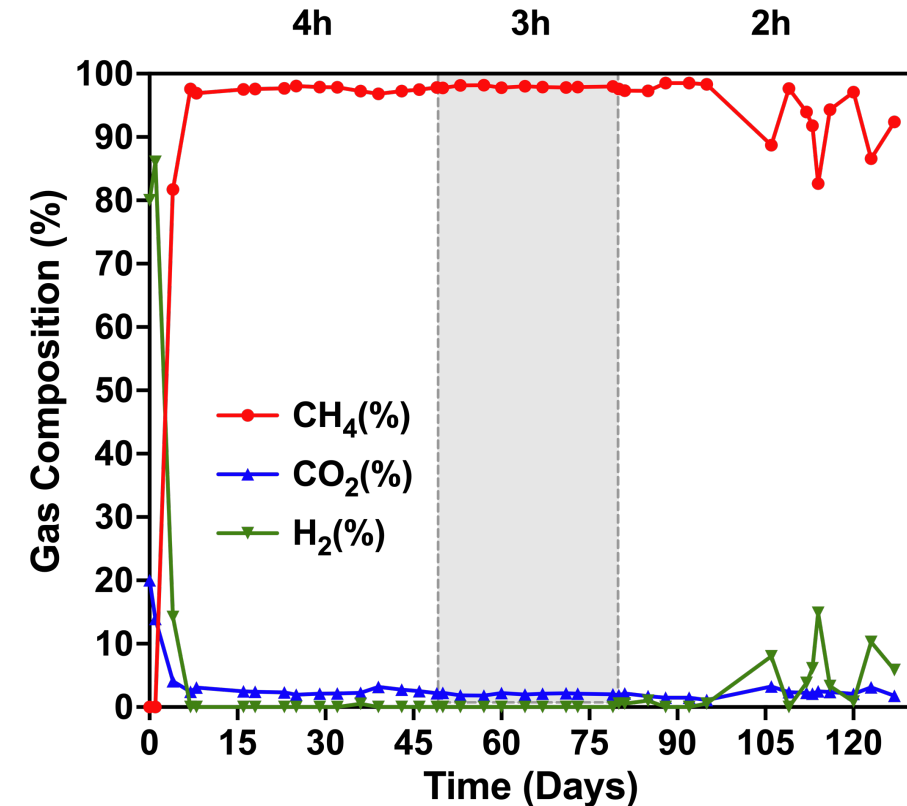
- **Quick adaptation** (4 days) for the microbial community, applying 4 h GRT
- **No decline** in the process efficiency after the reduction from 4 to 3 and to 2 h GRT
- Increased  $\text{CH}_4$  composition for 2 h GRT (>98%)
- A drop in the 1<sup>st</sup> day of 1 h GRT, **consistent with other similar research**
- Relatively unstable operation during 1 h GRT



# Results and Discussion

## Output gas composition of TBR3 (Biochar)

- Necessary adaptation time: 4 h GRT (7 days)
- **No decline** in the process efficiency after the shift from 4 to 3 h GRT
- Increased  $\text{CH}_4$  composition, by using 3 h GRT (>98%)
- Restart of the operation during the application of 2 h GRT

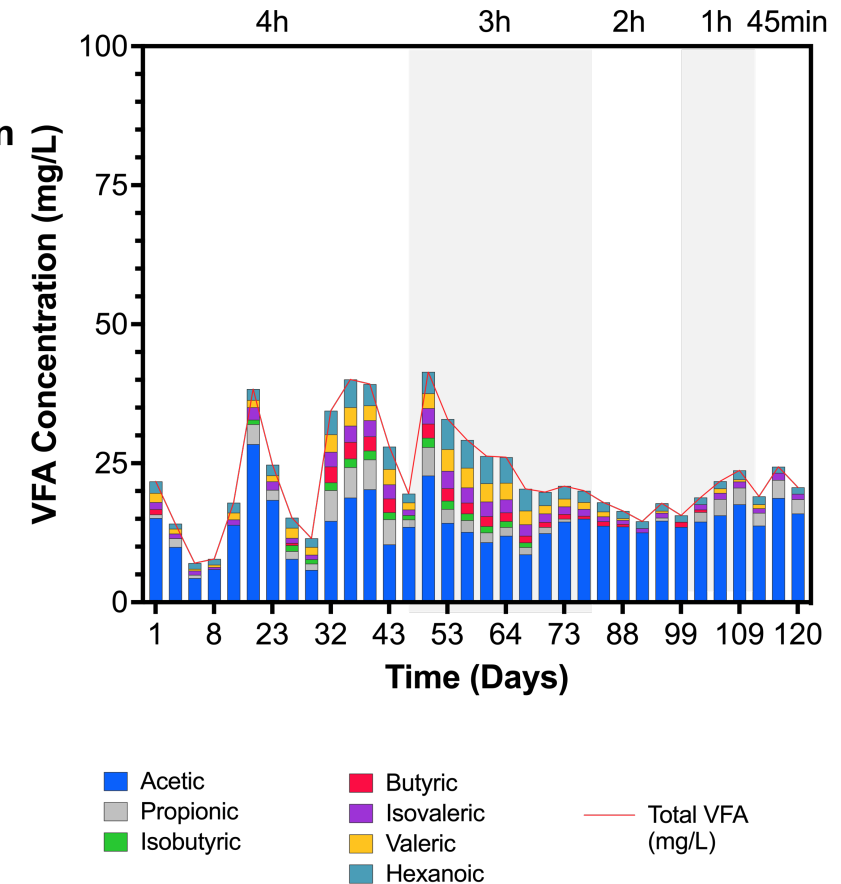
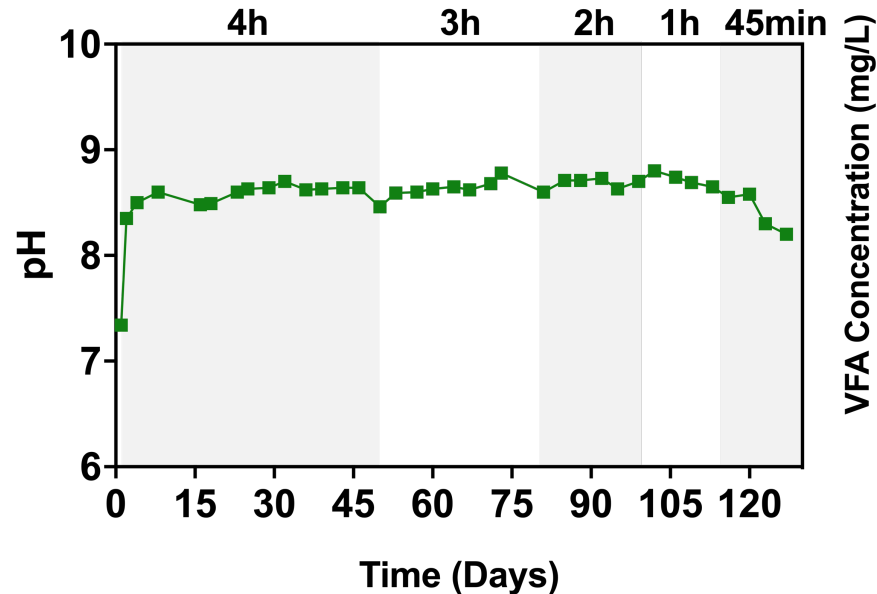


# Results and Discussion



## pH values and VFA concentrations of TBR1 (Raschig rings)

- TBR1 slightly out of the optimum range of pH values (8.5-8.6), **consistent with other similar research**
- pH stable during all the examined GRTs of TBR operation
- **Total VFAs concentration quite low** (Highest recorded value: 41.4 mg/L) in relation to the existing literature
- Slight upward trend of VFAs after the 18<sup>th</sup> day, due to the VFA contained in the nutrient/feed solution

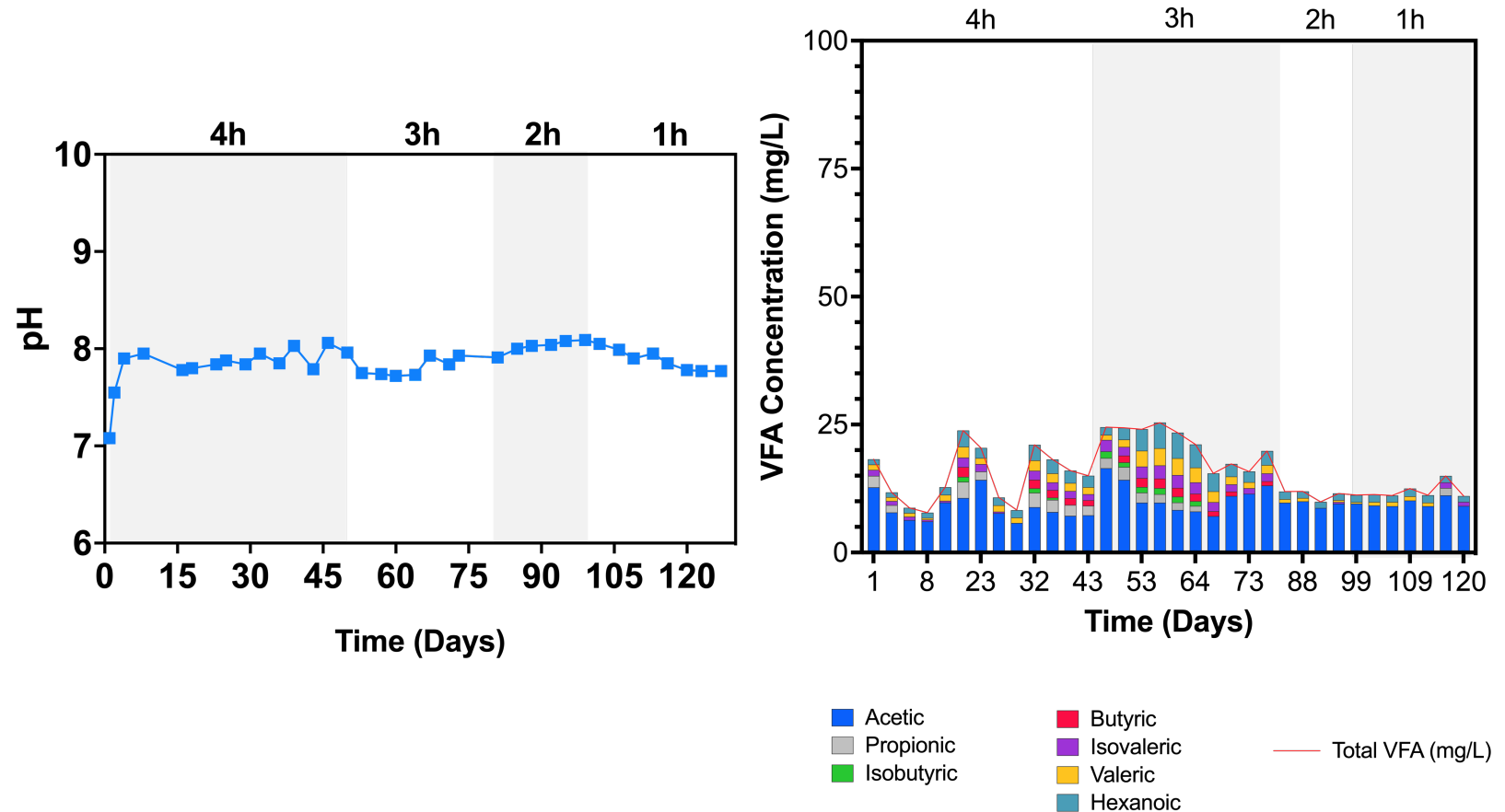




# Results and Discussion

## pH values and VFA concentrations of TBR2 (Activated Carbon)

- TBR2 in optimum range of pH values (7.7-8)
- pH stable during all the GRTs of TBR operation
- **Total VFAs concentration quite low** (Highest recorded value: 25.4 mg/L) in comparison with the existing literature
- Slight upward trend of VFAs after the 18<sup>th</sup> day, due to the VFA contained in the nutrient solution

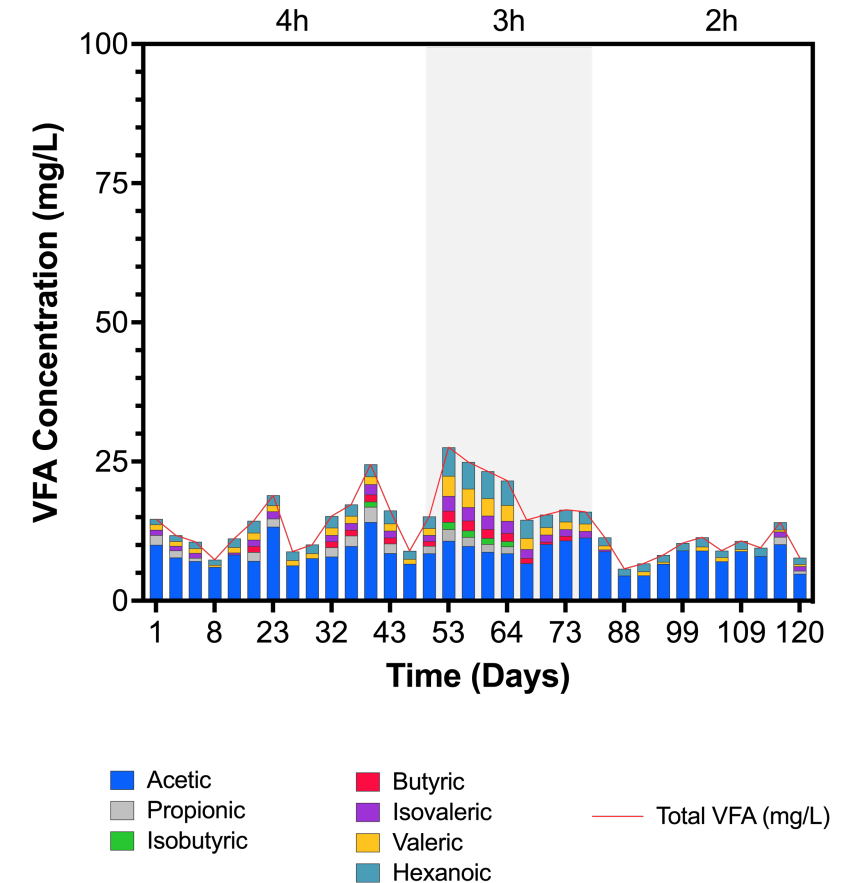
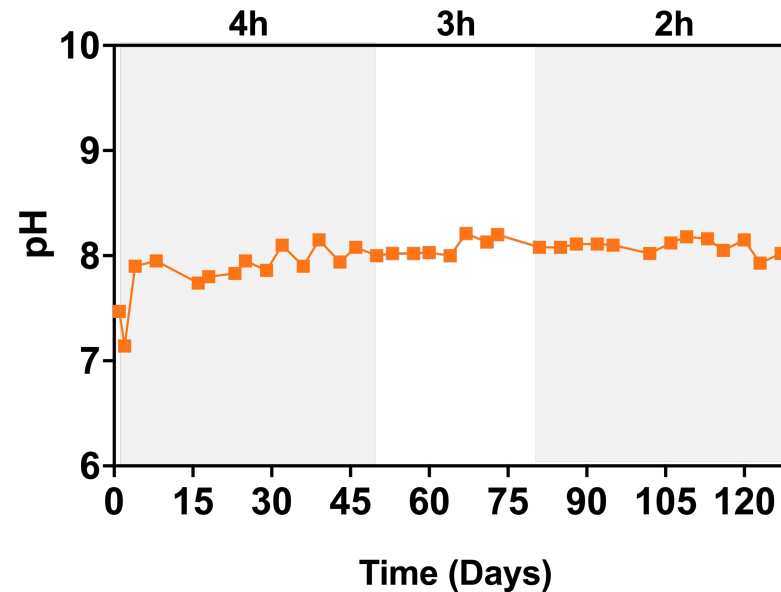


# Results and Discussion



## pH values and VFA concentrations of TBR3 (Biochar)

- TBR3 in the optimum range of pH values (7.9-8.1)
- pH stable during all the examined GRTs of TBR operation
- **Total VFAs concentration very low** (Highest recorded value: 27.6 mg/L) in relation to the existing literature
- Slight upward trend of VFAs after 18<sup>th</sup> day due to the VFA contained in the nutrient solution

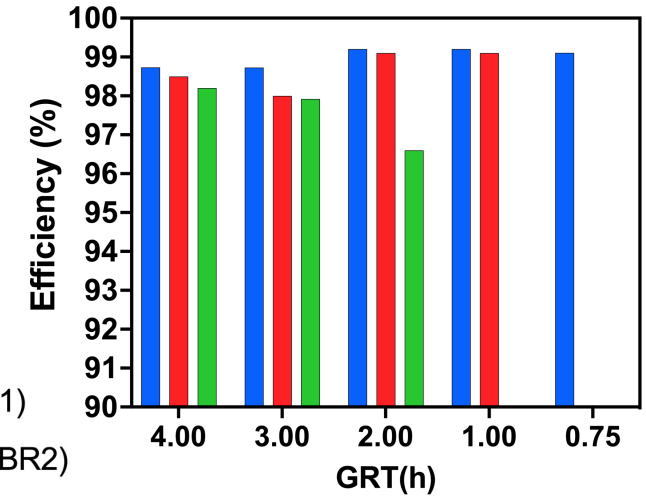


# Results and Discussion

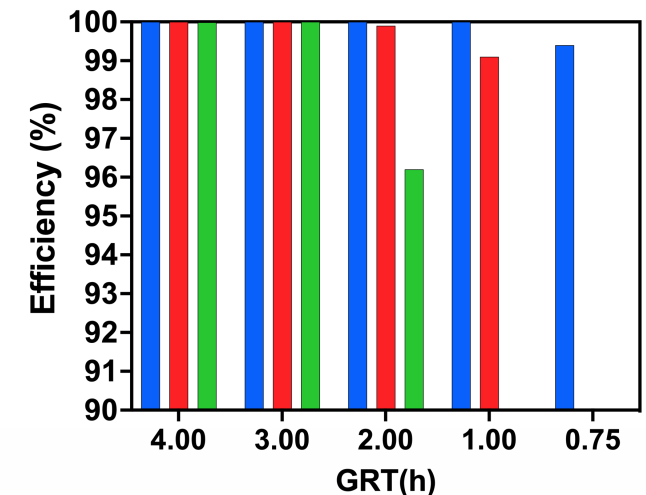
## Average CO<sub>2</sub>/H<sub>2</sub> utilization efficiency (%) of Trickle Bed Reactors (TBR)

- High H<sub>2</sub> utilization efficiency (100%), when applying 4 and 3 h GRT for all the three examined TBRs
- A sharp drop for the case of biochar and for 2 h GRT (96.2%), unstable operation of TBR2
- Lower H<sub>2</sub> utilization efficiency for the case of activated carbon and for 1 h GRT
- High CO<sub>2</sub> utilization efficiency (over 98%), when applying 4 and 3 h GRT for all the examined three TBRs
- A sharp drop for the case of biochar by using 2 h GRT (96.6%), unstable operation of TBR2
- High CO<sub>2</sub> utilization efficiency for the case of Raschig rings even for 45 min GRT (99%)

Average CO<sub>2</sub> Utilization Efficiency (%) per GRT



Average H<sub>2</sub> Utilization Efficiency (%) per GRT



# Conclusions



- **Raschig ring** found as more suitable packing material, than activated carbon and biochar
- Raschig rings achieved:
  - Output CH<sub>4</sub> composition in TBR1 higher than 98% for GRT 4, 3, 2 and 1 h
  - **Satisfactory and stable pH values for the operation**, although slightly higher than the optimal range
  - Low VFA concentrations (lower than 50mg/L)
- Comparing GRT 2 h → **Distinction between biochar-Raschig rings performance**
- Comparing GRT 1 h → **Distinction between activated carbon-Raschig rings performance**
- Biochar needs further investigation for lower GRT values



# Acknowledgements

The “Demonstration of a mobile unit for hybrid energy storage based on CO<sub>2</sub> capture and renewable energy sources (LIFE CO<sub>2</sub>toCH<sub>4</sub> - LIFE 20/CCM/GR/001642)” project has received funding from the LIFE Programme of the European Union.





# Thank you for your attention!

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