Thermochemical methanation

Basics

Selina Nieß, DBFZ Deutsches Biomasseforschungszentrum gGmbH

Hydrogen and Hydrogen Derivates – Possibilities and Constraints Webinar Series, 07.02.2024

On behalf of:
Federal Ministry for Digital and Transport

This publication was carried out on behalf of the Federal Ministry for Digital and Transport under file number 3544.1/ Pilot-SBG Phase 1b The sole responsibility for the content lies with the author.

From the Basics to the Pilot-SBG Project

BASICS

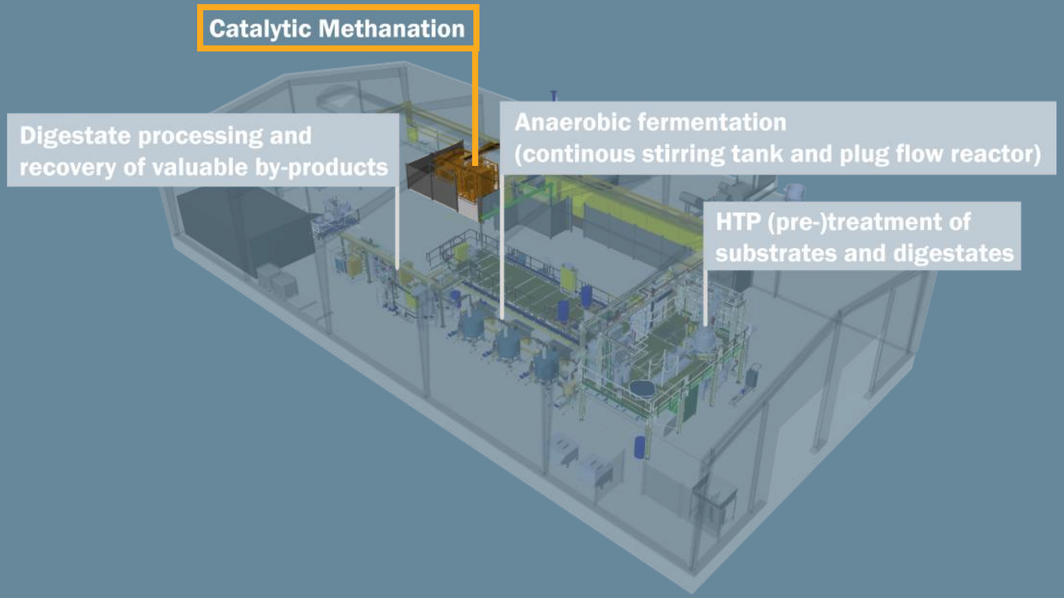
WHAT
Basic principles

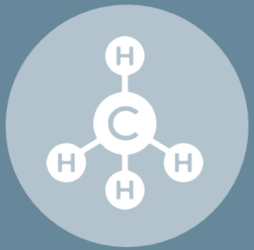
HOW
Operating conditions

WHY
Common applications

Pilot-SBG

Usage of **residual and waste materials for biofuel production**





Climate-friendly, renewable methane as fuel

Background

Interesting facts on thermocatalytic methanation

1. Disovered in **beginning of 20th century** by Sabatier and Senderens

2. Sabatier **won Nobel prize in chemistry** in 1912

3. CO methanation **used for SNG production during oil crisis** in 70s

4. **NASA research** to utilize CO_2 and produce water

©2024 DBFZ | Pilot-SBG | Selina Nieß

NASA: https://arc.aiaa.org/doi/pdf/10.2514/6.2005-2706; Nobel prize: https://www.nobelprize.org/prizes/chemistry/1912/sabatier/biographical/ ; SNG production: https://www.sciencedirect.com/science/article/pii/S0016236115011254

Thermochemical Methanation

Methanation reactions

Water-Gas-Shift:	CO_2	$+ H_2$	$\rightleftarrows$	CO	+	H_2O	$\Delta H_R^{298\,K} = +\ 41\ kJ\ mol^{-1}$
CO methanation:	CO	$+ 3\ H_2$	$\rightleftarrows$	CH_4	+	H_2O	$\Delta H_R^{298\,K} = -\ 206\ kJ\ mol^{-1}$
CO_2 methanation:	CO_2	$+ 4\ H_2$	$\rightleftarrows$	CH_4	+	$2\ H_2O$	$\Delta H_R^{298\,K} = -\ 165\ kJ\ mol^{-1}$

The thermochemical methanation is the hydrogenation of a carbon source to methane and water.

→ CO or CO_2 as carbon source and hydrogen
→ Low temperature
→ Reactor with catalyst
→ High pressure

Thermochemical CO_2 Methanation

Temperature requirements

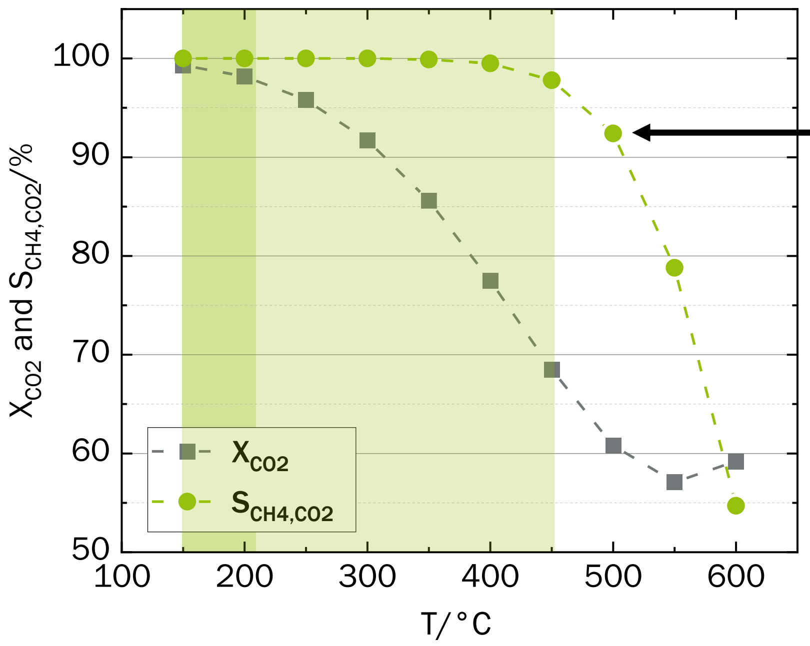
8 electron reduction

CO_2 methanation: $\overset{+IV}{CO_2} + 4\,H_2 \rightleftarrows \overset{-IV}{CH_4} + 2\,H_2O$ $\Delta H_R^{298\,K} = -165\ kJ\ mol^{-1}$

Thermodynamic equilibrium:
(1 bar, H_2/CO_2 = 4)

- Lower T for high conversion
- But: **kinetic limitation**!

→ Active catalysts at low T needed



Side reactions at higher T

Thermochemical CO_2 Methanation

<u>Choosing the right catalyst</u>

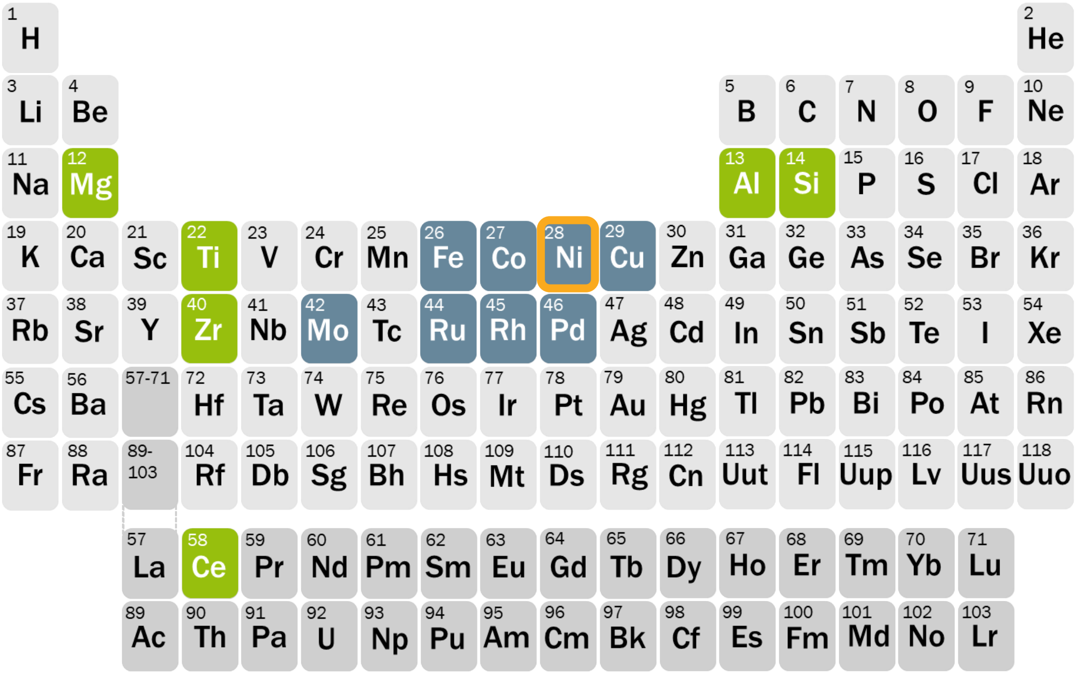
Usually, supported catalysts are used for high dispersion of metal

→ Active metal

→ Oxidic support material

Ni is a good choice as catalyst, because:

- Good catalytic perfomance
- High CH_4 selectivity
- <u>Low price</u>



Literature on catalysts: https://www.mdpi.com/2073-4344/7/2/59

Thermochemical CO_2 Methanation

Reactors for thermochemical methanation

Most commonly: fixed-bed reactors

→ adiabatic

→ cooling

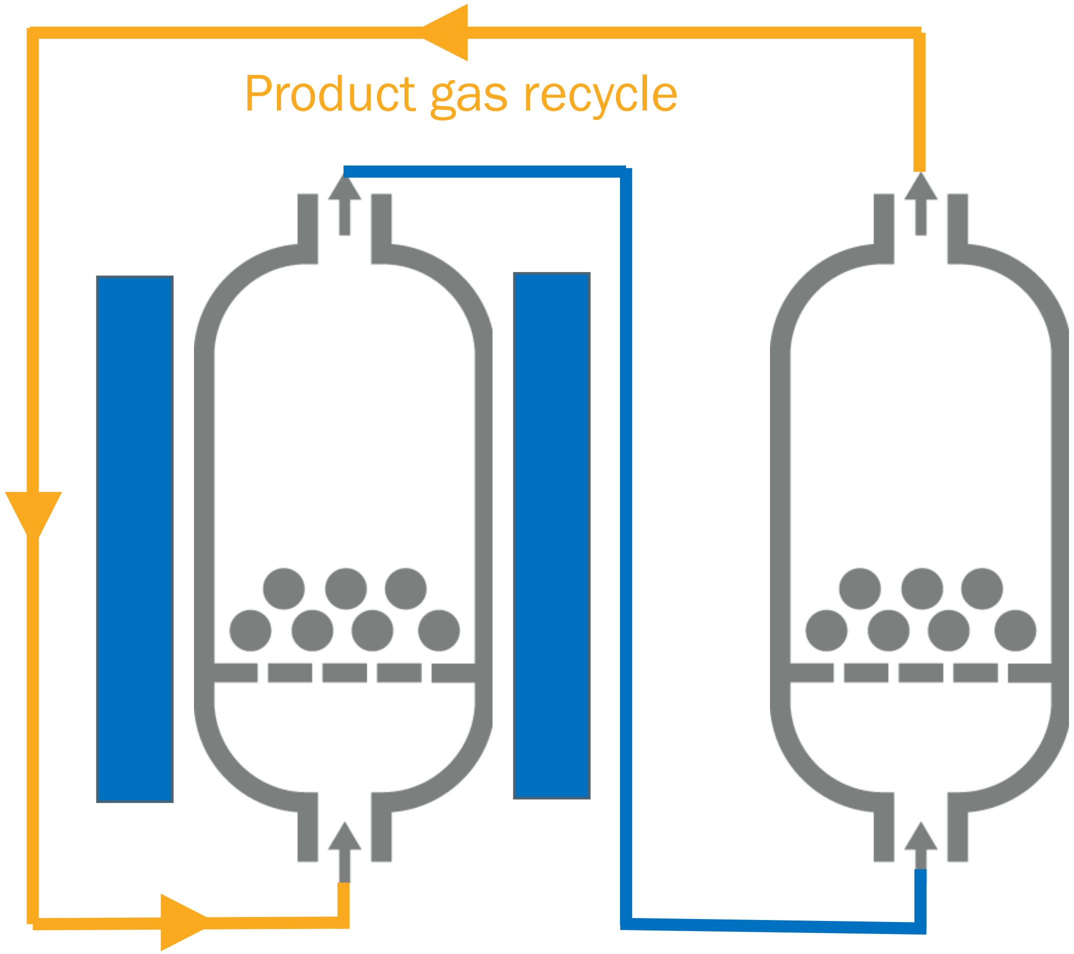
Multi-stage fixed-bed reactors

→ Intermediate cooling

→ Gas recycling

Research:

e.g. Fluidized bed reactors, Structured reactors, multi phase reactors



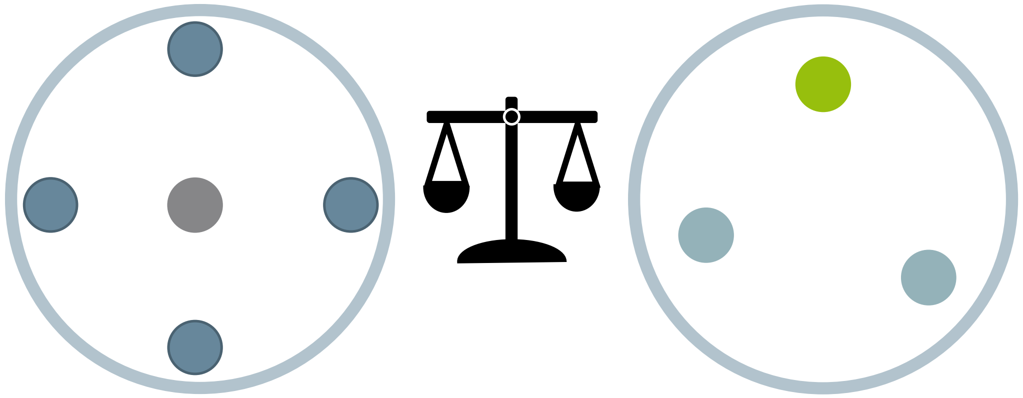
Literature on reactors: https://www.sciencedirect.com/science/article/pii/S0016236115011254

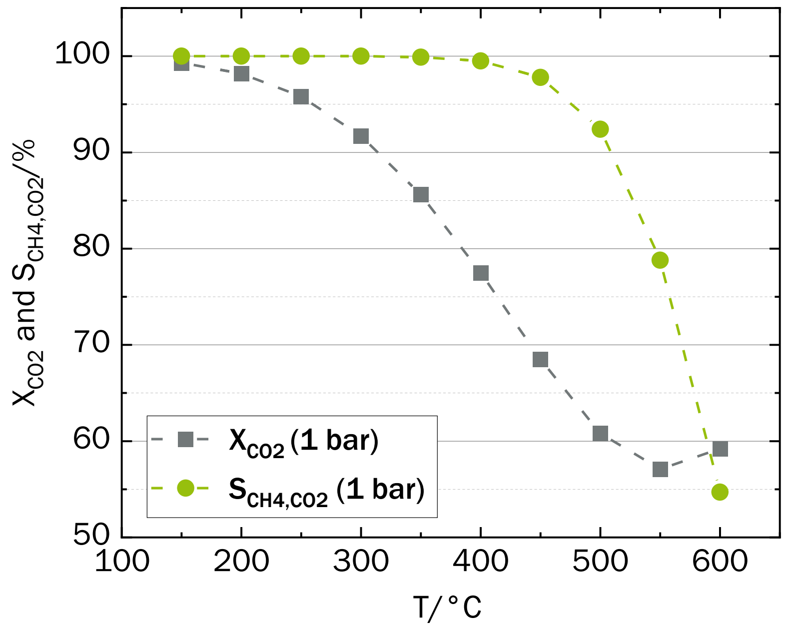
Thermochemical CO_2 Methanation

High pressures for high conversions

CO_2 methanation:	CO_2 + 4 H_2	⇄	CH_4 + 2 H_2O	$\Delta H_R^{298\ K} = -165\ kJ\ mol^{-1}$
	5 molecules		3 molecules	

1 bar





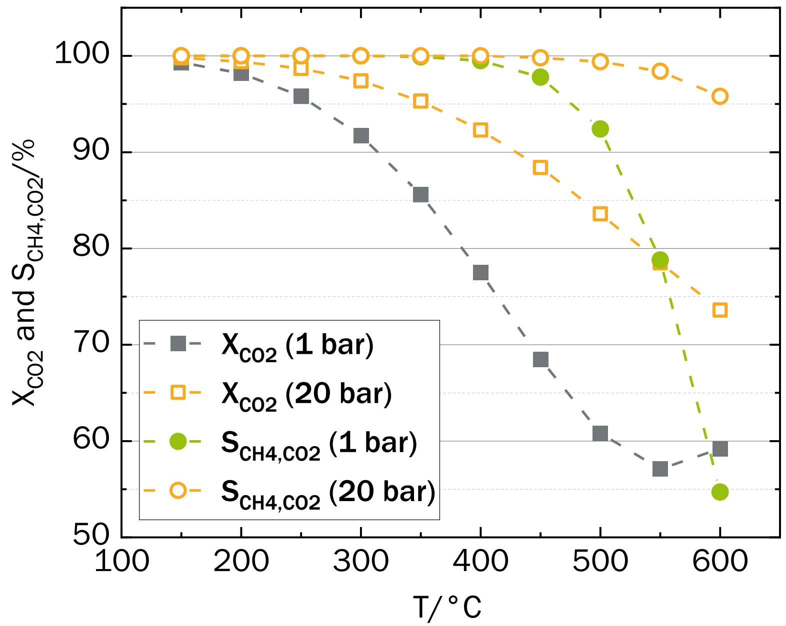
Thermochemical CO_2 Methanation

High pressures for high conversions

CO_2 methanation: $CO_2 + 4\,H_2 \rightleftarrows CH_4 + 2\,H_2O$ $\Delta H_R^{298\,K} = -165\ kJ\ mol^{-1}$

5 molecules 3 molecules

20 bar



Thermochemical CO_2 Methanation

Why Methane?

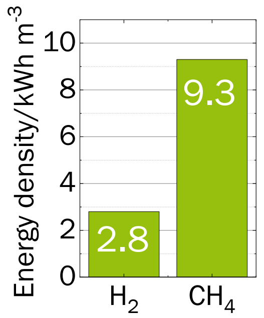
- Energy carrier (9.3 kWh/m³)
- High temperature generation
- Fuel
- Precursor for chemical synthesis

→ **Especially interesting with renewable methane**

And why transform H_2 into Methane?

1. Energy density:

→ CH_4 has 3-fold higher energy density



2. Infrastructure:

- CH_4: distribution network in GER ~ 530.000 km
- H_2: no nationwide infrastructure of its own yet

→ Theoretically, 10 % H_2 can be added to the gas grid

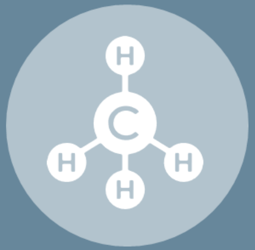
Gas network in GER: https://gas.info/gas-im-energiemix/gas-infrastruktur and https://gas.info/gas-im-energiemix/gas-infrastruktur/wasserstoff-im-gas-netz

Pilot-SBG project

A pilot scale biorefinery

An example for the production of renewable methane

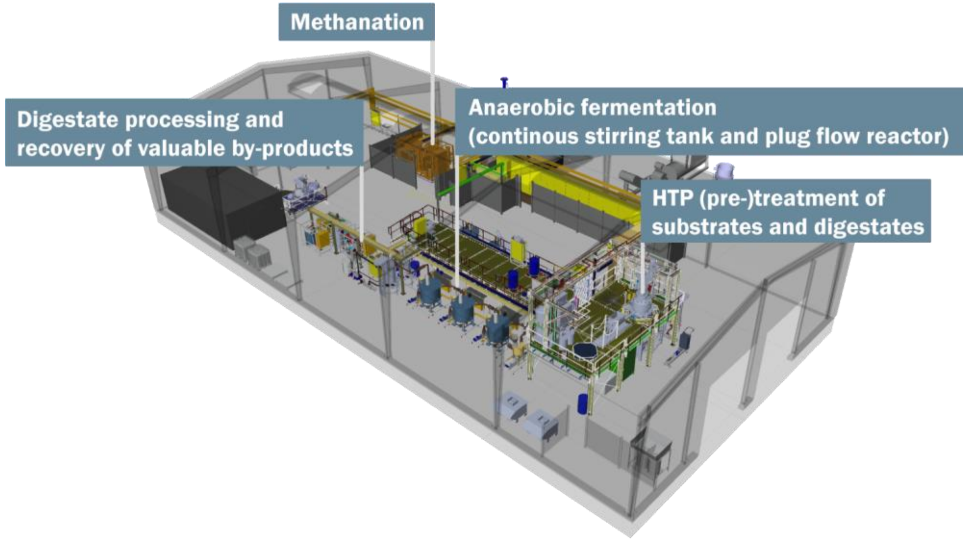
Usage of **residual and waste materials for biofuel production**

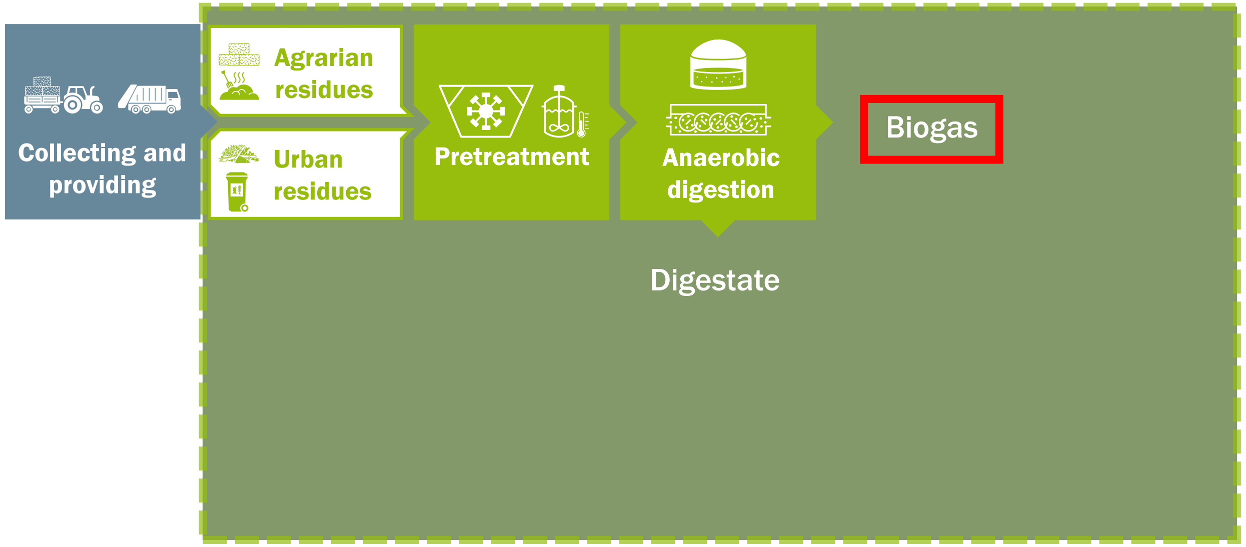


Climate-friendly, renewable methane as fuel

Pilot-SBG project

A pilot scale biorefinery

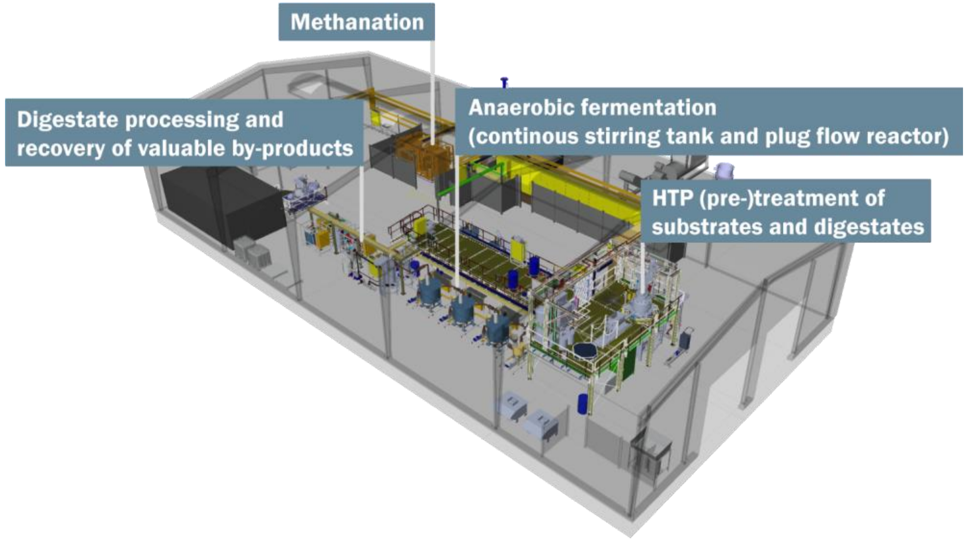




Biogas component	concentration
CH_4	40 – 75 vol%
CO_2	25 – 60 vol%
Traces*	Rest

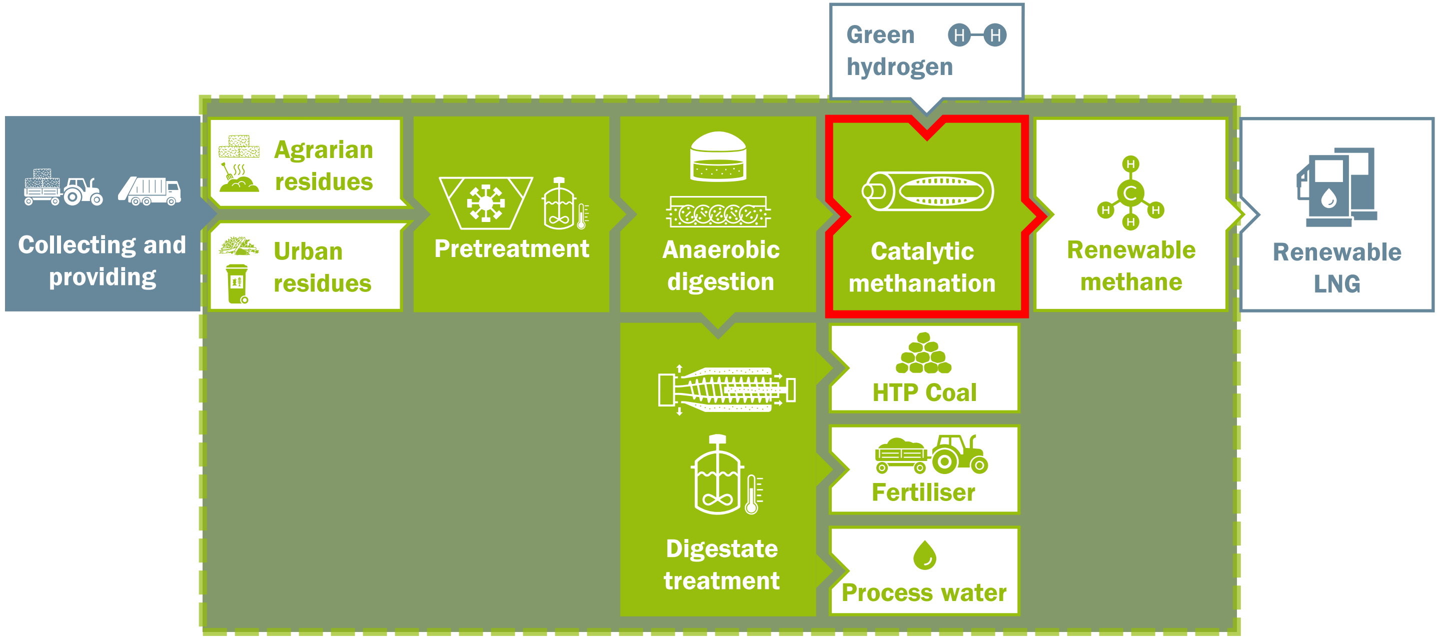
*Traces may contain catalyst poisons like H_2S, NH_3 and siloxanes

A pilot scale biorefinery



Biogas component	concentration
CH_4	40 – 75 vol%
CO_2	25 – 60 vol%
Traces*	Rest

*Traces may contain catalyst poisons like H_2S, NH_3 and siloxanes



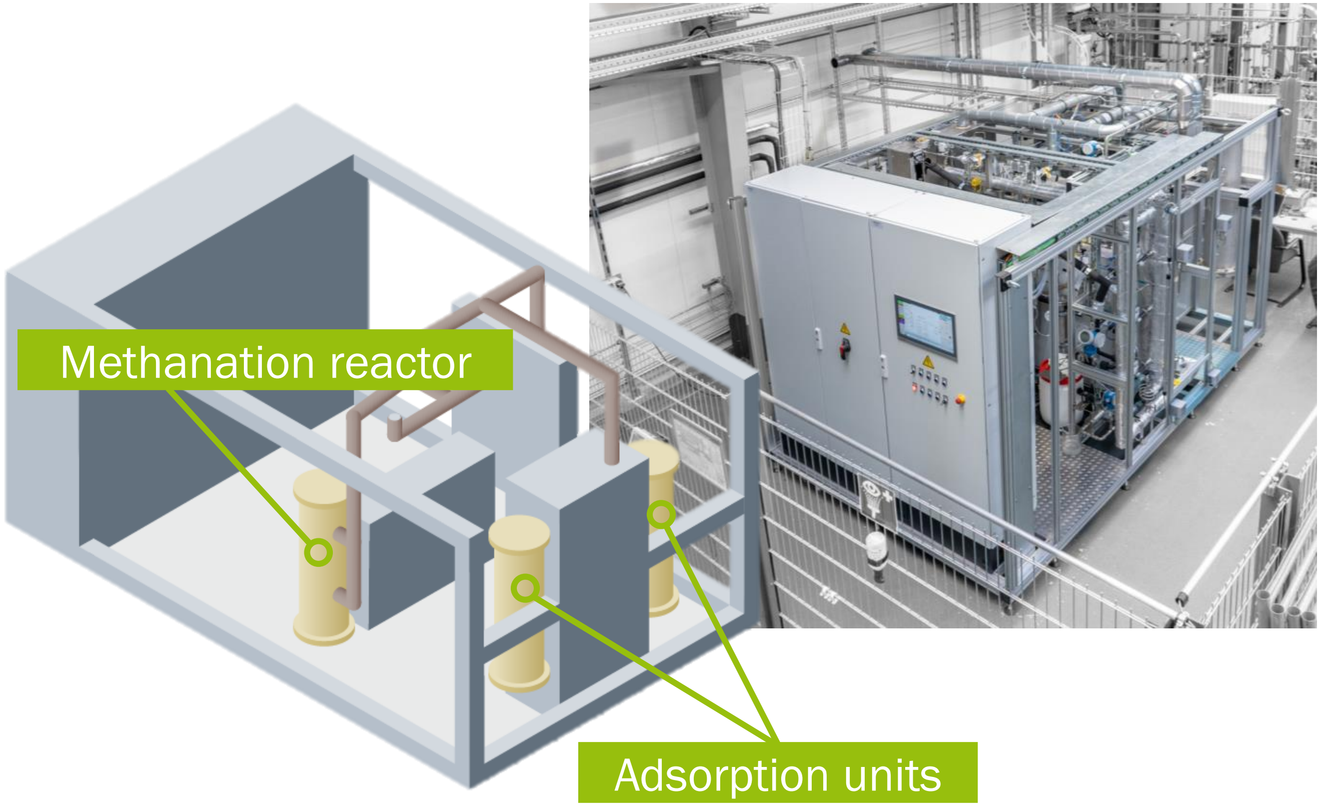
Biogas Methanation

Biogas component	concentration
CH_4	40 – 75 vol%
CO_2	25 – 60 vol%
Traces*	Rest

*Traces may contain catalyst poisons like H_2S, NH_3 and siloxanes

Special features of biogas methanation:

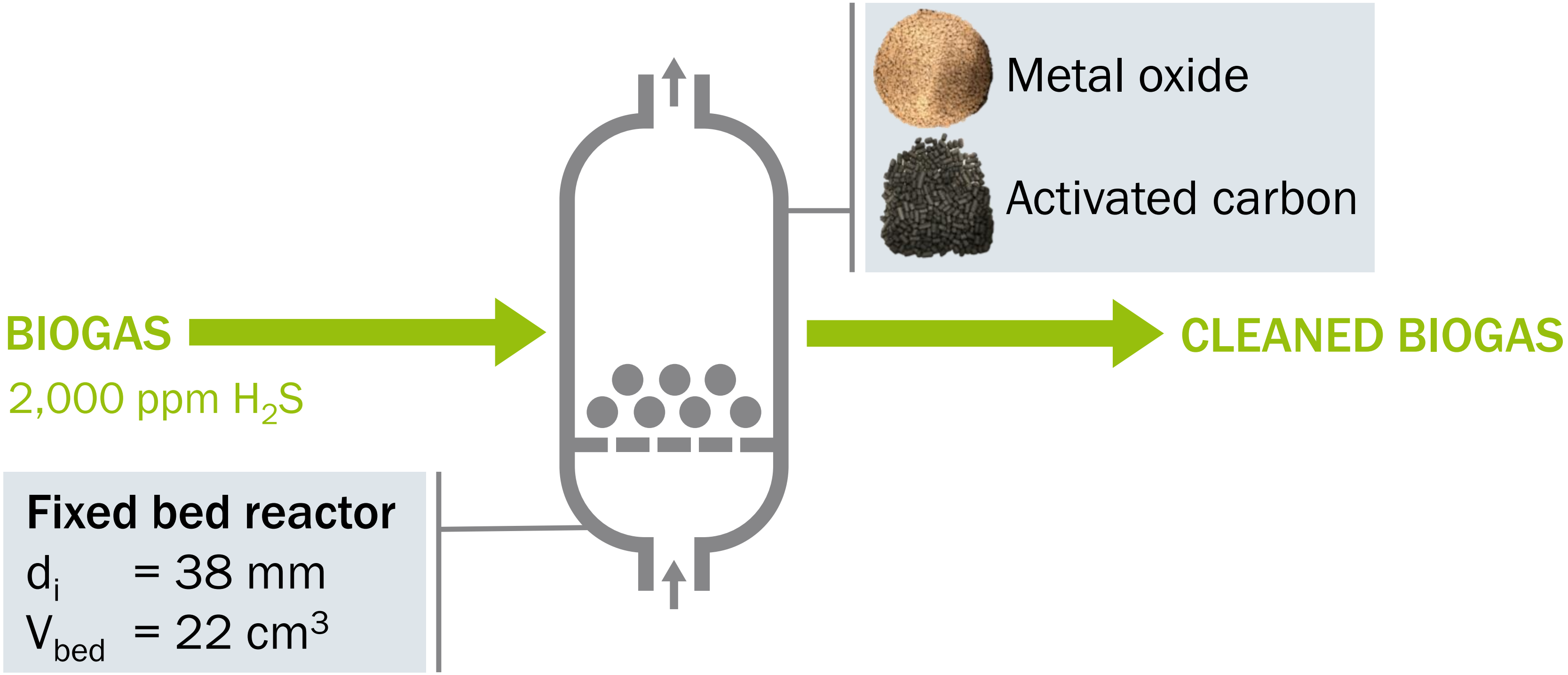
- Biogas cleaning required
  - ⟶ Usually with activated carbon or metal oxide adsorbents
- No need to separate CH_4 and CO_2 for methanation
  - ⟶ CH_4 improves temperature distribution



Research on methanation

Adsorbents

Breakthrough tests (lab): How long does it take until **50 ppm H_2S** are detected in the product gas?



Research on methanation

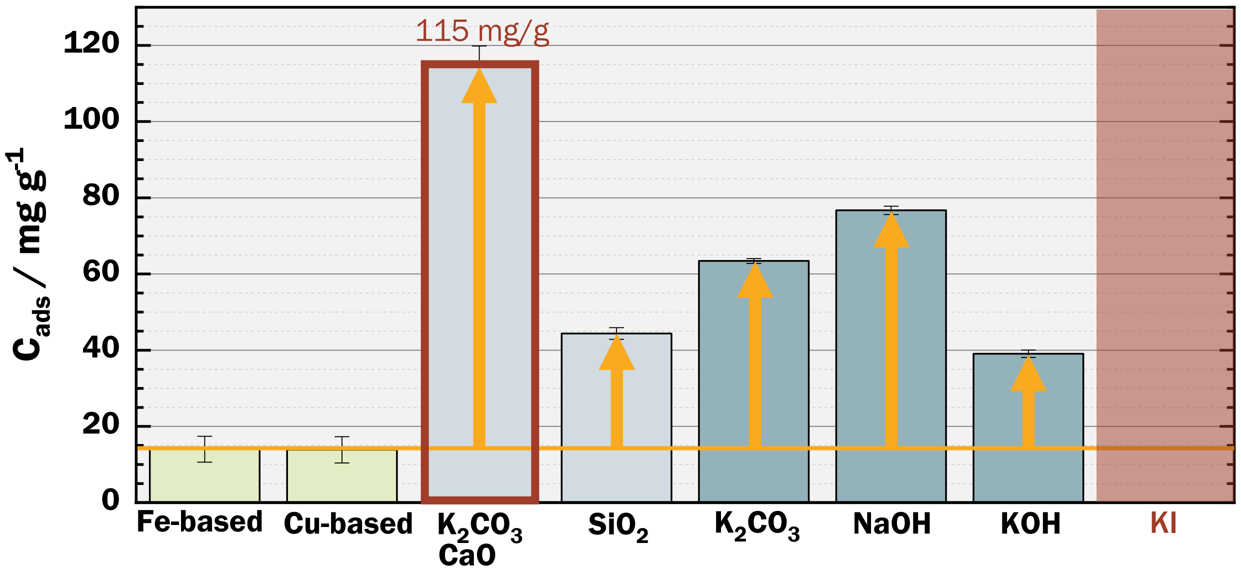
Adsorbents

Breakthrough tests (lab): How long does it take until **50 ppm H_2S** are detected in the product gas?

- **Adsorption capacities:**
  Calculated for H_2S uptake until 50 ppm H_2S are detected in product gas

  → Higher H_2S uptake with activated carbons

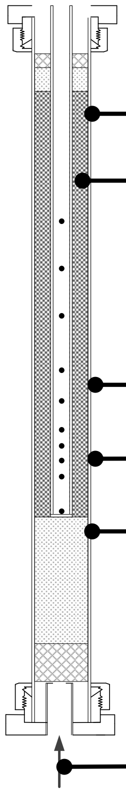
  → KI not suitable



Research on methanation

Catalysts

Small-scale testing of pilot plant operating parameters



Catalyst:

Fixed bed reactor

64 ml | 570 ml

Operating parameters:

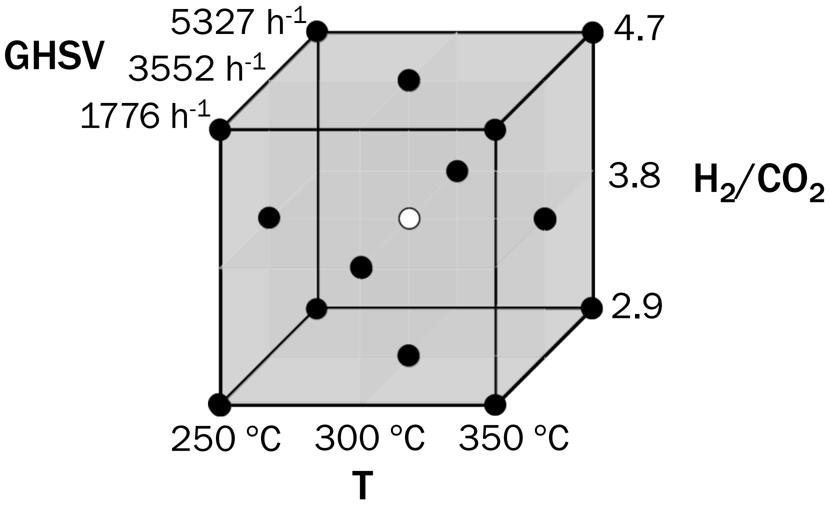
8 bar(a) | 20 bar(a)

250 – 400 °C | variable

1776 – 5327 h^{-1} | variable

Inlet gas:

CH_4, CO_2, (H_2S) + H_2 | biogas + H_2



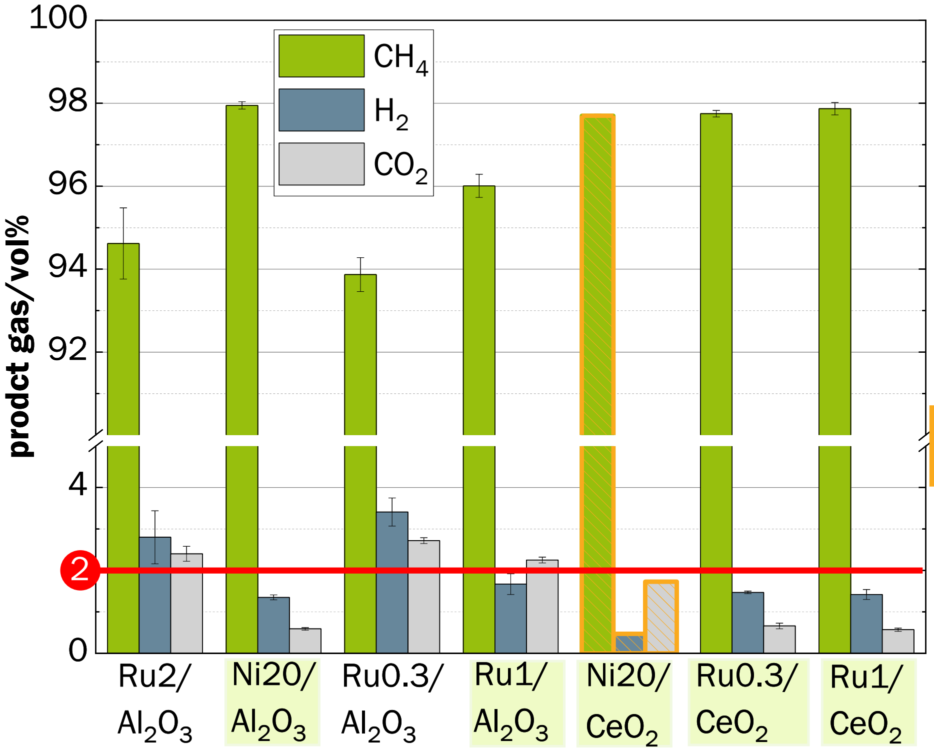
3 easy-to-change parameters for DoE (small scale):

- **T**
- **GHSV**
- **H_2/CO_2**

Research on methanation

Catalysts

- CH_4 has no adverse effect
- Fuel conditions (CH_4↑, CO_2↓, H_2 < 2 vol%) met with several catalysts
- Especially promising is catalyst with Ni and CeO_2



catalyst	T | GHSV | H_2/CO_2
$Ru2/Al_2O_3$	350 °C | 1776 h^{-1} | 2.9
$Ni20/Al_2O_3$	300 °C | 1776 h^{-1} | 3.8
$Ru0.3/Al_2O_3$	400 °C | 1776 h^{-1} | 2.9
$Ru1/Al_2O_3$	350 °C | 1776 h^{-1} | 2.9
$Ni20/CeO_2$	250 °C | 1776 h^{-1} | 2.9
$Ru0.3/CeO_2$	300 °C | 1776 h^{-1} | 3.8
$Ru1/CeO_2$	300 °C | 5327 h^{-1} | 3.8

Next step: Pilot plant operation

Interested?
Contact us!

Contact

Selina Nieß
Deutsches Biomasseforschungszentrum gGmbH
Torgauer Straße 116
04347 Leipzig

Phone: +49 341 24 34 420

Email: Selina.Niess@dbfz.de

www.dbfz.de/pilot-sbg