State of the Art and Perspectives of CO₂ Methanation
Process Concepts for Power-to-Gas Applications

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Overview

- Introduction
- Biological methanation concepts
- Catalytic methanation concepts
- Comparison
- Summary
Introduction
Fundamentals of methanation

Equations

\[ \text{CO} + 3 \text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \ (g) \]
\[ \Delta_{R} h^0 = -206 \text{ kJ/mol} \]

\[ \text{CO}_2 + 4 \text{H}_2 \rightleftharpoons \text{CH}_4 + 2 \text{H}_2\text{O} \ (g) \]
\[ \Delta_{R} h^0 = -165 \text{ kJ/mol} \]

\[ \text{CO}_2 + 4 \text{H}_2 \rightleftharpoons \text{CH}_4 + 2 \text{H}_2\text{O} \ (l) \]
\[ \Delta_{R} h^0 = -253 \text{ kJ/mol} \]

- Methanation is highly exothermic
- Removal of reaction heat is a significant issue
- Usually, nickel-based catalysts are used for catalytic methanation

Concepts

- Methanation concepts
  - Biological methanation (40 - 70 °C, 1 - 10 bar)
  - Catalytic methanation (250 - 550 °C, 1 - 100 bar)
    - Fixed bed: - Adiabatic - Isothermal
    - Fluidized bed
    - Three phase: - 3 phase fluidized bed - Bubble column
    - Structured: - Honey comb - Microchannel reactor
Introduction
Equilibrium conversion ($H_2/CO_2/CH_4 = 4/1/1$)

- No thermodynamic limitation for biological methanation
- Catalytic methanation is limited by equilibrium, especially at 1 bar
Overview

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Biological methanation concepts
Overview and tasks

Process Overview
- Microorganisms serve as biocatalysts
- Proceeds at low temperatures (40 to 70 °C)
- Discovered in 1906
- So far no technical application for SNG production

Technical tasks
- Upscaling from lab scale reactors to industrial plants
- Supply of hydrogen to the microorganisms
  ⇒ Poor solubility of $H_2$ in fermentation liquid ($CO_2$ is 25 times more soluble than $H_2$)
Biological methanation concepts

Concepts

Biogas plant

H₂ addition to biogas digester

Simplified process schema

Biogas plant

Biogas upgrading

Digesters

Biological methanation

External reactor

Source: www.bbfm.de
Biological methanation concepts
In situ vs. external

Methanation in the biogas digester
- No further reactor necessary
- Limited to biogas as carbon source
- Process conditions determined by biogas process
- Increase in CH₄ content (e.g. 50 to 75 %)
- Safety aspects need to be considered

External biological methanation
- Further reactor necessary
- Pure cultures are used
- Process conditions and reactor design adjusted to biol. methanation
- High CO₂ conversion possible

<table>
<thead>
<tr>
<th></th>
<th>in situ</th>
<th>external</th>
</tr>
</thead>
<tbody>
<tr>
<td>T in °C</td>
<td>40</td>
<td>65</td>
</tr>
<tr>
<td>p in bar</td>
<td>1</td>
<td>&gt; 4</td>
</tr>
<tr>
<td>CO₂ Conversion &gt; 95 %?</td>
<td>No</td>
<td>yes</td>
</tr>
<tr>
<td>Electrical Energy Demand in kWh/m³ SNG</td>
<td>1.8</td>
<td>0.4 - 1.3</td>
</tr>
<tr>
<td>Specific Investment Cost for a 5 MW SNG Plant in €/kWh SNG</td>
<td>≈ 400</td>
<td>≈ 600</td>
</tr>
</tbody>
</table>
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- **Catalytic methanation concepts**
- Comparison
- Summary
Catalytic methanation concepts

Adiabatic fixed-bed methanation (AFB)

- Reactor is packed with catalyst
- Several reactors in series with interstage cooling
- Some concepts use recycle streams
- State of the art
- Commercial SNG plants are based on this concept (e.g. Great plains, USA)
Catalytic methanation concepts

Three phase methanation (3PM)

- Catalyst (< 100 µm) is suspended in an inert liquid and (indirectly) fluidized by the feed gas
- $p = 20$ bar; $T \approx 300 \, ^\circ C$
- Developed at EBI, KIT

Advantages

- High heat capacity of the liquid
- High thermal conduction
- Simplified removal of reaction heat
- Isothermal operation possible
- Simple process design
- Catalyst replacement during operation

Drawbacks

- Evaporation and decomposition of the suspension liquid
- Liquid-side mass transfer limitations
Catalytic methanation concepts

3PM: dynamic operation

- Less than 10 min to reach steady-state operation after load change
- Reactor reset time only depends on the gas velocity
  \( \Rightarrow \) Reactor hydrodynamics and reaction kinetics are not the limiting factors
- Fast load change possible

Graph:

- Methane content: \( y_{CH_4} \)
- Load in %
- Elapsed time \( t \) in min

- 20 bar, 300 °C
- \( GHSV = 209 \) to \( 844 \) h\(^{-1}\)
- \( F_V = 1.3 \) m\(^3\)/h (100 % load)
- 100 % load
- 25 % load
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Comparison

Technical parameters

Gas Hourly Space Velocity (*GHSV*)
- Fixed-bed: highest operation temperature
  - Highest *GHSV* and therefore smallest reactor volume for a certain feed stream

Tolerance to impurities
- High tolerance of impurities for biological methanation
- Low tolerance of impurities such as $\text{H}_2\text{S}$ for catalytic processes (3PM, AFB)

Flexibility
- Limiting factor for load changes is related to the process control system
- Adiabatic fixed-bed: minimum load of 40% (lower for cooled fixed-bed such as in Welte PtG plant)
- 3PM: minimum load of 10 - 20%
- Low minimum load for biological methanation
Comparison
Efficiency

Biological methanation
- Additional power demand from the stirrer
- Opportunities for utilization of waste heat are sparse (low temperature level)

Catalytic methanation
- Heat can be used for steam/power production

Power supply of the plant covered by steam turbine
Further power (therm. and el.) can be integrated into biogas plant
# Comparison

## Efficiency

### Comparison of methanation technologies

<table>
<thead>
<tr>
<th></th>
<th>Biological</th>
<th>Catalytic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolysis</td>
<td>9000 kW</td>
<td></td>
</tr>
<tr>
<td>Chemical output in product</td>
<td>5200 kW</td>
<td></td>
</tr>
<tr>
<td>Power demand for PtG plant</td>
<td>150 – 560 kW</td>
<td>-</td>
</tr>
<tr>
<td>Further power/heat utilization</td>
<td>420 kW</td>
<td>1000 kW</td>
</tr>
<tr>
<td>Efficiency PtG in %</td>
<td>59 – 61</td>
<td>69</td>
</tr>
</tbody>
</table>

Higher efficiency for catalytic methanation
Comparison Economics

- Small plant size: production costs for biological methanation are only slightly higher
- Large plant size: production costs for biological methanation are nearly 2.5 times that of catalytic methanation
- For all cases the costs for hydrogen production are the most significant contributor
Summary

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Biological methanation</th>
<th>Three phase methanation</th>
<th>Adiabatic fixed-bed</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>$T$ in °C</strong></td>
<td>40 - 70</td>
<td>300 - 350</td>
<td>250 - 550</td>
</tr>
<tr>
<td><strong>$p$ in bar</strong></td>
<td>&gt; 4</td>
<td>&gt; 20</td>
<td>&gt; 5 - 10</td>
</tr>
<tr>
<td><strong>Stage of development</strong></td>
<td>lab scale/pilot</td>
<td>lab scale</td>
<td>commercial</td>
</tr>
<tr>
<td><strong>$GHSV$ in h⁻¹</strong></td>
<td>&lt; 100</td>
<td>500 - 1,000</td>
<td>2,000 - 5,000</td>
</tr>
<tr>
<td><strong>Tolerance of impurities</strong></td>
<td>high</td>
<td>medium</td>
<td>low</td>
</tr>
<tr>
<td><strong>Dynamic behaviour</strong></td>
<td>good</td>
<td>good</td>
<td>medium</td>
</tr>
<tr>
<td><strong>Efficiency PtG in %</strong></td>
<td>60</td>
<td>69</td>
<td>69</td>
</tr>
</tbody>
</table>

- SNG costs depend on plant size, full load hours, methanation concept…
- ≈ 20 ct/kWh SNG
Take-home message

- Biological methanation is a robust process that is better suited for small plant sizes

- Catalytic methanation enables heat utilization and therefore higher efficiency

- Costs for hydrogen production dominate the SNG costs
Appendix
Introduction
Possible process chains

Power-to-Gas (PtG) + biogas

- Carbon exploitation can be increased by H₂ integration with biogas and BtG processes
- So far enough carbon sources are available
Catalytic methanation concepts

AFB: dynamic operation

Catalyst

- Temperature must always be in the range of 220 – 550 °C
- Effect of load change on catalyst lifetime?
  - Recent results indicate that load change does not significantly reduce the catalyst lifetime

Reactor reset time and minimum load

- Reaction responds immediately to load changes
- Reactor reset time is dominated by the process control, especially by the heat exchangers
  - The complex heat management for adiabatic fixed-bed methanation leads to a comparatively inflexible process
- Minimum load: 40 %

Improved dynamic behaviour if cooled fixed-bed reactors are used (such as in the Werlte PtG plant)