Gasaufbereitung mit Membranen

Gas Treatment Using Membranes

Michael Harasek
Vienna University of Technology
Institute of Chemical Engineering
michael.harasek@tuwien.ac.at

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Regenerative Energien als Zukunftstechnologien
Gas Treatment Using Membranes

Agenda

- Short intro – why biogas upgrading?
- Quality issues
- Gas permeation process
- Scale-up to pilot and full scale - process integration
  - Two-stage grid injection (Bruck/Leitha)
  - Single-stage CNG production (Margarethen/Moos)
- Energy demand
- Biogas pretreatment (desulphurisation)
- Costs
- Technology roll-out & future
Introduction

Why biogas upgrading?

- Standardized product „biomethane“ (compatible with natural gas)
- Higher efficiencies in energy utilization than conventional gas engines without heat integration
- Access to new markets – the gas grid
- Automotive utilization (CNG)
## Biogas Composition and Gas Grid Standards

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Raw Biogas</th>
<th>Quality according to Austrian Standard OEVGW G31 / G33</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane ($\text{CH}_4$)</td>
<td>45 - 70</td>
<td>unspecified ( &gt; 97.0)</td>
<td>mol%</td>
</tr>
<tr>
<td>Carbon dioxide ($\text{CO}_2$)</td>
<td>30 - 45</td>
<td>≤ 2.0</td>
<td>mol%</td>
</tr>
<tr>
<td>Ammonia ($\text{NH}_3$)</td>
<td>&lt; 1,000</td>
<td>technically free</td>
<td>mg/m$^3_{\text{STP}}$</td>
</tr>
<tr>
<td>Hydrogen sulphide ($\text{H}_2\text{S}$)</td>
<td>&lt; 5,000</td>
<td>≤ 5</td>
<td>mg/m$^3_{\text{STP}}$</td>
</tr>
<tr>
<td>Oxygen ($\text{O}_2$)</td>
<td>&lt; 2</td>
<td>≤ 0.5</td>
<td>mol%</td>
</tr>
<tr>
<td>Nitrogen ($\text{N}_2$)</td>
<td>&lt; 8</td>
<td>≤ 5</td>
<td>mol%</td>
</tr>
<tr>
<td>Water ($\text{H}_2\text{O}$) - Dewpoint</td>
<td>&lt; 37 @ 1bar</td>
<td>≤ - 8 @ 40bar</td>
<td>°C</td>
</tr>
<tr>
<td>Upper Heating Value</td>
<td>6.7 – 8.4</td>
<td>10.7 – 12.8</td>
<td>kWh/m$^3_{\text{STP}}$</td>
</tr>
<tr>
<td>Wobbe-Index</td>
<td>6.9 – 9.5</td>
<td>13.3 – 15.7</td>
<td>kWh/m$^3_{\text{STP}}$</td>
</tr>
</tbody>
</table>

**ÖVGW G31** defines natural gas, **ÖVGW G33** specifies grid injection standards for biogases – German standards **DVGW G260/G262**
Gas Treatment Using Membranes

Biogas Upgrading – A Separation Problem

- Ammonia ($\text{NH}_3$)
- Hydrogen Sulphide ($\text{H}_2\text{S}$)
- Carbon dioxide ($\text{CO}_2$)
- Water vapour ($\text{H}_2\text{O}$)
- Bio-Methane ($\text{CH}_4$)
- Other Contaminants (Particles, Droplets, Siloxanes, Hydrocarbons, Mercaptanes)
Biogas Upgrading Steps

1. Preconditioning / pretreatment
   • Removal of particles, droplets, siloxanes, other trace components

2. Biogas desulphurization

3. Compression

4. Biogas upgrading
   • Separation of CO₂ and H₂O

5. Final conditioning
   • Dewpoint control, adjustment of heating value, offgas treatment
Upgrading of Biogas using Gas Permeation (GP)

- **Separation principle**: different permeabilities of methane and components to be separated.
- **Important parameter**: permeability ratio = selectivity.
- **After compression biogas is fed to membrane modules.**

Separation performance = $f(T, \Delta p, x_i)$

$p(F) > p(P)$

Diagram showing biogas components (CH$_4$, CO$_2$, H$_2$O, H$_2$S, NH$_3$, N$_2$, O$_2$) being separated by a membrane (polyimide Hollow fibres) with CO$_2$-rich permeate.
Membrane Test Equipment at TU Wien

- Preparation of CO$_2$/CH$_4$/N$_2$ gas mixtures with mass flow controllers
- Thermostatic chamber
- Industrial NDIR gas analyzer for CO$_2$ and CH$_4$ + gas chromatography / mass spectrometry
- Test control, visualization and data collection using a PLC with HMI/SCADA system
Pilot Test Equipment at TU Wien

• Mobile pilot plant for flexible treatment of many gas mixtures including H₂
• Magnet-coupled two-stage piston compressor (up to 15 bar, 0-6 m³/h)
• Fully automated upgrading plant for remote operation (industrial PLC)
  • 3 adsorber fillings in series
  • Cryo condenser
  • Reheater
• One/two stage membrane separation with/without gas recycling
• NDIR online continuous gas
Gas Treatment Using Membranes

Compression Energy Consumption per m³ Product

Biogas: 60% CH4
Biomethane: 98% CH4
2-stage upgrading
2-stage polytropic compression
p(absolute) = 10 bar
kappa = 1.3
Compressor efficiency: 80%
Mechanical efficiency: 90%

Economically feasible plant design

CO2/CH4-selectivity

10 20 35 50

Biomethane recovery [%]
Gas Treatment Using Membranes

**Membrane Area as Function of Recovery**

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- Biomethane: 98% CH4
- 2-stage upgrading
- 2-stage polytropic compression
- p(absolute) = 10 bar
- \( \kappa = 1.3 \)
- Compressor efficiency: 80%
- Mechanical efficiency: 90%

**Economically feasible plant design**
- **Two-stage separation process** with recycle and a single compressor
- Biological desulphurisation prior to membrane treatment
- Permeate is recycled to CHP plant – „zero methane“ emission of upgrading system
Biogas Upgrading Plant in Bruck/Leitha (Austria)
Biomethane Fuel Station: Single Stage Upgrading

Fuel Station

High Pressure Storage

High Pressure Compressor

Product Gas Biomethane

CH₄ rich

Compressor

Freeze Dryer

Refrigerant

Reheater

H₂S-Adsorber

Membrane Modules

Offgas

CO₂ rich

Q IRC 1

CO₂

Q IRC 2

CH₄
- **In-situ desulphurisation** (addition of iron salts into the fermentation broth to catch sulphides)
- **Permeate is recycled to CHP plant** – „zero methane“ emission of upgrading system
Biomethane Fuel Station using Membrane Technology

- Permeate recycle to CHP plant
- Further information: www.methapur.com
  Biomethane fuel station Margarethen/Moos

35 m³/h biomethane
Energy Consumption Analysis

• Main energy consumer of upgrading is the raw biogas compressor.

• Energy demand for constant product gas quality and quantity depends also on raw biogas methane content.

• **Effect of plant layout** (number of stages) on energy consumption:
  • Two stage gas grid injection plant: 0.38 kWh/m³STP of product gas
  • Single stage Bio-CNG-plant: 0.28 kWh/m³STP of product gas

• Energy consumption of <0.2 kWh/m³ STP of raw biogas possible!

• Related to the methane content of the produced biomethane gas stream:
  • Two stage gas grid injection plant: 3.2% (98.1vol% CH₄)
  • Single stage Bio-CNG-plant: 2.8% (96.1vol% CH₄)

• All values are valid for a product gas delivery pressure of about 3 bar(g).
Costs for CO₂ Separation

Calculations by Fraunhofer Institut UMSICHT

Excellent chances for membranes

Spezific costs for CO₂ separation
Offgas Treatment & Costs

- **Offgas treatment** depends on process integration:
  - Mixing with biogas and utilisation in CHP plants
  - Thermal oxidation (flameless oxidation systems or direct combustion of low-cal gas)
  - Catalytic oxidation
  - Further treatment using additional membrane separation stage

- **Specific costs of upgrading** (depends on plant capacity):
  - **Investment** (depreciation 10 years, 8%): 
    0,05 – 0,08 €/m³ biomethane
  - **Operation** (> 8000 h/a):
    0,10 – 0,14 €/m³ biomethane
Compatible Desulphurisation Technologies

Compatible:

- External biological desulphurisation in combination with pure oxygen injection
- In-situ desulphurisation using iron salts
- External chemical scrubber with oxidation using NaOH/H₂O₂, recommended for fluctuating H₂S concentrations in the biogas
- Adsorptive desulphurisation technologies with low excess of O₂ (impregnated activated carbon adsorbents)

Not suitable / incompatible:

- Air injection
- External biological desulphurisation with air injection

Project „BiogasOxiSulf“
Supply of max. 100 Vehicles with Biomethane

- Capacity up to 500 kg/d biomethane
- Operation of the first biogas driven tractor in Austria
Austrian Upgrading Technology - Export to Germany

- Capacity: 500 m³/h biogas, 300 m³/h biomethane, approx. 8 km pipeline to injection point (@ 60 bar)
- Axiom – gas permeation membrane system
- Capacity: 220 (300) m³/h biogas, grid injection @ 4bar
- Axiom – gas permeation membrane system
Thank you for your interest!

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