Membranes for Green processes

Elisa Esposito
Green chemistry, also called sustainable chemistry, is an area of chemistry and chemical engineering focused on the designing of products and processes that minimize or eliminate the use and generation of hazardous substances.
Design and development of new materials for membrane preparation
Objective

- Biorefinery
- Biomass
- Biogas
- MEMBRANE SEPARATION
- Biomethane
- BioCO₂
- Biofuel
- Electricity
- Heating
- Food and beverage application
- REDUCE
- REUSE
- RECYCLE
Gas transport in Membrane

Feed mixture
e.g. CO₂/CH₄

Membrane
(selective barrier)

Retentate
Enriched in methane
CH₄ >> CO₂

Permeability (P) = \( \frac{n \cdot \ell}{t \cdot A \cdot \Delta P} \)

Permeate
Enriched in CO₂
CO₂ >> CH₄

\[
\text{selectivity } \alpha_{AB} = \frac{P_A}{P_B}
\]
Robeson plot

B.D. Freeman, Basis of permeability/selectivity tradeoff relations in polymeric gas separation membranes, Macromolecules. 32 (1999) 375–380
A highly rigid and gas selective methanopentacene-based polymer of intrinsic microporosity derived from Tröger's base polymerization†

Rhodri Williams, Luke A. Burt, Elisa Esposito, Johannes C. Jansen, Elena Tocci, Carmen Rizzuto, Marek Lanč, Mariolino Carta and Neil B. McKeown

Polymers of intrinsic microporosity (PIMs) have been identified as potential next generation membrane materials for the separation of gas mixtures of industrial and environmental relevance. Based on the exceptionally rigid methanopentacene (MP) structural unit, a Polymer of Intrinsic Microporosity (PIM-MP-TB) was designed to demonstrate high selectivity for gas separations. PIM-MP-TB was prepared using a polymerisation reaction involving the formation of Tröger’s base linking groups and demonstrated an apparent BET surface area of 257 m² g⁻¹ at room temperature. The microporosity of PIM-MP-TB was also...
Membrane preparation

PIM-MP-TB polymer solution

Mechanical stirring

Slow solvent evaporation

Dense and homogenous membrane

SEM image
Mixed gas permeation test

Selectivity $\alpha_{\text{CO}_2/\text{CH}_4}$

- Aged 110 g
- $T^\circ C$
- MeOH
- PIM-MP-TB
- Mix
- PIM-1

$PCO_2=3500$ Barrer
$\alpha_{\text{CO}_2/\text{CH}_4} = 13$
Mixed matrix membranes based on MIL-101 metal–organic frameworks in polymer of intrinsic microporosity PIM-1

Muhammed Khdhayyer, Alexandra F. Bushell, Peter M. Budd, Martin P. Attfield, Dongmei Jiang, Andrew D. Burrows, Elisa Esposito, Paola Bernardo, Marcello Monteleone, Alessio Fuoco, Gabriele Clarizia, Fabio Bazzarelli, Amalia Gordano, Johannes C. Jansen

PIM-1

MIL-101

Mixed Matrix membranes
Single gas permeation test
Overview of Single and Mixed gas performance

![Graph showing selectivity \( \alpha (CO_2/CH_4) \) vs. CO₂ permeability (Barrer). The graph compares PIM-1 and MMMs.](image)
Scale-up

- Laboratory scale
- Large-scale
- Industrial-scale
Simultaneous production of biomethane and food grade CO₂ from biogas: an industrial case study†

Elisa Esposito,† Loredana Dellamuzia,† Ugo Moretti,† Alessio Fuoco,† Lidietta Giorno† and Johannes C. Jansen†,†,*

Impact factor: 33
Three-stage membrane separation

Biogas
- 1 bar
- 1000 Nm³/h

1st module
- Raw CH₄
- Raw CO₂

2nd module
- Recycle CO₂ + CH₄

Retentate

Permeate

3rd module
- BioCO₂ 98.06%

Recycle 2nd permeate and 3rd retentate → minimum CH₄ loss

Biomethane

<table>
<thead>
<tr>
<th>Gas</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>96.3%</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.9%</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.6%</td>
</tr>
<tr>
<td>O₂</td>
<td>0.2%</td>
</tr>
<tr>
<td>N₂</td>
<td>0</td>
</tr>
</tbody>
</table>

Liquid CO₂ 99.99%

CO₂ = 750 Kg/h
Composition of Biomethane and Bio\(\text{CO}_2\) after membrane separation

- Biomethane suitable for injection into the natural gas grid

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limits allowed</th>
<th>Biomethane Membrane stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity</td>
<td>&gt;80%</td>
<td>96.3%</td>
</tr>
<tr>
<td>Wobbe Index (MJ/Sm(^3))</td>
<td>47.31-52.33</td>
<td>50.02</td>
</tr>
<tr>
<td>Density (g/cm(^3))</td>
<td>0.5548-0.8</td>
<td>0.56</td>
</tr>
<tr>
<td>Heating value (MJ/Sm(^3))</td>
<td>34.95-45.28</td>
<td>37.48</td>
</tr>
</tbody>
</table>

- Further removal of trace impurities from \(\text{CO}_2\) needed

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limits EIGA/ISBT</th>
<th>(\text{CO}_2) Membrane stage</th>
<th>Liquefied (\text{CO}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purity</td>
<td>99.9% v/v max</td>
<td>98.06% v/v max</td>
<td>99.998% v/v</td>
</tr>
<tr>
<td>Humidity</td>
<td>20 ppm v/v max</td>
<td>120 ppm v/v max</td>
<td></td>
</tr>
<tr>
<td>Acidity</td>
<td>comply with the test</td>
<td>comply with the test</td>
<td>comply with the test</td>
</tr>
<tr>
<td>Oxygen</td>
<td>30 ppm v/v max</td>
<td>200 ppm v/v max</td>
<td>1.9 ppm v/v</td>
</tr>
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</table>

\(\text{CH}_4\) 96.3%  
\(\text{CO}_2\) 98.06%
Additional advantage: CH₄ recycle from this step back to the membrane separation unit leads to 100% CH₄ recovery and zero CH₄ emission
The final liquefied CO\textsubscript{2} is chemically and microbiologically pure, respecting the limits of food grade quality proposed by the EIGA/ISBT.

### BIOLOGICAL ANALYSIS

- **High contamination**: < 10,000 UFC/m\textsuperscript{3}
- **High contamination**: < 2,500 UFC/m\textsuperscript{3}
- **Low contamination**: < 50 UFC/m\textsuperscript{3}
- **Very low contamination**: < 50 UFC/m\textsuperscript{3}

### CHEMICAL ANALYSIS

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<th>Limits EIGA/ISBT</th>
<th>CO\textsubscript{2} Membrane stage</th>
<th>Liquefied CO\textsubscript{2}</th>
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<tr>
<td></td>
<td>Threshold</td>
<td>Measured values</td>
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Membrane processes produces simultaneously renewable energy and re-cycle of CO₂

The energy cost of CO₂/CH₄ membrane separation (0.3 kWh/m³) is lower compared to that the traditional separation techniques (0.6 kWh/m³).

3000 m³/h of Biomethane from organic waste that can be fed directly into the natural gas grid.

32.000 tonnes/year of CO₂ from a useless by-product to a food-grade quality gas for food and beverage industry

No CO₂ and CH₄ are released into the atmosphere and organic waste is consumed: first “carbon negative” plant in Italy
Future challenges
Future challenges: To green materials

Pebax® membrane

Hismox-MOF

Bio-MOF

OH \( \text{C}_2\text{H}_4 \text{O} \) \( \text{C} \) \( \text{N} \) \( \text{C}_5\text{H}_{10} \text{O} \) OH

Green solvent: mixture of EtOH/H\(_2\)O 70/30 vol%

Histidin amino acid linker
The basic idea is to mimic the reaction that takes place inside the erythrocytes.

**Potential use of membrane contactors for CO₂/CH₄ separation by facilitated CO₂ transport in Hollo fiber membranes**

**Enzyme**

*Carbonic anhydrase*
- Metal protein
- Zinc functional group
- Catalyzes hydration of carbon dioxide

**Hydration of carbon dioxide**

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+. 
\]
Thank you for your attention