Breakthrough Curves of CO$_2$ and CH$_4$ on Carbon Molecular Sieves - Experiment and Modelling

A. Möller$^1$, J. Guderian$^2$, R. Staudt$^3$, J. Möllmer$^4$

$^1$ Quantachrome GmbH, Odelzhausen/D
$^2$ FH Münster, Fachbereich Chemieingenieurwesen, Steinfurt/D
$^3$ HS Offenburg, Fakultät Maschinenbau, Offenburg/D
$^4$ Institut für Nichtklassische Chemie e.V., Leipzig/D

Introduction

Carbon molecular sieves (CMS) are widely used for the refinement of biogas to biomethane [1]. This application is based on kinetic separation due to size selective adsorption in PSA processes [2]. Modern CMS are tuned towards maximum sorption capacities regarding to the component, which is to be adsorbed. By means of dynamic measurements, it is possible to examine such materials at realistic process conditions with respect to sorption kinetics and capacities.

In this study breakthrough curves of CO$_2$, CH$_4$ in He and their mixtures were measured on Shirasagi MSC CT-300. It can be shown, that an evaluation of the performance of such materials, based on isotherms are not always correct and will lead sometimes to misinterpretation of the whole separation process.

Objectives

Purification of biogas to biomethane necessary for grid feeding:

<table>
<thead>
<tr>
<th>Typical distribution of main components in biogas / %</th>
<th>Requirements to gas composition according to DVGW G 260 and 262 / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$: CO$_2$, H$_2$O, H$_2$, S, Other Components</td>
<td>CH$_4$, CO$_2$, H$_2$O, H$_2$, S, Other Components</td>
</tr>
<tr>
<td>40–75, 25–55, &lt;10, &lt;0.5 Balance</td>
<td>acc. to Wobbe index, &lt;6, &lt;50 mg m$^{-3}$, &lt;5 mg m$^{-3}$ Balance</td>
</tr>
</tbody>
</table>

H$_2$S: Removal of H$_2$S with biological methods (first step), chemical/physical methods

CO$_2$: Removal of CO$_2$ with carbon molecular sieves (PSA process) or treatment with chemicals (amines)

Test procedures to evaluate the performance of Carbon Molecular Sieves:

Determination of breakthrough at different gas velocities and pressures with dynaSorb BT, modeling and simulation of CH$_4$ purification.

Experimental

The experiments were carried out with the commercial available device dynaSorb BT from QuantaChrome Instruments at 40 °C. This device is designed for dynamic test routines under process relevant conditions.

As adsorbent the carbon molecular sieve Shirasagi MCS CT-350 from CarboTech AC was used. This material has been especially developed for removal of CO$_2$ from CH$_4$ rich gas mixtures. Before the measurements the material was regenerated at 150 °C for 4 h.

The predefined test routines and the mathematical model for evaluation are all included in the software package of dynaSorb BT.

Mathematical Model – Equations [5, 6, 7]

Mass Balance

\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( \frac{\partial C}{\partial x} + u \frac{\partial C}{\partial x} \right) - 1 \frac{\partial q}{\partial x} + 1 \frac{\partial C}{\partial x} \frac{\partial q}{\partial x} \]

Energy Balance for Fixed Bed (simplified)

\[ \rho \left( \frac{\partial}{\partial t} \left( \frac{\partial E}{\partial x} \right) + U \frac{\partial E}{\partial x} \right) = \rho c_p \frac{\partial T}{\partial t} \]

Operation conditions for breakthrough experiments on MSC CT-350 with dynaSorb BT

<table>
<thead>
<tr>
<th>conditions</th>
<th>CO$_2$ in He</th>
<th>CH$_4$ in He</th>
<th>CH$_4$/CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [K]</td>
<td>313</td>
<td>313</td>
<td>313</td>
</tr>
<tr>
<td>Pressure [MPa]</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Fraction CH$_4$ [%]</td>
<td>-</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>Fraction CO$_2$ [%]</td>
<td>10</td>
<td>10 - 60</td>
<td></td>
</tr>
<tr>
<td>Flow rate [cm$^3$ s$^{-1}$]</td>
<td>16.7 - 83.3</td>
<td>16.7</td>
<td>33.3 - 83.3</td>
</tr>
</tbody>
</table>

References


Conclusion

All breakthrough curves of CO$_2$ show the expected behaviour for a thermodynamic controlled system. However the curves for CH$_4$ have spontaneous breakthroughs due to the very low kinetic of the CH$_4$ molecules on MCS CT-350. This different behaviour increases the effective selectivity of the investigated material for the desired separation process considerably. This results in higher selectivity performance compared to the predicted thermodynamic selectivity from isotherms.

Therefore, detailed investigations of kinetics with dynamic methods, i.e. breakthrough experiments, are necessary for a reliable assessment of such materials. The evaluation of isotherms from static methods without considering kinetic effects will lead to considerable misinterpretation of such materials.