



# Carbon membrane gas separation of binary CO<sub>2</sub> mixtures at high pressure



N. Kruse<sup>a,\*</sup>, Y. Schießer<sup>a</sup>, S. Kämnitz<sup>b</sup>, H. Richter<sup>b</sup>, I. Voigt<sup>b</sup>, G. Braun<sup>a</sup>, J.U. Repke<sup>c</sup>

<sup>a</sup> TH Köln, Betzdorfer Straße 2, 50679 Cologne, Germany

<sup>b</sup> Fraunhofer IKTS, Michael-Faraday-Straße 1, 07629 Hermsdorf, Germany

<sup>c</sup> TU Bergakademie Freiberg, Leipziger Straße 28, 09599 Freiberg, Germany

## ARTICLE INFO

### Article history:

Received 1 February 2016

Received in revised form 17 March 2016

Accepted 18 March 2016

Available online 21 March 2016

### Keywords:

Carbon membrane

High pressure

Gas separation

CO<sub>2</sub>

## ABSTRACT

The key feature of inorganic membranes is the ability to operate at high temperature and pressure. Even supercritical solvents can be processed by these membranes, whereas polymer membranes tend to swell and consequently suffer from reduced selectivity and mechanical strength. The combination of chemical and mechanical stability of ceramic membranes opens completely new fields of applications, e.g. in membrane reactors for chemical reactions like H<sub>2</sub>-synthesis by dehydrogenation. This work investigates the selectivity and permeance of carbon membranes for binary mixtures composed of Helium, Nitrogen, Oxygen or Carbon dioxide in a pressure region up to 20 MPa and a temperature range from 300 to 450 K. A Maxwell–Stefan diffusion approach has been applied to study the gas to gas and gas to membrane interactions under high pressure condition.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

The separation of gas mixtures employing inorganic membranes is an established part of the current membrane research activities. One reason for investigating the performance of these membranes is their excellent selectivity and permeability compared to other recent membrane types [1]. Another reason is their capability to operate at high temperature and high pressure. For polymer membranes successful operation at higher pressure is reported as well [2]. However, high fugacities of components that are well soluble in the membrane material leads to plasticization [3] and therefore to serious reduction in mechanical strength. Since it is thermodynamically impossible to increase the fugacity of one component from feed to permeate side a high transmembrane pressure, compared to the feed pressure, is required to achieve an increase of concentration and a decrease of fugacity from feed to permeate side at the same time. Therefore mechanical strength is necessary to separate mixtures of small molecules without using sweep gas. In comparison to polymer membranes, the mechanical strength of carbon based membranes is not affected by sorption

which makes them predestined for operation at high transmembrane pressure.

Despite their potential applicability to high pressure gas separation, very limited research has been carried out on this topic. As far as we know, less than a half dozen of articles has been published in journals on gas separation with carbon membranes at pressures above 2 MPa [1,4–7] and none at pressures above 10 MPa.

For modelling gas transport through carbon membranes, many approaches have been published as summarised by Ismail and David [8]. Obviously, size exclusion (molecular sieving) and adsorption phenomena play a significant role for the selective transport through the membrane. Both factors can be taken into account by using Fick's law and deriving the local concentrations from the adsorption isotherms. This has been shown for example by Koresh and Soffer [9]. For higher pressures this attempt is not practical because the Fick diffusivity coefficients become strongly dependent on the local concentrations of all components.

Therefore, the more general approach of Maxwell–Stefan diffusion has to be applied, which is better suited to deal with the fluid to membrane and fluid to fluid interactions. Krishna [10,11] proposed the following implementation for binary mixtures in zeolites and other crystalline materials:

$$\begin{aligned} -\frac{\rho q_1}{RT} \cdot \nabla \mu_1 &= \frac{x_2 \cdot j_1 - x_1 \cdot j_2}{D_{12}} + \frac{j_1}{D_1} \\ -\frac{\rho q_2}{RT} \cdot \nabla \mu_2 &= \frac{x_1 \cdot j_2 - x_2 \cdot j_1}{D_{12}} + \frac{j_2}{D_2} \end{aligned} \quad (1)$$

\* Corresponding author.

E-mail addresses: [Nicolas.Kruse@th-koeln.de](mailto:Nicolas.Kruse@th-koeln.de) (N. Kruse), [yuliya.schiesser@th-koeln.de](mailto:yuliya.schiesser@th-koeln.de) (Y. Schießer), [susanne.kaemnitz@ikts.fraunhofer.de](mailto:susanne.kaemnitz@ikts.fraunhofer.de) (S. Kämnitz), [hannes.richter@ikts.fraunhofer.de](mailto:hannes.richter@ikts.fraunhofer.de) (H. Richter), [ingolf.voigt@ikts.fraunhofer.de](mailto:ingolf.voigt@ikts.fraunhofer.de) (I. Voigt), [gerd.braun@th-koeln.de](mailto:gerd.braun@th-koeln.de) (G. Braun), [Jens-Uwe.Repke@tun.tu-freiberg.de](mailto:Jens-Uwe.Repke@tun.tu-freiberg.de) (J.U. Repke).

where  $\rho q$  is the volumetric adsorption,  $R$  the universal gas constant,  $T$  the temperature,  $\mu$  the chemical potential,  $x$  the molar fraction in the adsorbate phase,  $j$  the molar flux and  $D$  the Maxwell–Stefan diffusion coefficient for gas to gas and gas to membrane interactions. Assuming no temperature gradients in the separation layer the chemical potential can be described by the fugacity  $f$ :

$$d\mu = RT \frac{1}{f} df \quad (2)$$

For estimating the adsorption equilibrium of two mixture components in the membrane, a modified Langmuir isotherm described by Markham and Benton [12] can be applied (Eq. (3)). The model takes into account the competing adsorption as seen in the following equation, where  $q_s$  is the saturation loading,  $b$  the Langmuir-coefficient and  $f$  the fugacity:

$$q_1 = \frac{q_{s,1} f_1 b_1}{1 + f_1 b_1 + f_2 b_2} \quad (3)$$

This theoretical approach combined with mixed gas permeance measurements should contribute to a better understanding of the mass transport in carbon membranes at high pressure to advance membrane technology into new industrial applications.

## 2. Experimental

### 2.1. Membrane

The tested membrane type has a tubular configuration with an inner diameter of 7 mm, outer diameter of 10 mm and a total length of 250 mm. The carbon separation layer is placed on the inside wall of a porous aluminium oxide ceramic tube and has a thickness of 2  $\mu\text{m}$ . Multiple intermediate layers ensure a smooth interface between separation layer and support tube (Fig. 1). The effective membrane area is  $5.3 \cdot 10^{-3} \text{ m}^2$  and the pore size of the separation layer is below 0.5 nm. A maximum mechanical strength of 9.2 MPa transmembrane pressure was determined. The membrane has been developed and manufactured by Fraunhofer IKTS/Hermsdorf. A comprehensive and detailed overview on carbon membrane fabrication is given by Saufi and Ismail [13].

### 2.2. Membrane cell

To investigate the membrane behaviour, a specialized high pressure membrane cell has been developed and built (Fig. 2).

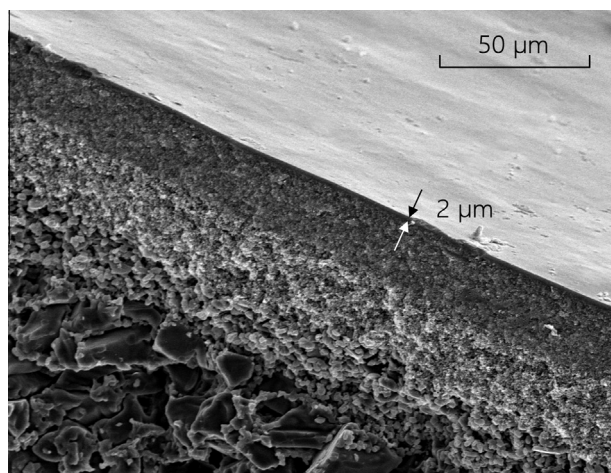


Fig. 1. SEM image showing the cross section of the carbon separation layer, the intermediate layers and the support tube.

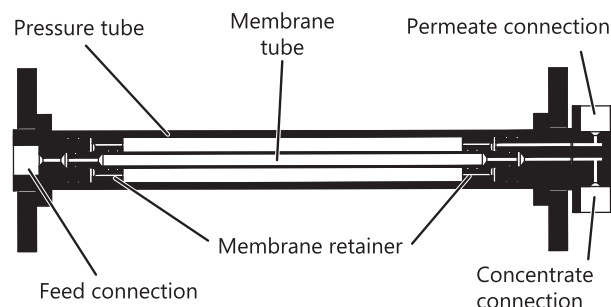


Fig. 2. High pressure membrane test cell.

Besides mechanical strength and temperature resistance, the different thermal expansion coefficients of steel and the membrane material were considered. Therefore, the membrane is mounted to retainer elements which are freely movable in axial direction to prevent thermal strain on the membrane. Furthermore, the sealing cross section of the retainer elements are dimensioned in such a manner that transmembrane pressure does not cause any axial force on the membrane. All machined parts are made from stainless steel. Sealing is implemented by FKM O-rings.

### 2.3. Experimental plant

For this research a high pressure test plant (Fig. 3) has been designed. The plant is capable of conducting measurements with pressures up to 20 MPa. Feed and permeate pressure can be controlled independently. The possible operating temperature ranges from 300 to 450 K.

Feed gas components are supplied by 30 MPa cylinders or by a cooled high pressure pump for fluids with low vapour pressure (e.g.  $\text{CO}_2$ , propane, butane). A real time capable PLC controls pressures, retentate flow rate and feed composition as well as the cell temperature. Moreover, the PLC ensures that the strain on the membrane is kept below its maximum strength during pressure changes.

Pneumatic valves on the feed, retentate and permeate sides of the module allow a fast control of pressures and flows. The feed side valve between gas cylinder and membrane controls the feed pressure by a PID loop. On the permeate side a feedback controlled valve between the membrane module and ambient pressure ensures the desired permeate pressure.

The retentate flow is measured by a coriolis flow meter and the permeate flow by a thermal flow meter. Both are manufactured by Bronkhorst High-Tech. To derive molar flows, the thermal capacity flow signal, measured by the thermal flow meter, is combined with data from an online composition measurement system.

The online composition measurement system utilizes thermal conductivity sensors in the permeate and retentate stream. The method described by Wassiljewa, Saksena and Saxena [14] is used to determine the thermal conductivity of binary mixtures. It is solved numerically on the PLC to derive the compositions from the measured thermal conductivities in real time. The online composition data allows a feed-back-control of the feed pump to set the specified feed composition.

To guarantee the desired temperature inside the membrane module, the test plant controls multiple electric heat sources. One heater evaporates the liquid fluid stream from the high pressure pump before it is mixed with the second component from the gas cylinder. This mixture is then preheated to the temperature of the membrane test cell. A third heater keeps the test cell temperature constant. Measuring accuracy for temperature is better than 2 K. Composition measuring accuracy depends significantly

Download English Version:

<https://daneshyari.com/en/article/639923>

Download Persian Version:

<https://daneshyari.com/article/639923>

[Daneshyari.com](https://daneshyari.com)