

Supplementary Information

Desorption-controlled separation of natural gas alkanes by zeolite membranes

R. Dragomirova,^a M. Stöhr,^a C. Hecker,^b U. Lubenau,^c D. Paschek,^d S. Wohlrab*^a

^a Leibniz Institute for Catalysis at the University Rostock, Albert-Einstein-Str. 29a, D-18059 Rostock, Germany

^b Technical University Freiberg, Institute for Electronic and Sensor Materials, Gustav-Zeuner-Str. 3, D-09599 Freiberg, Germany

^c DBI Gas-und Umwelttechnik GmbH, Karl-Heine-Straße 109/111, D-04229 Leipzig, Germany

^d Institute für Chemie, Abteilung Physikalische Chemie, Universität Rostock, Dr.-Lorenz-Weg 1, D-18059 Rostock, Germany

Table of Contents

1. Membrane preparation.....	3
2. Single gas permeation.....	4
2.1 Single gas adsorption isotherms and calculation of the permeation flux	4
2.2 Single gas permeation fluxes	6
3. Binary permeation	8
3.1 Mixture adsorption isotherms	8
3.2 Separation experiments.....	9
4. References	10

1. Membrane preparation

MFI membranes were grown at the inner side of porous tubular α -Al₂O₃ supports (purchased from Fraunhofer IKTS, Hermsdorf, Germany) with pore sizes of 200 nm in the top layer. The dimensions of the support tubes were 12.5 cm in length with an outer diameter of 10 mm and an inner diameter of 7 mm. The support tubes were glass sealed at both ends in a length of 15 mm. An approximately 40 μ m thick MFI layer with a Si/Al ratio of 270 was prepared in a two-step synthesis procedure described earlier in detail.¹ Here, only a brief explanation of the preparation procedure is given. First, a micrometre sized seeding layer acting as heterogenous nucleation side and mechanical stabilizer was coated from slurry of ball-milled silicalite particles TZP9023 (from Süd-Chemie Zeolite GmbH, Bitterfeld, Germany). In the second step, the MFI membrane layer was formed by hydrothermal synthesis for 72 h at 453 K under autothermal pressure. The synthesis solution with a molar composition of 100 SiO₂: 0.19 Al₂O₃: 3.33 TPAOH: 3.33 TPABr: 6,66 NaOH: 2000 H₂O was filled in Teflon insets and put into stainless steel autoclaves (270 ml total volume). The pre-treated tubular supports were fixed vertically into the autoclaves. After hydrothermal synthesis, the samples were washed thoroughly with deionized water, dried at 100°C and calcined at 723 K for 5 h at 1 K/min in air to remove the template.

To evaluate and to detect the formation of intercrystalline defects in the membranes permoporometry was used. The principle, based on monitoring the permeation of nitrogen as non-condensable component in the presence of zeolitic pore blocking adsorptive, here n-hexane, was described elsewhere in more detail.² Figure S1 depicts permoporometry data for the membrane (M1) used in the permeation experiments showing a low residual flux after pore blocking with n-hexane from which a low number of defects can be derived. As p/p_s increases from 0 to 0.1, the relative flux of nitrogen drops by more than 98 %. As stated before, such membranes possess an overall good permeation ability.²

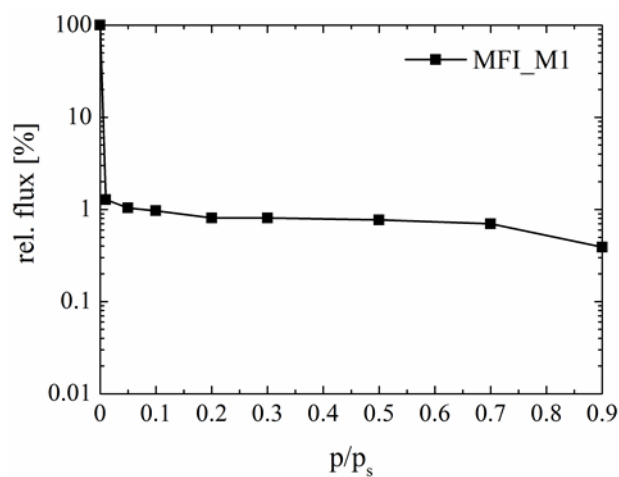


Figure S1: Permporometry measurement of the used MFI-membrane (M1) showing the dependency of relative flux ($\text{flux}_{\text{nitrogen+n-hexane}}$ at p/p_s related to $\text{flux}_{\text{nitrogen+n-hexane}}$ at $p/p_s = 0$) on p/p_s (p_s = vapour pressure of n-hexane in nitrogen).

2. Single gas permeation

To illustrate the adsorption of the pure components methane and n-butane in MFI and the related loading at the feed and permeate side of the MFI membrane layer, configurational biased Monte Carlo (CBMC) simulations were carried out. For all simulations the BIGMAC³ simulation code has been employed. A more detailed description of the CBMC method can be found elsewhere⁴.

Single gas permeation experiments with both gases methane and n-butane were performed as a function of step-wise reduced permeate pressure at constant feed pressure of either 1 or 2 bar. First, the membrane was sealed with Viton O-rings in a stainless steel permeation reactor. The applied setup for the measurements is described elsewhere in more detail.² A combination of pressure regulator at the feed side with a back pressure regulator at the retentate side was used for pressure adjustments. The permeate side of the membrane was set under reduced pressure by the aid of a vacuum pump. The total feed flow was kept constant at either 6 or 12 L h⁻¹. The operating temperature was adjusted to 298 K, 323 K and 348 K, respectively. Before each experiment the membrane was evacuated for at least 1 h at room temperature in order to remove adsorbed components and assure reproducible results. Every measurement was performed twice for confirmation.

2.1 Single gas adsorption isotherms and calculation of the permeation flux

Figure S2 represents the sorption isotherms of methane and n-butane in a temperature range between 298 K and 348 K. From the depicted data, it is obvious that in the operating pressure range of either 1 or 2 bar on the feed side and 10⁻² bar on the permeate side, we operate in low loading regime for the case of methane and high loading regime for n-butane. Moreover, increase in processing temperature leads to decline in the loading of methane on the feed side, whereas in the case of n-butane changes in the feed loading are minimal.

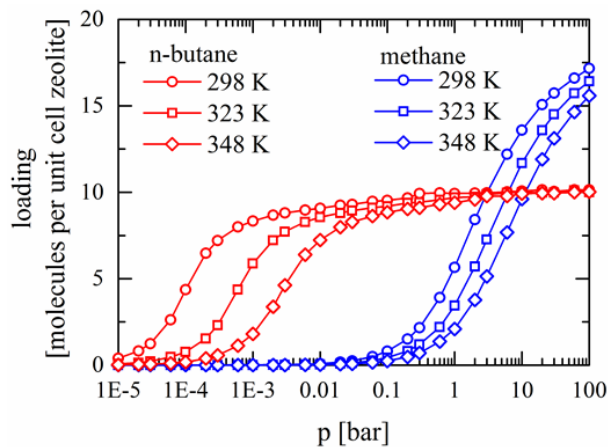


Figure S2: CBMC simulation of adsorption isotherms for methane and n-butane at 298 K (circles), 323 K (squares) and 348 K (diamonds). The heavy lines correspond to dual-site Langmuir fits.

We wanted to find out if the experimentally observed permeation fluxes for both gases are in accordance with the surface diffusion model expressed by eqn. (1). In order to predict the permeation rates, we took the individual loadings from adsorption isotherms (see Figure S2), computed from configurational biased Monte Carlo (CBMC) simulations of methane and n-butane in silicalite which are well represented by a dual site Langmuir isotherm model

$$q_i(p) = q_{\text{sat},a,i} \cdot \frac{b_{a,i} p}{1 + b_{a,i} p} + q_{\text{sat},b,i} \cdot \frac{b_{b,i} p}{1 + b_{b,i} p} \quad (1)$$

and fractional loading being $\theta_i = q_i / (q_{\text{sat},a,i} + q_{\text{sat},b,i})$.

The fitted parameters for the Langmuir model are given in Table S1.

Table S1: Parameter for the dual-site Langmuir model fitted to represent the isotherm data obtained from CBMC simulations.

T / K	$q_{\text{sat},a}$	$q_{\text{sat},b}$	b_a / bar^{-1}	b_b / bar^{-1}
n-butane:				
298	9.33	0.88	8330	3.10
323	9.29	0.87	1390	0.627
348	9.22	0.97	308	0.249
methane:				
298	16.85	4.77	0.477	$1.0 \cdot 10^{-3}$
323	16.71	4.68	0.244	$6.9 \cdot 10^{-4}$
348	16.53	4.79	0.140	$5.0 \cdot 10^{-4}$

We determined the flux of each component i according to the surface diffusion model⁵

$$N_i^s = D_i^s \rho q_{\text{sat},i} \nabla \ln(1 - \theta_i) \quad (2)$$

Here $q_{\text{sat},i}$ represents the saturation loading of the individual components and θ_i is the fractional loading. For the temperature dependence of the diffusion coefficient we assume Arrhenius behaviour

$$D_i^s = D_i^{s,0} \exp\left\{\frac{-E_a}{RT}\right\} \quad (3)$$

with activation energy $E_a = 12 \text{ kJmol}^{-1}$ for methane and $E_a = 38 \text{ kJmol}^{-1}$ for n-butane. For computing the flux data, the ratio between the individual mobilities of methane and n-butane at 348 K is about $D_{\text{methane}} / D_{\text{n-butane}} = 10$, which is compatible with recent self-diffusion data.

The permeation fluxes thus obtained and presented in Fig 2b und 2c indicate that the experimentally observed permeation fluxes of n-butane are in accordance with the surface diffusion model. Moreover, it was shown that the surface diffusion model is applicable for the case of methane since it fits the experimental findings.

2.2 Single gas permeation fluxes

In order to prove that the flattening of the methane permeation flux at reduced permeate pressure (see Fig. 2b) is due to the insufficient feed flux, we conducted single gas permeation experiments at higher permeation flux at a feed pressure of 1 bar. Considering Figure S3 which plots the permeation flux of

methane in [$\text{L h}^{-1} \text{m}^{-2}$] versus step-wise reduced permeate pressure it can be concluded that increasing the feed flux from 6 L h^{-1} to 12 L h^{-1} results in approximately linear permeance of methane. Here, the same temperature dependence of the permeation flux as the one observed for the permeation experiments with 6 L h^{-1} was found. Temperature increase leads to lower permeation fluxes at the applied permeate pressure. More importantly, permeation fluxes at the relevant temperature window from 293 K up to 323 K do again fit to the calculated values (see Fig. 2b) indicating the applicability of the surface diffusion model independently from the feed flux.

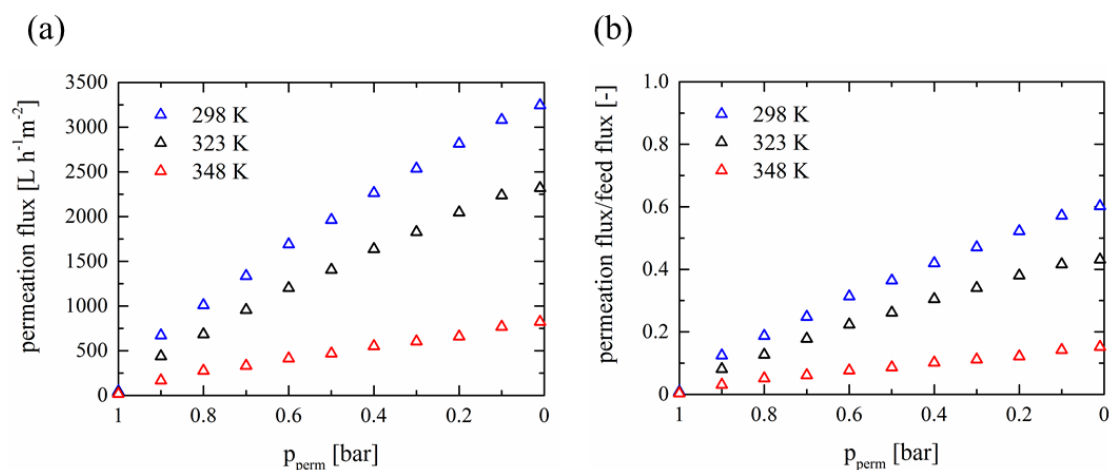


Figure S3: Permeation fluxes of methane (a) through MFI-membrane (M1) and the respective ratios between permeation flux and feed flux (b) as function of permeate pressure at different temperatures; feed pressure = 1 bar; feed stream = 12 L h^{-1} .

Additionally, single gas permeation experiments at a feed pressure of 2 bar were conducted. The findings of this study are consistent with the features for single gas permeation at 1 bar. The experiments presented in Figure S4c and Figure S4d demonstrates the positive influence of the increased feed pressure on the permeation fluxes of n-butane. Here, at a temperature of 348 K and permeate pressure of approximately 0.01 bar the permeation flux of n-butane increase up to level of $1000 \text{ L h}^{-1} \text{m}^{-2}$ compared to $650 \text{ L h}^{-1} \text{m}^{-2}$ at a feed pressure of 1 bar. Moreover, at reduced permeate pressure and feed pressure of 2 bar the exponential diffusion behavior of n-butane is maintained. On the contrary, the higher transmembrane pressure difference and the low feed flux of 6 L h^{-1} give rise to a complete permeance of methane at permeate pressure of 0.7 bar (see Figure S4a and S4b).

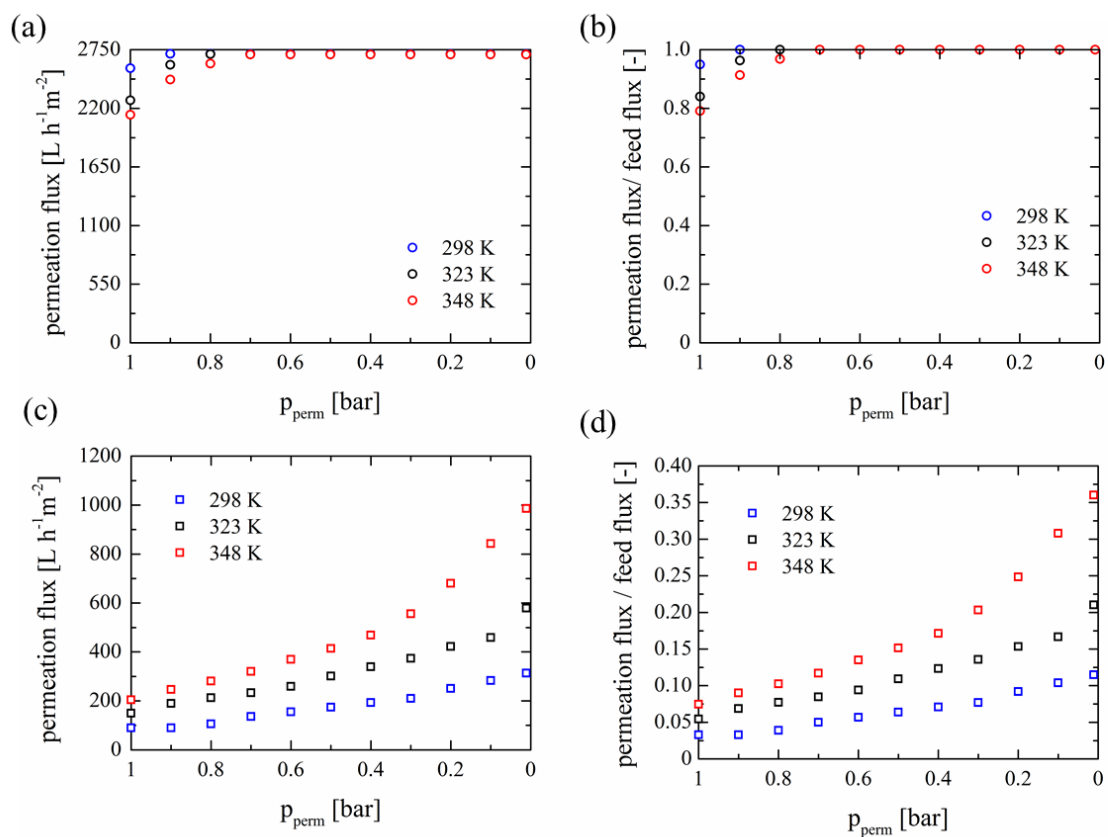


Figure S4: Permeation fluxes of methane (a) and n-butane (c) through MFI-membrane (M1) and ratio between permeation flux and feed flux for methane (b) and n-butane (d) as function of permeate pressure at different temperatures; feed pressure = 2 bar; feed stream = 6 L h⁻¹.

3. Binary permeation

The adsorption of a model mixture comprising 92 vol% methane and 8 vol% n-butane in MFI and the related loading at the feed and permeate side of the MFI membrane layer were calculated using configurational biased Monte Carlo (CBMC) simulations.

Additionally, binary permeation experiments with the model mixture were performed using the same setup as the one for the single gas permeation. The total feed flow was kept at 6 L h⁻¹ and the retentate flow was measured by an ADM flowmeter (Agilent). The composition of the retentate side was continuously analysed using an online coupled capillary GC HP 6890 from Hewlett Packard (GS-Q column; TCD detector; carrier gas: Ar). The permeate composition was calculated according to

$$c_{C_4, perm} = (c_{C_4, feed} \cdot V_{feed} - c_{C_4, ret} \cdot V_{ret})/V_{perm} \quad (4)$$

$$c_{C_1, perm} = (c_{C_1, feed} \cdot V_{feed} - c_{C_1, ret} \cdot V_{ret})/V_{perm} \quad (5)$$

where c_{C_4} and c_{C_1} are the concentrations of n-butane and methane in vol% of either the retentate or the feed calculated from the GC analysis; V_{feed} , V_{ret} and V_{perm} are the flows in feed, retentate and permeate, respectively.

Before each GC analysis the system was kept at least 30 min at the applied pressure or temperature in order to assure a steady state process.

The separation factor α of the binary mixture C_4/C_1 was calculated according to the IUPAC recommendations by the following equation⁶

$$\alpha_{C_4/C_1} = \frac{c_{C_4, perm} \cdot c_{C_1, ret}}{c_{C_1, perm} \cdot c_{C_4, ret}} \quad (6)$$

In this equation $c_{C_1, perm}$ and $c_{C_4, perm}$ are the concentrations of methane and n-butane in permeate and $c_{C_1, ret}$ and $c_{C_4, ret}$ the concentrations in retentate.

3.1 Mixture adsorption isotherms

Figure S5 shows simulation of adsorption isotherms for a mixture comprising 92 vol% methane and 8 vol% n-butane in temperature range from 298 K up to 348 K revealing the preferred adsorption of n-butane under competitive conditions.

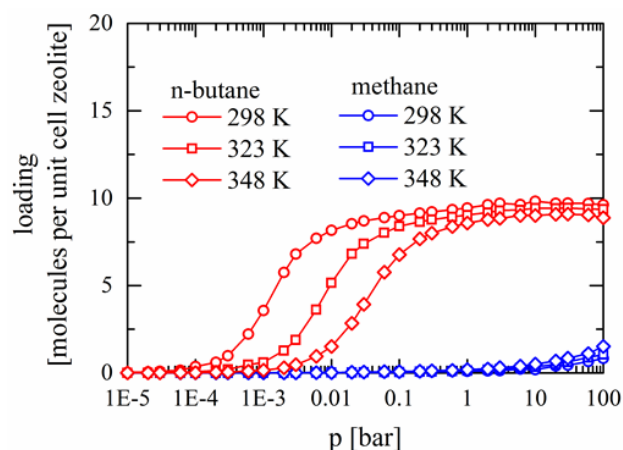


Figure S5: CBMC simulation of adsorption isotherms for a mixture comprising 92 vol% methane and 8 vol% n-butane at 298 K (circles), 323 K (squares) and 348 K (diamonds).

3.2 Separation experiments

The separation performances at a feed pressure of 1 bar, reduced permeate pressure and temperatures of 298 K, 323 K and 348 K, respectively, are depicted in Figure S6. Reducing the permeate pressure leads to exponential increase in the permeation flux. At feed pressure of 1 bar, a permeate pressure of at least 0.6 bar is required for permeation. However, the observed permeation fluxes and separation factors are lower than the one obtained at higher feed pressure of 2 bar due to a lower transmembrane pressure difference. Here, at permeate pressure of 0.01 bar an increase in temperature up to 348 K leads to a lower separation factor compared to that at 323 K. This behavior could be attributed to temperature dependent window blockage effect at the applied conditions.

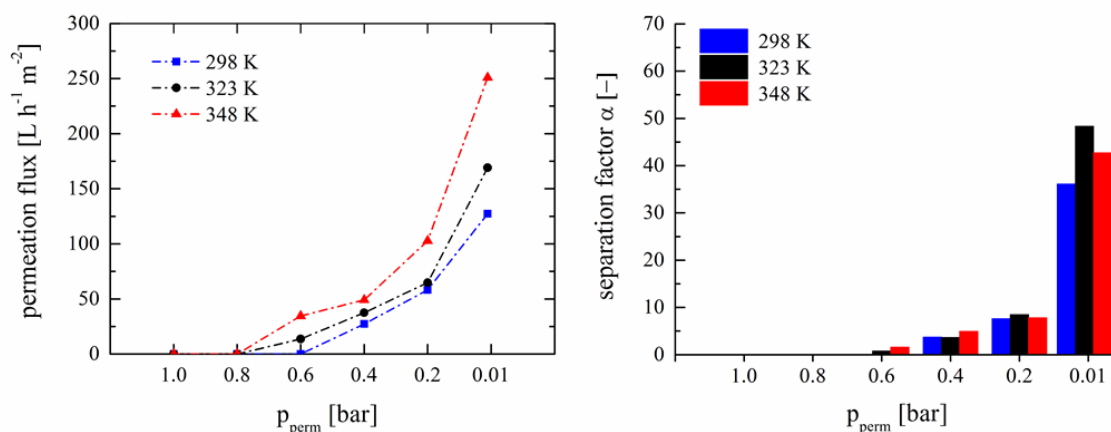


Figure S6: Separation factor α_{c_4/c_1} and permeation flux for the separation of a mixture comprising 92 vol% methane and 8 vol% n-butane at constant feed pressure of 1 bar and varying permeate pressure.

In second series of experiments, the effect of increased feed pressure under reduced permeate pressure was studied for the model mixture comprising 92 vol% methane and 8 vol% n-butane at 298 K. The operating conditions as well as the separation factors and permeation fluxes are listed in Table S2.

Table S2: Experimental conditions, separation factor α_{C_4/C_1} and permeation flux for the experiments conducted at 298 K with a mixture comprising 92 vol% methane and 8 vol% n-butane.

pRet	pPerm	feed	separation factor	permeation flux
[bar]	[bar]	[L h ⁻¹]	[-]	[L h ⁻¹ m ⁻²]
5	0.01	30	6.9	467
4	0.01	24	13.3	308
3	0.01	18	17.9	257.5
2	0.01	12	35.5	155.5
1	0.01	6	39.0	120

As a consequence of the increased feed pressure an increase in the permeation flux was observed, whereas the separation performance drastically decreased. In Figure S7 the alkane compositions of the permeate and retentate are plotted in [%].

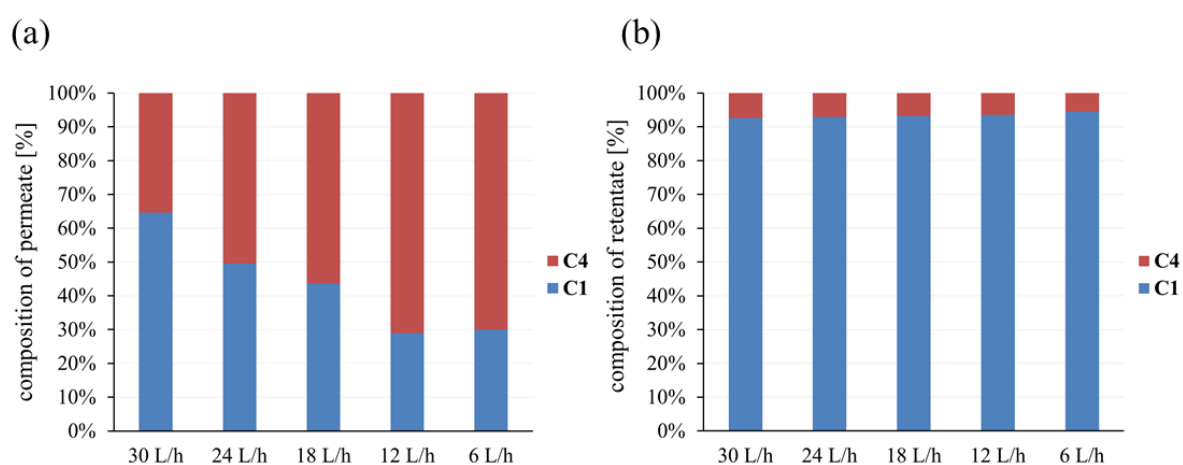


Figure S7: Composition of the permeate stream (a) and composition of the retentate stream (b) at 298 K for the separation experiments conducted with a feed mixture comprising 92 vol% methane and 8 vol% n-butane.

From Figure S7a it is obvious that by increasing the feed pressures the enrichment of n-butane in the permeate stream is reduced. At the same time light enrichment of the less permeable component methane up to 94.6 % was observed in the retentate gas streams for the experiments conducted at feed pressure of 1 bar (see Figure S7b).

4. References

1. S. Wohlrab, T. Meyer, M. Stöhr, C. Hecker, U. Lubenau and A. Oßmann, *J. Membr. Sci.*, 2011, **369**, 96-104.
2. M. Noack, P. Kölsch, R. Schäfer, P. Toussaint, I. Sieber and J. Caro, *Microporous Mesoporous Mater.*, 2001, **49**, 25-37.
3. *The BIGMAC program is authored by T.J.H. Vlugt and B. Smit. Information is available via <http://molsim.chem.uva.nl/bigmac>.*
4. T. J. H. Vlugt, M. G. Martin, B. Smit, J. I. Siepmann and R. Krishna, *Mol. Phys.*, 1998, **94**, 727-733.
5. J. M. van de Graaf, F. Kapteijn and J. A. Moulijn, *J. Membr. Sci.*, 1998, **144**, 87-104.
6. W. J. Koros, Y.H. Ma and T. Shimidzu, *Pure & Appl. Chem.*, 1996, **68**, 7, 1479-1489.