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Combination of membrane separation and gas condensation for advanced natural gas conditioning



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ABSTRACT

Membrane separation and gas condensation are combined to reveal an advanced method for the separation of alkanes. First, the applicability of MFI membranes for alkane separation is principally demonstrated by means of realistic adsorption isotherms computed by configurational biased Monte Carlo (CBM) simulations. Next, dew point curves of mixtures comprising different ratios of n-butane (C₄) and methane (C₁) were calculated according to the thermodynamic methods of Soave–Redlich–Kwong (SRK) and Peng Robinson (PR). From that, isothermal phase boundaries in dependence on the composition of the gas mixture were derived and process parameters under which condensation of the alkane mixture occurs were predetermined. Experimentally, the separation performance of MFI membranes was recorded during separation of n-butane from methane. It was found that liquefied n-butane in the feed and a further liquefaction in the permeate enhance the separation selectivity of MFI zeolite membranes under sweeping conditions tremendously. At the dew point of the feed mixture a sudden rise of the separation factor α is observed. At a temperature of 258 K a mixture with $\chi_{C_4} = 0.5$ can be separated with a separation factor $\alpha_{C_4/C_1} = 174$ due to liquefaction. Experiments without sweeping show a similar behaviour. When forming a two phase mixture in the feed an increase in overall condensation efficiency η_{C_4} is detected in the permeate. At 258 K and $p_{\text{feed}} = 2$ bar and $p_{\text{permeate}} = 1$ bar 29.6% liquefied n-butane was isolated in the permeate from a mixture comprising $\chi_{C_4} = 0.5$.

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1. Introduction

Natural gas is a widely variable mixture of different hydrocarbons and side components like nitrogen, carbon dioxide, hydrogen sulphide, water vapor and helium [1]. The composition of natural gas varies according to its geographical origin and the nature and depth of the gas reservoir [2–4]. Hence, before supplying natural gas into gas grids, different processing steps have to be executed in order to achieve a constant gas quality [5]. First, free liquids have to be removed. Besides, desulphurization and elimination of carbon dioxide have to be processed. Since condensation of hydrocarbons can occur during the transport in pipelines, the hydrocarbon dew point has to be adjusted which is currently the most energy consuming process during the conditioning of natural gas [5,6]. Without a partial removal of C₃₊-alkanes, condensates can entail plant malfunctions and

system failures [7]. Substituting this energy intensive step by a low energy membrane based alternative would be a great benefit for gas conditioning in future. The fundamentals for such a new strategy are complex due to the different hydrocarbon contents of the available gases. Basically, natural gases can be divided into dry and wet gas qualities [8] with a varying amount of the C₃₊-fraction. Dry gases contain mostly methane and a lesser amount of other hydrocarbons, whereas wet gases possess higher amounts of alkanes like propane, butanes and pentanes. Additionally, traces of higher alkanes up to C₂₀ (below 0.1 Mol%) can be present in natural gas streams [7].

Due to the fact that the pore system can be defined by the zeolite structure membranes with uniform pore diameters can be manufactured for the application of selective separation processes [9]. For instance, besides energy intensive sorptive natural gas sweetening through packed columns filled with zeolites [10] the separation of carbon dioxide from natural gases was already demonstrated by using ZSM-5 zeolite membranes [11]. Moreover, inorganic membranes have the potential for an application in alkane separation during natural gas conditioning. In comparison

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to polymer membranes inorganic membranes are nearly non-swelling [12]. In addition, with zeolite membranes high pressure differences between feed and permeate can be applied [13].

Several works were previously performed dealing with alkane separation by zeolite membranes. For example, the applicability of MFI membranes for the separation of alkane mixtures was already demonstrated by several authors [5,14,15]. Molecularly considered, the substance transport through such zeolite membranes can occur by different processes [16]. Key mechanisms are Hagen–Poiseuille flow, Knudsen diffusion and surface diffusion. Furthermore, for zeolite membranes separation efficiencies can be ascribed to specific adsorption, capillary condensation or molecular sieving [17,18]. Hence, nonpolar MFI membranes possess a stronger affinity for higher alkanes than for methane what makes the enrichment in permeate possible [5,19].

Recently we could report a significant improvement of customized MFI membranes for the separation of alkane mixtures at elevated feed pressures allowing a higher adsorption probability at the membrane surface. We could show that mechanically stabilized MFI layers possess a separation selectivity for n-butane/methane mixtures of nearly 14 [19]. In this paper we describe the influence of gas condensation on the performance of MFI membranes during the separation of n-butane from methane. Gas condensation occurs at the dew point of a gas mixture. The dew point itself is defined as the temperature at which saturation of one component in a gas mixture occurs at a specific pressure [2]. In natural gases, long-chained alkanes possess higher dew points than short-chained alkanes. However, in practice it is difficult to measure the exact hydrocarbon dew point mainly due to its dependency on the low amounts of higher alkanes in the raw gas mixture [7]. Furthermore, the position of the dew point curve within a temperature–pressure diagram is primarily depending on the fraction of the hydrocarbon with the highest boiling point [2]. Due to these determination problems our experiments are based on the calculated dew point curves. For further simplification we calculated dew point curves for different two component mixtures consisting of methane and n-butane. Based on these results we can experimentally demonstrate the influence of a liquefied fraction on the separation properties of porous membranes.

2. Materials and methods

2.1. Simulations

2.1.1. Calculation of dew points

Calculations of dew point curves were performed using Pro/II 8.3 simulation software (Invensys SimSci-Esscor, Invensys Systems, USA) according to the thermodynamic methods of Soave–Redlich–Kwong (SRK) and Peng Robinson (PR) for different methane/n-butane compositions. On the basis of dew point curves the isobaric and isothermal curves for the different gas compositions were determined.

2.1.2. Grand canonical Monte Carlo simulations

In order to compute realistic adsorption isotherms for the alkane mixtures we use configurational biased Monte Carlo (CBMC) simulations of a realistic model of n-butane and methane in silicalite. The simulations were carried out in the grand canonical ensemble, where the chemical potentials of the adsorbed species and the temperature were fixed. For all simulations the BIGMAC [20] simulation code has been employed. In order to ensure chemical equilibrium, it is essential to successfully exchange particles with the reservoir. In the present simulations, a flexible alkane is grown atom by atom in such a way that the ‘empty spaces’ in the zeolite are found. The bias of the growing scheme is removed by a modification of the

acceptance rules [21]. A more detailed description of the CBMC method can be found in [22]. The interaction potential used has been specifically tailored for zeolite/alkane interactions by Dubbeldam et al. [23] treating the zeolite as rigid and the CH_n groups of alkanes as ‘united atoms’ via pure Lennard–Jones interactions. The results shown here refer to simulation consisting of 3×10^5 Monte–Carlo cycles, where the final 10^5 steps were used for analysis.

2.2. Preparation

2.2.1. Chemicals

A slurry of ball milled silicalite TZP9023 (Süd-Chemie Zeolite GmbH, Bitterfeld, Germany) in water was used for seeding. Tetrapropyl ammonium hydroxide (TPAOH, 20.0 wt% solution in water, Aldrich), tetrapropyl ammonium bromide (TPABr, 98%, Acros Organics), sodium hydroxide (NaOH, 99%, Roth) were premixed in deionized water. As aluminium containing colloidal silica source Levasil® 30/300 was used (Obermeier GmbH & Co. KG).

2.2.2. Preparation of membranes

For all membranes porous tubular supports from Fraunhofer IKTS (Hermsdorf, Germany) were used. The supports consisted of $\alpha\text{-Al}_2\text{O}_3$ with an asymmetric layer sequence and pore sizes of 200 nm in the top layer. The tubes used were 125 mm long single tube elements with an outer diameter of 10 mm and a channel diameter of 7 mm. Both ends of the tubes were sealed with glass in a length of 15 mm each. Two of these tubes were used for each synthesis approach.

Coating and hydrothermal synthesis of a microfiltration zeolite layer was performed as described previously [19]. First, polymer stabilised silicalite (TZP9023) dispersion was sucked into the tubes whereas a micrometer sized seeding layer is formed. In a second step the synthesis solution (molar ratio of 100 SiO_2 : 0.19 Al_2O_3 : 3.33 TPAOH: 3.33 TPABr: 3.33 NaOH: 2000 H_2O) was filled in Teflon insets of stainless steel autoclaves and the tubular membrane supports were placed into autoclaves. Then, the tubes were hydrothermally treated at 453 K for 48 h and calcined at 723 K for 5 h in air.

2.3. Characterization

2.3.1. Permeation measurements

The permeation behaviour through the membranes was tested in stainless steel permeation cells where the tubes were embedded by Viton O-rings. A pressure regulator at the feed side in combination with a back pressure valve at the retentate side was used for pressure adjustments. Gas streams of methane and n-butane were used as premixed compressed gas mixtures of different compositions (Linde, Germany) or pure gases (Air Liquide, Germany) were mixed. For all experiments $Q_{\text{perm}} + Q_{\text{ret}}$ was set to $2900 \text{ L h}^{-1} \text{ m}^{-2}$ (Q_{perm} = volumetric flow rate of permeate; Q_{ret} = volumetric flow rate of retentate). In some cases helium as sweep gas was streamed over the retentate with different flow rates. Compositions of permeate and retentate were analysed continuously using an online coupled capillary GC HP 6890 from Hewlett Packard. The applied setup for measurements was described elsewhere in more detail [24].

The separation factor α of the binary mixture C_4/C_1 was calculated by the following equation:

$$\alpha_{\text{C}_4/\text{C}_1} = \frac{c_{\text{C}_4,\text{perm}}c_{\text{C}_1,\text{ret}}}{c_{\text{C}_1,\text{perm}}c_{\text{C}_4,\text{ret}}} \quad (1)$$

whereas $c_{\text{C}_1,\text{ret}}$ and $c_{\text{C}_4,\text{ret}}$ are the concentrations of methane and n-butane in retentate and $c_{\text{C}_1,\text{perm}}$ and $c_{\text{C}_4,\text{perm}}$ are the concentrations of methane and n-butane in permeate. All values measured

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