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Hydrocarbon Gas Streams Using Polyethylene –
Polybutyleneterephthalate (POLYACTIVE®) Thin Film
Composite Membranes**

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Pilot Scale Investigations of the Removal of Carbon Dioxide from Hydrocarbon Gas Streams Using Poly (Ethylene Oxide) – Poly (Butylene Terephthalate) (Polyactive®) Thin Film Composite Membranes

Torsten Brinkmann^{a,*}, Céline Naderipour^{a,1}, Jan Pohlmann^a, Jan Wind^a, Thorsten Wolff^a

Erik Esche^b, David Müller^b, Günter Wozny^b

Björn Hoting^c

^a: Helmholtz-Zentrum Geesthacht, Institute of Polymer Research, Max-Planck Straße 1, D 21502 Geesthacht, Germany

^b: Technische Universität Berlin, Process Dynamics and Operations Group, Sekr. KWT-9, Str. des 17. Juni 135, D-10623 Berlin, Germany

^c: Borsig Membrane Technology GmbH, Egellsstrasse 21, D 13507 Berlin, Germany

*: corresponding author:

E-mail: torsten.brinkmann@hzg.de

Telephone: +49 (4152) 87 2400

Fax: +49 (4152) 87 4 2400

Address: Helmholtz-Zentrum Geesthacht,
Institute of Polymer Research,
Max-Planck Straße 1,
D 21502 Geesthacht,
Germany

Keywords

gas separation; CO₂ removal; high flux thin film composite membranes; pilot plant operation; biogas

Abstract

The focus of this contribution is the separation of carbon dioxide from biogas and hydrocarbon containing gaseous reaction products using a high flux flat sheet membrane. The thin selective layer of the membranes is made from the commercial blockcopolymer Polyactive®. The membrane

¹: Present address: Helmholtz-Zentrum Geesthacht, Institute of Coastal Research, Max-Planck Straße 1, D 21502 Geesthacht, Germany

material is manufactured reproducibly on a technical scale and installed into membrane modules. The modules were investigated in three pilot plants: two for the removal of carbon dioxide from methane and one for the separation of carbon dioxide from gaseous hydrocarbon streams. The pilot plant experiments confirmed a rapid approach to steady state operation and the dependence of the separation result on the employed pressure ratio. For the biogas applications it was shown that a single stage process is sufficient to achieve methane purities in excess of 95 mol-% in the retentate at methane recoveries of 70 %, as well as carbon dioxide mole fractions larger than 60 mol-% in the permeate. Carbon dioxide could also be removed successfully from gaseous, hydrocarbon containing product streams employing the investigated high flux membranes. The employed simulation model for the modules predicted the experimental results well and proofed to be a valuable tool.

1 Introduction

The separation of carbon dioxide from gaseous feed streams is becoming an ever more important task in various industrial sectors. This separation is especially important with respect to the world's changing energy and raw material supply situation. Next to conventional separation technologies such as physical or chemical absorption and adsorption processes, membrane technology is well suited for carbon dioxide applications. Examples for the separation of carbon dioxide by gas permeation are the conditioning of natural gas [1, 2], the separation of carbon dioxide from flue gases [3-7] and the upgrading of biogas to natural gas standard [8-11]. Membrane processes and hybrid processes involving gas permeation stages for the removal of carbon dioxide from gaseous reaction products are also under investigation [12, 13].

For the separation tasks mentioned above, integral asymmetric cellulose acetate [1] and various polyimide membranes [8-10, 12] are employed on industrial and pilot scale. In research, also mixed matrix concepts are investigated [14].

The separation of carbon dioxide from nitrogen or hydrogen has been one focus in gas separation membrane research for several years now. The reason is the requirement to reduce carbon dioxide emissions in order to tackle the greenhouse gas effect. A basic concept is to equip fossil fuel fired power plants with carbon dioxide separation stages to render a carbon dioxide rich gas stream that can be stored underground, *i.e.* carbon capture and storage according to the post combustion principle [3, 4]. Another example is the separation of carbon dioxide from hydrogen. This application is typical for the processing of synthesis gas stemming from biomass gasification [15]. Blockcopolymers containing poly (ethylene oxide) as a component of high carbon dioxide selectivity and permeability were found to be excellent materials for the active separation layer of multilayer composite membranes. Two membranes that have been produced in technical scale are described in the literature: the POLARIS™ membrane [3, 15] and membranes employing Polyactive®, a blockcopolymer made from poly (ethylene oxide) and poly (butylene terephthalate) [16-18]. The latter material was developed within the scope of the Mem-Brain alliance, funded by the Helmholtz Association in Germany [4]. These membranes exhibit an excellent carbon dioxide permeance of about $3 \text{ Nm}^3/(\text{m}^2 \text{ h bar})$ at carbon dioxide/nitrogen selectivities of 60 at 20°C [3, 18, 19, 20].

Polyimide membranes are predominantly manufactured in hollow fibre geometry [8-10]. A flat sheet membrane approach was selected for cellulose acetate [1] and the poly (ethylene oxide) containing blockcopolymers. The latter are manufactured in a multilayer, thin film composite configuration where the active separation layer is as thin as 70 nm [18]. The membrane module types for the flat

sheet membranes are either spiral wound [21] or envelope type modules [19, 22]. For these modules, rigorous process simulation tools were developed and validated [19, 25] in order to assess their performance and develop processes superior to their conventional counterparts.

Since the Polyactive® membranes also exhibit reasonable selectivities for carbon dioxide with respect to methane and other hydrocarbon gases, the application of these membranes for the upgrading of biogas and the separation of carbon dioxide from gaseous reaction products was investigated. This paper focusses on the application of Polyactive® multilayer composite membranes mounted in envelope type membrane modules for pilot scale experiments.

2 Membrane Material, Membrane Production and Membrane Module

The formation and application of Polyactive® membranes for the separation of carbon dioxide from other gases was thoroughly investigated by several researchers in the recent years [16-18]. An important result was the identification of the optimum contents of poly (ethylene oxide) and poly (butylene terephthalate) and their preferable molecular weights [17].

The Polyactive® membrane was manufactured on pilot scale in a multilayer composite configuration. The support structure consisted of polyester non-woven onto which a porous poly (acrylonitrile) structure was cast [23]. Subsequently, this support was coated with dense polymer layers. The first of the layers was a poly (dimethyl siloxane) (PDMS) gutter layer [18, 21]. The following layer was the actual Polyactive® separation layer, having a thickness of about 70 nm [18]. The final protection layer consisted again of PDMS. No problems relating to the compatibility between Polyactive® and PDMS were found. The membranes were produced employing the pilot scale membrane production infrastructure at Helmholtz-Zentrum Geesthacht [22]. Several batches of 200 m length and breadths of 0.3 or 0.6 m were prepared, resulting in 60 and 120 m² of membrane area, respectively. The quality of the produced membranes was controlled by determining their oxygen and nitrogen permeances and the resulting oxygen/nitrogen selectivities. Figure 1 shows the homogenous quality of the produced membrane. The more important parameter for the quality assessment is the selectivity. Membrane segments exhibiting a O₂/N₂ selectivity larger than 2.5 were used for membrane envelope production. A minimum value of 0.05 Nm³/(m² h bar) was required for the N₂ permeance in order to pass the quality criterion.

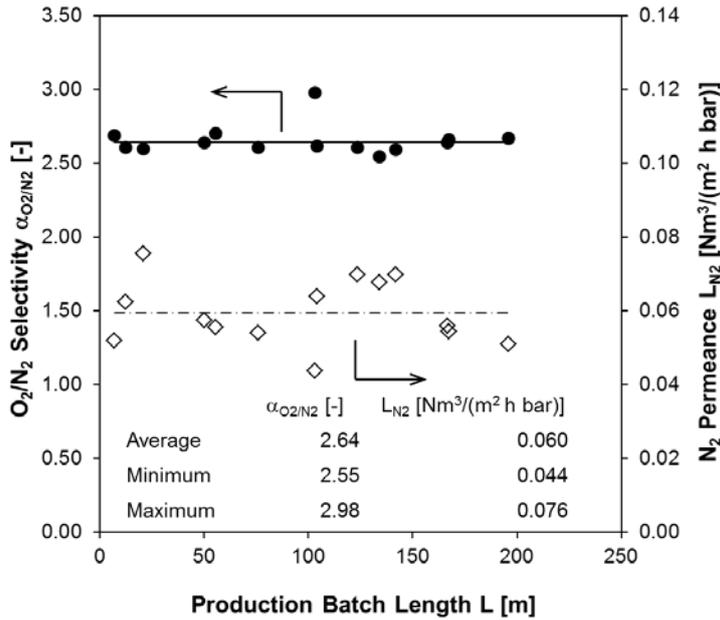


Figure 1: Oxygen/nitrogen selectivity and nitrogen permeance of produced Polyactive® multilayer composite membrane

The membrane material was cut into sheets for membrane envelopes. The membrane envelopes are of circular geometry with a segment cut off at two sides and a central hole for permeate withdrawal (see Figure 3, left). A envelope consist of two sheets with the separation layer facing outwards. The membrane sheets are separated by spacer material in order to form the permeate pathway in radial direction towards the central hole. The thickness of the envelopes can be adjusted as required by the individual application, *i.e.* for a vacuum assisted, high stage cut applications a thicker membrane envelope is selected allowing for lower permeate side pressure drops. The membrane envelopes are thermally welded at the outer circumference. The design involves no additional glue and hence chemical compatibility is more easily ensured. The membrane envelopes employed in this study were manufactured with a diameter of 100 or 310 mm and thicknesses of 1 and 1.5 mm, respectively. Each manufactured membrane envelope is again tested for oxygen and nitrogen permeance as well as oxygen/nitrogen selectivity. The minimum quality acceptance criteria for O_2/N_2 selectivity and N_2 permeance were 2.55 and $0.05 Nm^3/(m^2 h bar)$, respectively. Figure 2 shows the results for a manufactured batch. When comparing Figures 1 and 2 it is apparent that there is considerably less deviation from the average value between the membrane envelopes than there is between the membrane samples taken during production. This is due to the fact that inevitable deviations created during membrane production are more likely to level out for the $0.119 m^2$ membrane envelopes than for the $0.00342 m^2$ production samples. This is also the reason for a more stringent quality acceptance criterion for membrane envelopes.

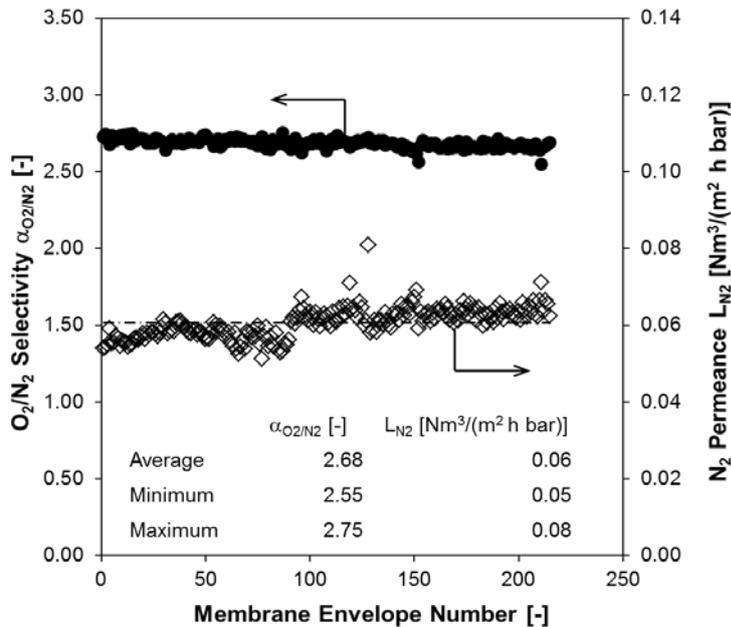


Figure 2: Quality control results of a membrane envelope batch

Figure 3 shows the geometry of the membrane envelope as well as the principal set-up of the envelope type membrane module. The membrane envelopes are stacked onto a perforated permeate tube. They are separated from one another by sealing elements in order to provide the seal between feed and permeate sides. Spacer material is placed between the envelopes to form the feed flow pathways. Furthermore, the membrane envelope stack is divided into compartments by baffle plates. Hence, the flow velocity can be controlled within narrow bounds relative to a design velocity. This is because the cross sectional area available for the feed flow can be adjusted according to the decreasing feed flow caused by the permeation process.

The envelope type membrane modules for the 100 and 310 mm envelopes can house up to 1 m² and 75 m², respectively. For the latter module this results in a packing density up to 950 m²/m³, depending on envelope and feed spacer thickness. The membrane modules can be manufactured with a pressure rating of up to 150 bar.

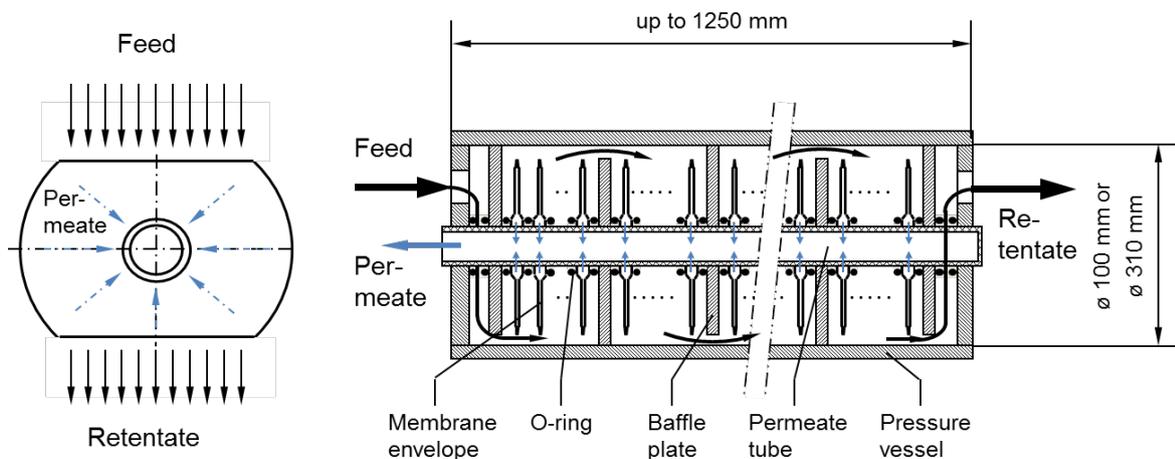


Figure 3: Membrane envelope and envelope type membrane module principle

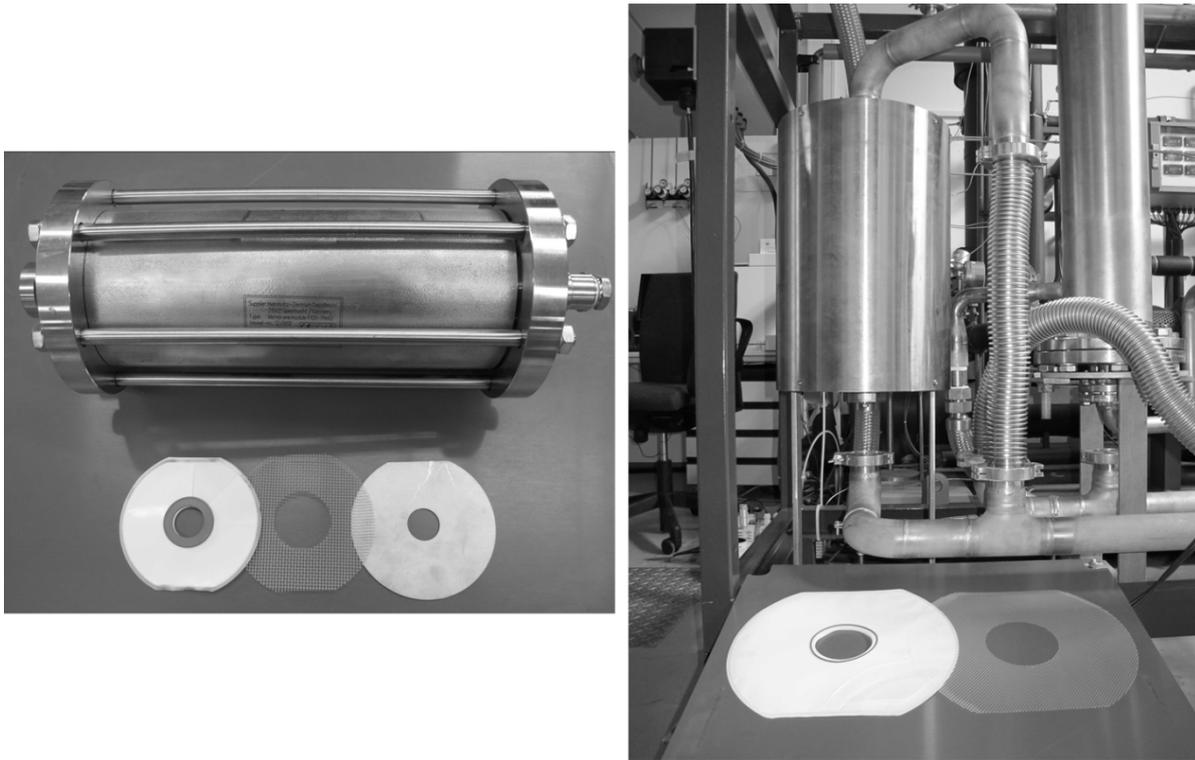


Figure 4: Envelope type membrane modules, membrane envelopes and feed spacers: left 100 mm type for mini plant and piloting applications, right 310 mm type for commercial scale applications

3 Permeation Properties

A fully automated constant volume – variable pressure apparatus was employed to determine the permeation characteristics of the Polyactive® membrane [18, 22]. It operates according to the pressure increase principle. A selected gas is filled into a feed vessel of calibrated volume to a pre-selected pressure and temperature. The employed feed pressures were between 0.36 and 1.25 bar for carbon dioxide, hydrogen, methane and nitrogen, 0.194 and 0.96 bar for ethylene and ethane and 0.4 and 0.25 bar for water vapour. At the start of the measurement, valves are opened allowing the gas to flow into the membrane test cell. All gas supplied to the cell permeates through the membrane and is collected into a previously evacuated permeate vessel, also carefully calibrated. The pressure increase in the permeate vessel as well as the pressure decrease in the feed vessel are carefully recorded as functions of time. This recorded data allow the determination of permeances employing the permeation relationship:

$$\dot{n}_i'' = L_i^{mol} \cdot (f_{F,i} - f_{P,i}) \quad (1)$$

in combination with a dynamic material balance around the permeate vessel. In Equation (1), \dot{n}_i'' represents the molar flux through the membrane, L_i^{mol} represents the molar permeance and f_F and f_P represent the fugacities on feed and permeate side of the membrane, respectively. The measurements are repeated at different pressures and temperatures for the gases of interest. A more detailed description of the pressure increase apparatus can be found in [18, 22].

The single gas permeances of various gases for the Polyactive® multilayer composite membrane are shown in Figure 5 as functions of temperature. The permeance values are the averages of at least 10

measurements for each temperature. It is apparent that water vapour has the highest permeance with carbon dioxide, ethylene, ethane, hydrogen, methane, oxygen and nitrogen following in the given order. Figure 5 also clearly shows that the selectivities of carbon dioxide and water vapour with respect to the other investigated components are decreasing with increasing temperatures. The selectivity values for 20°C and 30°C for carbon dioxide are shown in Table 1. A value for the single gas water permeance at 20°C could not be determined experimentally, since the feed pressure of single permeation apparatus employed would have been too low to allow for meaningful measurement.

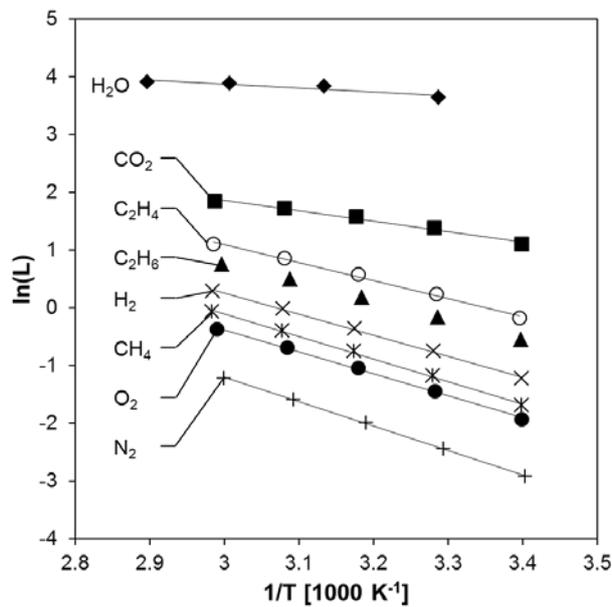


Figure 5: Single gas permeances of water vapour, carbon dioxide, ethylene, ethane, hydrogen, methane, oxygen and nitrogen in Polyactive® multilayer composite membranes as functions of temperature

Table 1: Selectivities of CO₂ with respect to component i for Polyactive® multilayer composite membranes calculated from single gas permeances for 20 and 30°C

	C ₂ H ₄	C ₂ H ₆	H ₂	CH ₄	O ₂	N ₂	H ₂ O
$\alpha_{\text{CO}_2,i}$ (20°C)	3.60	5.29	10.24	16.41	20.78	56.44	-
$\alpha_{\text{CO}_2,i}$ (30°C)	3.14	4.68	8.42	12.95	16.82	45.93	0.104

The pressure dependency of the permeances for carbon dioxide and ethylene within the investigated pressure ranges was small enough to justify the averaging without falsifying the results shown in Figure 5 and Table 1.

The experimental data for the single gas permeation experiments were described using an Arrhenius type relationship for water vapour, ethane, hydrogen, methane, oxygen and nitrogen whilst the Free Volume model [19, 24] was employed for carbon dioxide and ethylene. The Free Volume Model, shown in Equation (2), allows the prediction of multicomponent permeation based on single gas

experiments by accounting for the increase in flux of one component caused by the swelling induced by another. In case no swelling is caused by a component, the parameters m_0 and m_T are 0 and the model becomes an Arrhenius type relationship.

$$L_i = L_{\infty,i}^0 \cdot \exp\left(\frac{-E_i}{R \cdot T} + \sum_{j=1}^{nc} \left(\frac{\sigma_i}{\sigma_j}\right)^2 \cdot m_{0,j} \cdot f_{av,j} \cdot \exp(m_{T,j} \cdot T)\right) \quad (2)$$

$$f_{av,j} = 0.5 \cdot (f_{F,j} + f_{P,j}) \quad (3)$$

Where L is the permeance, L_{∞}^0 the permeance for infinite temperature and pressure approaching 0, E the apparent activation energy, *i.e.* the sum of the activation energy for diffusion and the heat of sorption, R the universal gas constant, T the temperature, and σ the Lennard-Jones molecule diameter. The Lennard-Jones diameters are a measure of the size of the molecules. f_{av} , f_R and f_P are the average, retentate and permeate fugacities, respectively. Swelling induced by individual components is considered to be a function of the average fugacity with m_0 being the swelling parameter for temperatures approaching 0 and m_T expressing the temperature dependency.

Table 2: Free-Volume model parameters of the investigated components

	L_{∞}^0 [Nm ³ /(m ² h bar)]	E [kJ/kmol]	m_0 [1/bar]	m_T [1/K]	σ [Å] [34]
CH ₄	59170.3	30405.3	0	0	3.758
C ₂ H ₄	36688.1	26030.8	-0.0003	-0.0296	4.163
C ₂ H ₆	13347.0	24356.3	0	0	4.443
CO ₂	1734.1	15302.6	0.0717	-0.0032	3.941
H ₂	36134.9	27929.6	0	0	2.827
H ₂ O	361.4	5588.1	0	0	2.641
N ₂	69166.7	33699.2	0	0	3.798
O ₂	24663.3	28746.8	0	0	3.467

In [19] it was shown that Polyactive® single gas permeation data derived using the described method can be employed to accurately describe the separation performance of a membrane module.

As can be seen from the presented results, the introduced Polyactive® multilayer composite membrane exhibits a high carbon dioxide permeance and good selectivities towards nitrogen and hydrogen. For these separations, the Polyactive® membrane is amongst the best in the world, *e.g.* it compares well to MTR's Polaris™ membrane [3]. The selectivities towards methane and other hydrocarbon gases are considerably lower than for polyimide and cellulose acetate based membrane materials [20]. However, due to the high carbon dioxide permeances, several feasible applications for the separation of carbon dioxide from hydrocarbon gases are possible, because of the low membrane area requirements. Further studies in order to develop a model accounting for the multilayer structure of the membrane as well as the swelling behaviour at higher pressures are currently underway.

4 Simulation Model

Process simulation is an important tool to design processes, plan experiments on pilot scale and assess and evaluate experimental results or operational performance. For this purpose, a numerical model for the envelope type membrane modules was employed in this study. The model was developed and implemented in the equation oriented process simulator Aspen Custom Modeler® [19, 25, 26]. The model rigorously describes the flow patterns on the feed and permeate sides of the membrane module by numerically solving the differential material, energy and momentum balances. Feed conditions and the permeate pressure form the boundary conditions of the model. The material and energy balances on the feed and permeate side are coupled by mass and heat transfer relationships for the permeating stream. The selective mass transfer through the membrane is described by Equation 1 employing permeances calculated by the Free-Volume model (Equation 2). The parameters of this model (Table 2) form the only experimental input of the model. Concentration polarisation on the feed side is considered by means of a Sherwood correlation. The heat transfer consists of a convective, *i.e.* enthalpy of the permeating flow, and a conductive part. The latter is calculated using an overall heat transfer coefficient. Hence temperature effects due to the Joule-Thomson effect are accounted for in the model. Real gas behaviour is also assumed when calculating driving forces (Equation 1). Densities, enthalpies, molar concentrations and fugacity coefficients were calculated using the Soave-Redlich-Kwong equation of state [27] as implemented in Aspen Process Modelling [26]. The methods implemented in this software were also used to calculate the required transport properties like viscosities and diffusion coefficients. The pressure drops were calculated using a friction factor approach. From the results shown in [19] it is apparent that the model is well suited to describe membrane gas separation employing modern, high flux membranes at operating conditions involving high pressures on the feed side as well as vacuum assisted operation on the permeate side. A more detailed description of the model including its validation can be found in [19].

5 Applications

5.1 Biogas Upgrading

Biogas can be an important element of an alternative energy mix since it is independent of meteorological and seasonal influences as it is the case for wind energy or photovoltaics. Conventionally, the produced biogas is fed to a decentralised combined heat and power generation facility. Whilst the produced electricity can be fed into the grid, the usage of the generated heat is more complicated due to the rural location of most biogas plants. The heat demand of biogas plants is lower than the heat produced and additional usages for decentralised heating are often difficult to identify. Biogas upgrading allows for a full usage of the energy content by separating the majority of the carbon dioxide and hence a direct methane source can be provided. It can be employed as a substitute for natural gas and used in existing infrastructures for heating and fuelling purposes as well as an industrial feedstock. Several process technologies can be employed for this purpose as *e.g.* physical and chemical absorption and pressure swing adsorption on carbon molecular sieves. Membrane gas separation is another option that has gained increasing interest in the recent years. This is due to its simple and easily adaptable process design, inherent steady state operation achieved almost instantaneously after start-up and the fact that no additional process streams like absorbent liquid and the associated regeneration are required. Several membrane materials have been investigated for this application. Predominant are polyimides [8 - 11], which generally exhibit carbon dioxide/methane selectivities in excess of 30. However, the permeances are rather low, hence large membrane areas are required, typically provided in hollow fibre configuration. Even with

these quite selective membranes, two stage or even three stage processes are required to achieve the required purities of at least 96 mol-% at the high recoveries typically demanded by governmental regulation as *e.g.* the German renewable energy law.

As illustrated in the section permeation properties, the carbon dioxide/methane selectivities of Polyactive® are considerably lower, albeit at almost tenfold the permeance of carbon dioxide. Hence these membranes can be employed in scenarios where only part of the biogas is to be upgraded to a defined methane purity level on the retentate side. The carbon dioxide rich permeate of a one stage process still contains a rather high fraction of methane, resulting in a low methane recovery. The permeate gas can *e.g.* be employed for onsite energy generation [20, 28]. A simulation of such a process is shown in Figure 6. The feed gas is a typical biogas consisting of 65 mol-% methane and 35 mol-% carbon dioxide which also is water vapour saturated. Low concentration contaminants like hydrogen sulfide and ammonia are not explicitly considered and assumed to readily permeate the membrane. A one stage gas permeation process equipped with Polyactive® membranes is employed to purify the biogas to a methane content of 96 mol-% at a methane recovery of 64 % in the retentate. The permeate consists of a carbon dioxide enriched stream, still containing 41 mol-% methane and hence is suitable as fuel for a gas engine [29]. The generated power can be used for the compressor, cooling aggregates or fed into the electrical grid. The generated heat is well within the range of a typical biogas plant's heat demand [30].

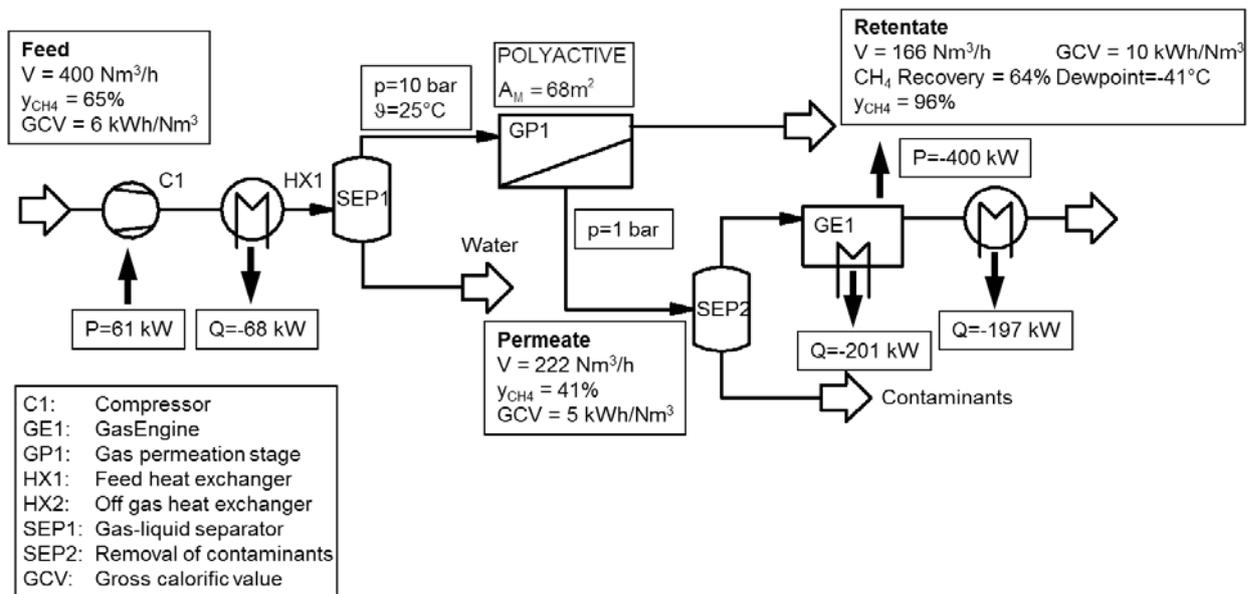


Figure 6: Process simulation of a one stage membrane process equipped with Polyactive® multilayer composite membranes for simultaneous upgrading of biogas and energy generation

5.2 Separation of Carbon Dioxide from Ethylene

Many industrial product streams contain carbon dioxide as a reaction byproduct, which has to be removed for further processing of the actual product. In some cases, the standard approach of using amine-based absorbents for the carbon dioxide removal has detrimental effects. Ethylene and ethane for example are to some degree physically dissolvable in amine solutions [31]. Therefore, the absorption needs to be performed at lower pressures, diminishing the energy efficiency of the

process. For this purpose, gas separation membranes and networks thereof pose a viable and energy efficient alternative.

6. Pilot Plant Investigations

In order to experimentally confirm the performance of Polyactive® multilayer composite membranes installed into envelope type membrane modules, pilot plant experiments were conducted. The experiments were also used to validate the simulation model for this application. Three pilot plants were employed: one located at Helmholtz-Zentrum Geesthacht, operated with synthetic gas mixtures (Pilot Plant 1), one located at an operating biogas plant (Pilot Plant 2) and one located at the Technical University of Berlin employed for the separation of carbon dioxide from gas mixtures containing ethylene, methane and nitrogen which closely resemble the product gas from the oxidative coupling of methane reaction (Pilot Plant 3) [12, 13].

6.1 Pilot Plant 1: Synthetic, humidified methane/carbon dioxide mixtures

The flowsheet of the pilot plant operated with synthetic gas mixtures is shown in Figure 7. Single gases are fed into feed vessel in order to achieve the required feed composition. A liquid ring compressor supplies the gas to the membrane module. Feed pressures of up to 4.5 bar at flowrates up to 50 Nm³/h can be achieved. A bypass control valve (V1) allows for the adjustment of the feed flowrate. The operating principle of liquid ring compressors ensures a saturation of the compressed gas with the employed service liquid, in this case water. Hence, the influence of water vapour was simultaneously assessed in the experiments. The membrane module separated the feed gas into a carbon dioxide enriched permeate and a methane enriched retentate stream. The details of the module are compiled in Table 3.

Table 3: Details of Membrane modules employed in pilot plant experiments

	Pilot Plant 1: Synthetic CH ₄ /CO ₂ Mixture (humidified)	Pilot Plant 2: Biogas	Pilot Plant 3: Synthetic CH ₄ /C ₂ H ₄ /CO ₂ /N ₂ Mixture
Membrane area A _M [m ²]	6.069	7.378	0.114
Module diameter D [m]	0.31	0.31	0.10
Number of envelopes	51	62	10
Compartments	5	20	10

The retentate stream is throttled via another control valve (V2) used to set the feed side pressure and subsequently recycled into feed vessel. Vacuum is applied to the permeate side of the membrane module by a liquid ring vacuum pump. The permeate pressure can be controlled by means of a further control valve (V3). Typically, permeate pressures between 100 and 500 mbar are applied. After recompression, the permeate is also recycled into the feed vessel. Hence the unit operates in a closed loop configuration.

The feed and retentate lines are equipped with sensors for flowrate, pressure and temperature. Composition analysis is conducted by means of a gas chromatograph (GC). The gas sample line supplying the sample loop of the GC is equipped with a vacuum pump in order to draw samples from the permeate side.

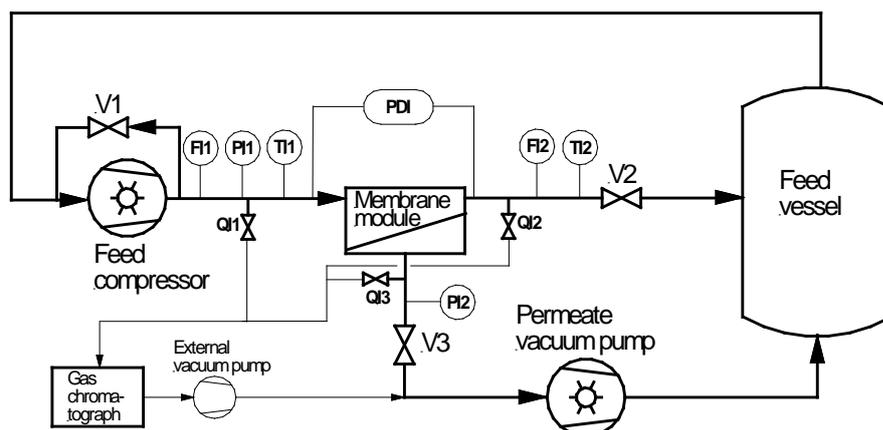


Figure 7: Flowsheet of Pilot Plant 1 operated with synthetic, humidified methane/carbon dioxide mixtures (FI: flow indicator, PI: pressure indicator, QI: sample port, TI: temperature indicator, V: valve)

A total of 167 experiments were conducted over a period of two month period. The feed conditions and the permeate pressures for the experiments presented in Figure 8 a-c are summarised in Table 4.

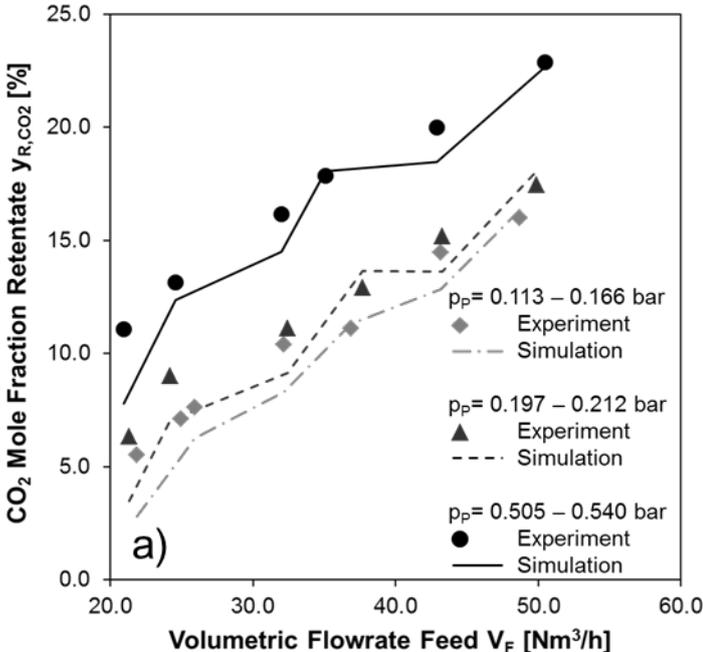
Table 4: Feed conditions and permeate pressures of the experiments conducted in Pilot Plant 1

Feed flowrate [Nm ³ /h]	20 - 50
Feed temperature [°C]	16 - 24
Feed pressure [bar]	4
Feed composition (dry basis) [mol-%]	
CH ₄	55.7 – 60.2
CO ₂	37.7 – 42.0
N ₂	0.0 – 3.4
H ₂ O	Saturated
Permeate pressure [bar]	0.11 – 0.54

Next to the experimental points, predictions of the previously described simulation model based on single gas permeation measurements are depicted in Figure 8 a-c. The membrane module performed as expected: with increasing feed flowrate at otherwise unchanged operating parameters, the carbon dioxide mole fraction in the retentate increased since not as much membrane area in relation to the feed flowrate was available (Figure 8 a). This increase is somewhat less than linear due to the more pronounced effect of concentration polarisation at the lower flowrates. Figure 8 b shows that the carbon dioxide permeate concentration also increases with increasing feed flowrate as the carbon dioxide concentration on the retentate side and hence the driving force for permeation is higher (*cf.* Equation 1). As the ratio of membrane area to feed flowrate is decreasing with increasing feed flowrates, the stage cut, i.e. the ratio of permeate flowrate to feed flowrate, is also decreasing with increasing feed flowrates as shown in Figure 8 c. It is apparent from Figure 8 that an increase in pressure ratio affects the achievable separation positively. Increasing the pressure ratio from 8 (*i.e.* feed pressure: 4 bar, permeate pressure 500 mbar) to 20 (*i.e.* feed pressure 4 bar, permeate pressure 200 mbar) increases the stage cut significantly. Increasing the pressure ratio further to 40 (*i.e.* feed pressure 4 bar, permeate pressure 100 mbar) did not result in much improvement. These findings are in good agreement with other studies [21, 32].

It is apparent that carbon dioxide concentrations of approx. 5.5 mol-% in the retentate can be achieved with Polyactive® membranes, provided that a carefully designed membrane module in combination with the right process conditions (*i.e.* $V_F = 22 \text{ Nm}^3/\text{h}$ and $p_p = 116 \text{ mbar}$ in Figure 8a) is used. This concentration allows the treated gas to be employed as a natural gas substitute. The methane recovery is approx. 80 % with a carbon dioxide permeate concentration of 70 mol-%.

The experimental data and the simulation predictions are in agreement.-This allows for the conclusion that the module’s performance is not affected by the presence of water vapour. Since the experiments were conducted over a period of two month, the agreement between experimental and simulation data indicates that the employed multilayer composite membrane is stable during longer term operation. Furthermore, the results can be regarded as a validation of the accuracy of the simulation model, especially at flowrates in excess of 30 Nm^3/h for the selected operating conditions. At lower flowrates, the prediction is not as good. One possible cause is an underestimation of the influence of concentration polarisation by the model at the investigated process conditions.



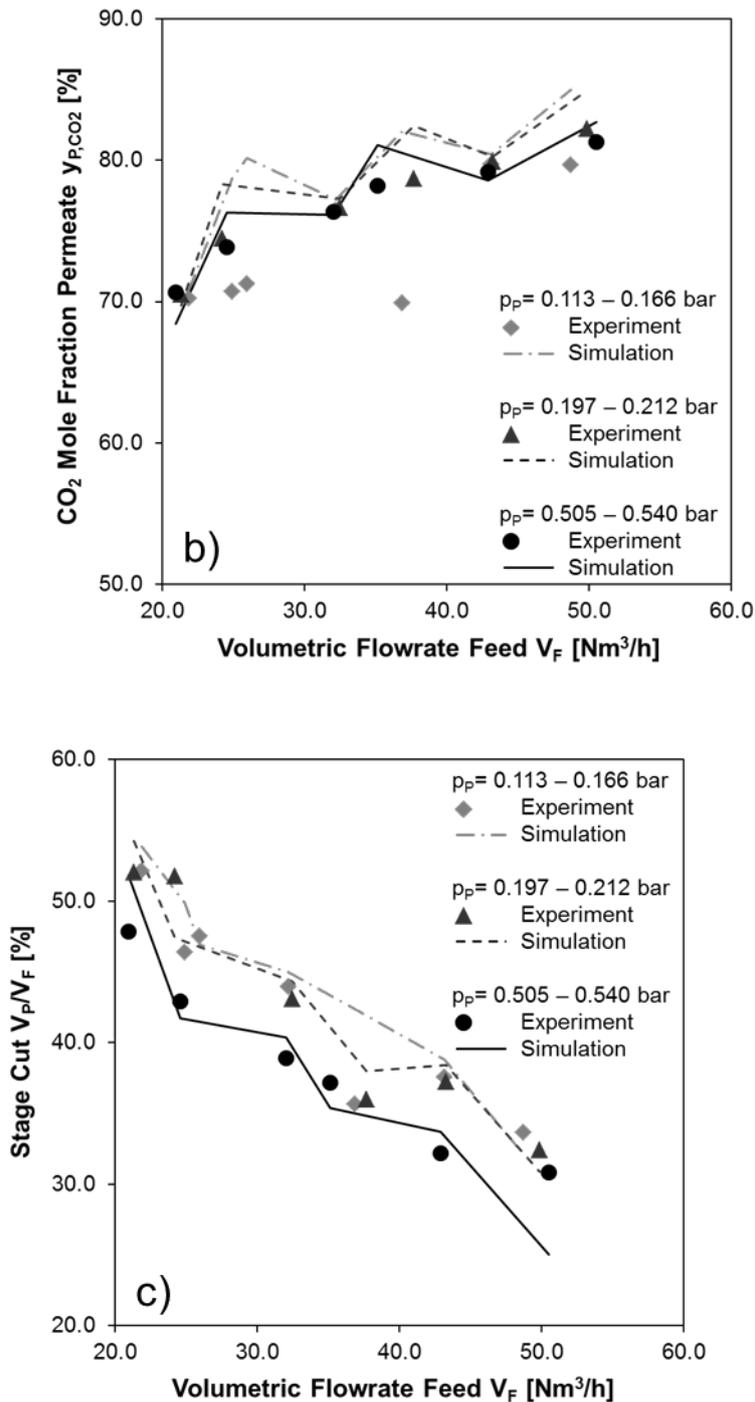


Figure 8: Experimental results of Pilot Plant 1 operated with synthetic, humidified methane/carbon dioxide mixtures at feed temperatures of 16 to 24°C, a feed pressure of 4 bar and feed carbon dioxide mole fractions of 38 – 42 % at varying feed flowrates and permeate pressures

6.2 Pilot Plant 2: Separation of carbon dioxide from Biogas

Figure 9 shows the flowsheet of the pilot plant operated at a biogas production facility. The feed of the unit was a fraction of the produced biogas directly drawn from the fermenter. A screw compressor was employed to compress the gas to pressures of 7 to 10 bar. The gas was subsequently cooled and condensates were removed. Particulates and droplets were hindered to enter the

membrane module by means of a filter-coalescer. However, the feed gas was still water vapour saturated at the feed temperatures of 16 to 25°C. The membrane module was equipped with 7.4 m² of Polyactive® membrane, as detailed in Table 3. A control valve was employed to set the retentate pressure. The permeate was at ambient pressure. Flowrates, temperatures and pressures were continuously logged in the feed (FI1, PI1, TI1) and retentate (FI2, PI2, TI2) streams. Sample ports were employed to collect samples from feed, retentate and permeate. These samples were analysed for composition using an infrared analyser. Experiments with this pilot plant were conducted over a period of three months. During this time the module was in constant contact with biogas. No changes in operating performance were observed when comparing experiments conducted at the start and at the end of the three month period.

The investigated experimental conditions are summarised in Table 5.

Table 5: Feed conditions and permeate pressures of the experiments conducted in Pilot Plant 2

Feed flowrate [Nm ³ /h]	40 - 100
Feed temperature [°C]	16 - 25
Feed pressure [bar]	7 - 9
Feed composition (dry basis) [mol-%]	
CH ₄	63.8 – 64.5
CO ₂	35.0 – 35.6
N ₂	0.3
H ₂ O	Saturated
Permeate pressure [bar]	1.01325

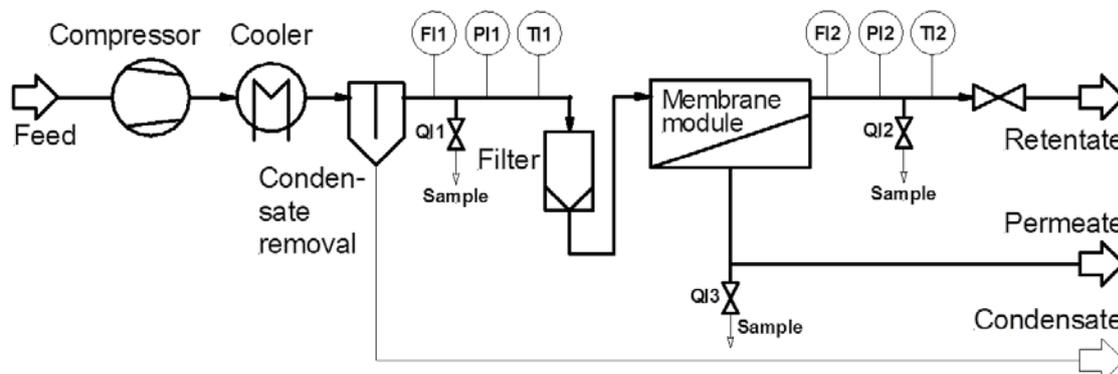
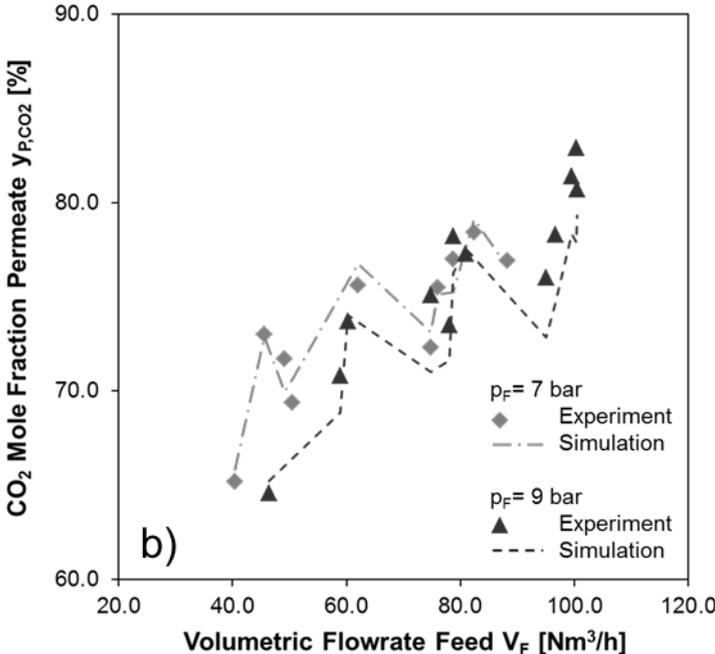
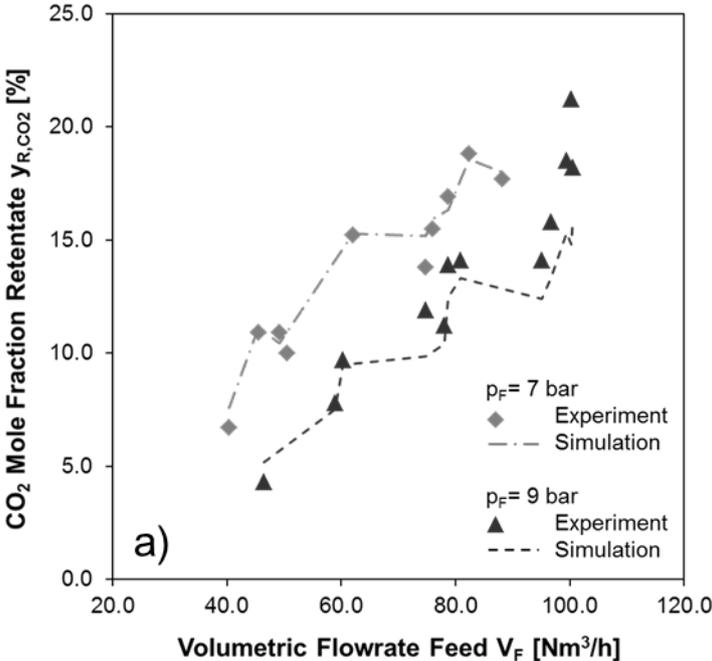


Figure 9: Flowsheet of Pilot Plant 2 operated at a biogas plant (FI: flow indicator, PI: pressure indicator, QI: sample port, TI: temperature indicator)

The results of the biogas experimental runs in Pilot Plant 2 shown in Figure 10 are in line with those discussed previously for the Pilot Plant 1. Figure 10 a shows that for a feed pressure of 9 bar and a feed flowrate of 46 Nm³/h, carbon dioxide compositions in the retentate of lower than 5 Mol-% can be achieved at methane recoveries of 71 %. Due to the lower pressure ratios realised in Pilot Plant 2 compared to Pilot Plant 1, the carbon dioxide permeate mole fractions (Figure 10 b) and the methane recoveries are lower at similar stage cuts and methane retentate purities.

The comparisons between experimental results and simulation predictions are also shown in Figure 10. The biogas treatment is predicted satisfactorily. The largest deviations can be observed for the

stage cuts (Figure 10 c). Furthermore, the prediction of the experimental data in general is better for the lower flowrates, which is in contrast to the observations of Pilot Plant 1. One possible cause is that the flow velocities in the membrane module used in Pilot Plant 2 are higher than those in Pilot Plant 1. The module used in Pilot Plant 1 had between 9 and 12 envelopes per compartment as it was designed for feed pressures as low as 2 bar and velocities should be kept low enough as not to cause high feed side pressure drops at these low feed pressures. The number of envelopes in the module used in Pilot Plant 2 was between 2 and 5 as this module was designed for a narrower pressure range, *i.e.* the capability of adjusting the flow velocity inside the envelope type module could be applied more advantageously.



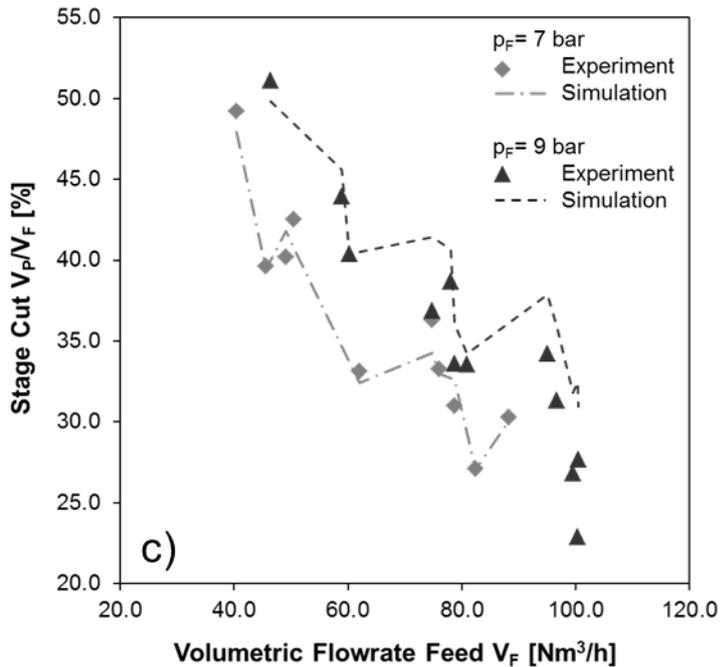


Figure 10: Experimental results of Pilot Plant 2 operated with biogas at feed temperatures of 16 to 25°C, ambient permeate pressure and feed carbon dioxide mole fractions of 35 – 36 % at varying feed pressures and flowrates

6.3 Pilot Plant 3: Separation of carbon dioxide from ethylene, methane and nitrogen

Pilot Plant 3 is operated at the Technische Universität Berlin in the scope of the excellence cluster UNICAT funded by the German Research Foundation (Grant no. DFG EXC 314). Within UNICAT, different catalysed reactions are investigated addressing the changing raw material basis of the chemical industry. One reaction investigated is the oxidative coupling of methane. Next to the desired product ethylene, the reaction product stream consists of non-converted methane, the side product carbon dioxide as well as water and nitrogen. In order to purify the product stream, a sequence of dehydration, removal of carbon dioxide and cryogenic distillation is investigated [12, 33]. The carbon dioxide removal step is designed as hybrid process consisting of carbon dioxide-selective gas permeation and amine-based, chemical absorption. One option for the membrane material of the gas permeation stage is Polyactive®.

A series of experiments were conducted employing the Polyactive® membrane installed in an envelope type membrane module of 100 mm internal diameter as detailed in Table 3. Feed, retentate and permeate flowrates were measured employing thermal mass flow meters. Likewise temperatures and pressures of these streams were continuously measured. The compositions of the gas streams were analysed employing online gas chromatography and IR spectroscopy. The feed mixtures were mixed from pure gases. The total operating time of membrane module was in excess of 400 h, where a continuous operation period of 160 h was achieved. The feed data as well as the permeate pressure are listed in Table 6.

Table 6: Feed data and permeate pressure of experiments conducted in Pilot Plant 3

No.	Feed	Permeate
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	Flowrate [Nm ³ h ⁻¹]	Pressure [bar]	Temperature [°C]	Mole fraction [-]				Pressure [bar]
				N ₂	CO ₂	CH ₄	C ₂ H ₄	
1	4.63	10.85	24.02	0.579	0.226	0.064	0.131	1.34
2	4.64	10.83	23.95	0.553	0.222	0.095	0.130	1.34
3	7.39	20.78	22.80	0.456	0.236	0.190	0.118	1.36
4	4.33	10.72	23.35	0.427	0.227	0.213	0.133	1.32

The experimental results as well as the comparison with the process simulation tool are given in Tables 7 and 8 for the retentate and permeate streams, respectively.

Table 7: Experimental and simulation results of the runs conducted in Pilot Plant 3 for the retentate stream

No.	Flowrate [Nm ³ h ⁻¹]		Pressure [bar]		Temperature [°C]		Mole fraction [-]					
							CO ₂		CH ₄		C ₂ H ₄	
							Exp.	Sim.	Exp.	Sim.	Exp.	Sim.
1	3.896	4.033	10.72	10.70	22.85	22.76	0.153	0.165	0.071	0.064	0.118	0.121
2	3.900	4.056	10.70	10.68	22.90	22.73	0.145	0.160	0.108	0.101	0.118	0.121
3	5.570	6.117	20.63	20.61	20.77	20.61	0.094	0.149	0.223	0.211	0.110	0.112
4	3.567	3.705	10.59	10.59	22.70	21.99	0.155	0.161	0.217	0.228	0.124	0.121

Table 8: Experimental and simulation results of the runs conducted in Pilot Plant 3 for the permeate stream

No.	Flowrate [Nm ³ h ⁻¹]		Temperature [°C]		Mole fraction [-]					
					CO ₂		CH ₄		C ₂ H ₄	
					Exp.	Sim.	Exp.	Sim.	Exp.	Sim.
1	0.734	0.597	23.318	23.367	0.615	0.670	0.026	0.032	0.204	0.192
2	0.742	0.587	23.301	23.318	0.627	0.653	0.027	0.051	0.191	0.194
3	1.817	1.270	21.661	21.029	0.671	0.678	0.091	0.089	0.139	0.161
4	0.759	0.621	23.200	22.650	0.562	0.640	0.199	0.105	0.174	0.181

It is apparent that the carbon dioxide recoveries in the permeate range between 44 % at 10 bar feed pressure and 70 % at 20 bar feed pressure. These values are sufficient, if indeed a hybrid process design is in the focus of the development, *i.e.* the remaining carbon dioxide will be separated by subsequent process units. However the ethylene losses of 24 % and 29 % at 10 bar and 20 bar, respectively, are hardly tolerable. In order to achieve an economically feasible operation, a further treatment of the permeate stream *e.g.* by an additional membrane stage is required in order to minimise the ethylene losses. The experiments show that a higher pressure ratio is advantageous since the increase in carbon dioxide recovery is more pronounced than the increase in ethylene loss due to the increased process selectivity.

The comparison between experimental and simulation results reveals that the calculated prediction is not as good as for the studies conducted in Pilot Plants 1 and 2. A probable reason is that the swelling of the membrane material at higher pressures and additional well permeating components

like ethylene are not considered adequately by the employed permeation model. A strong indication for this argument is the consistent underestimation of the permeate flowrate by the simulation (Table 8). The retentate pressures of the membrane module are predicted rather well. Likewise, experimental and simulated temperature decreases in permeate and retentate coincide. These decreases are likely due to the Joule-Thomson effect. However, the influence of this effect is rather small in the application considered.

7. Conclusions

Polyactive® multilayer thin film composite membranes show excellent carbon dioxide permeances at high CO₂/N₂ selectivities and reasonable selectivities of carbon dioxide towards hydrocarbon gases. The permeation behaviour of different single gases can be described well using an Arrhenius or a Free-Volume model approach. They can be manufactured in homogenous quality on technical scale and installed into membrane modules well suited for gas separation. The envelope type modules employed in this study allow for well ordered flow regimes and hence minimises detrimental effects like *e.g.* concentration polarisation.

Although the available selectivity is limited, Polyactive® membranes can be employed advantageously to the removal of carbon dioxide from hydrocarbon containing gas streams. For biogas treatment, natural gas equivalent product gases can be generated with a low membrane area, as was shown employing two pilot plants, one using synthetic, biogas equivalent mixtures and one operating with a feed stream from an operating biogas plant. The operation in these two pilot plants showed that the separation could be operated most effectively, if the pressure ratio was close to the selectivity ($\alpha_{\text{CO}_2/\text{CH}_4} = 16$ at 20°C) of the gases to be separated. Hence the best separation could be achieved for a pressure ratio of 20 as realised with vacuum assisted operation. Any further increase of pressure ratio did not markedly improve the separation. Polyactive® membranes can also be employed for the separation of carbon dioxide from feed streams containing ethylene. However, the process selectivity is lower compared to the biogas cases. In order to minimise methane or ethylene losses with the permeate stream, this gas could be further treated by additional membrane stages, hybrid process configurations or put to energetic usage in case of biogas treatment.

During the pilot plant studies no detrimental effect of water vapour present in the feed gases on the separation performance of Pilot Plants 1 and 2 was detected. The feed gas of Pilot Plant 3 did not contain water vapour. No decrease in permeation performance was detected during the period of operation in the three pilot plants. The membrane envelopes employed in Pilot Plant 2 were stored for a period 48 month. Subsequently they were installed into a membrane module used for the separation of carbon dioxide from power plant flue gas. The experiments carried out using this module provided further proof of the stability of the membrane, since no deviation from the expected performance was observed.

The experiments conducted in Pilot Plants 1 and 2 could be well predicted using a process simulation model implemented in Aspen Custom Modeler®. This proved the applicability of the model for design purposes as well as for checking the feasibility of experimental results. The predictions of the experiments of Pilot Plant 3 were not as good. This was most likely caused by an insufficient description of the permeance of carbon dioxide and ethylene at higher pressures. Improving the permeation model for these scenarios is in the focus of current research. However, the simulated

compositions represent the experimental results in close enough agreement for process design studies.

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Nomenclature

A	Area	m^2
D	Diameter	m
E	Apparent activation energy	kJ kmol^{-1}
f	Fugacity	bar
L	permeance	$\text{kmol m}^{-2} \text{h}^{-1} \text{bar}^{-1}$ or $\text{Nm}^3 \text{m}^{-2} \text{h}^{-1} \text{bar}^{-1}$
m_0	Swelling parameter	bar^{-1}
m_T	Swelling parameter	K^{-1}
\dot{n}''	molar flux	$\text{kmol m}^{-2} \text{h}^{-1}$
p	Pressure	bar
P	Power	kW
Q	Duty	kW
R	Universal gas constant	$8.31433 \text{ kJ kmol}^{-1} \text{K}^{-1}$
T	Temperature	K
V	Volumetric flowrate	$\text{Nm}^3 \text{h}^{-1}$
y	Mole fraction	-

Greek

α	selectivity	-
σ	Lennard-Jones molecule diameter	\AA
ϑ	Temperature	$^{\circ}\text{C}$

Superscripts

0	Pressure $\rightarrow 0$
mol	Molar

Subscripts

∞	Temperature $\rightarrow \infty$
av	Average

F	Feed
i	Component
j	Component
M	Membrane
P	Permeate
R	Retentate