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Evaluation of a membrane permeation system for biogas upgrading using model and real gaseous mixtures: The effect of operating conditions on separation behaviour, methane recovery and process stability

Nándor Nemestóthy[1], Péter Bakonyi[1,*], Eszter Szentgyörgyi[1], Gopalakrishnan Kumar[2], Dinh Duc Nguyen[3], Soon Woong Chang[3], Sang-Hyoun Kim[2], Katalin Bélafi-Bakó[1]

[1]Research Institute of Bioengineering, Membrane Technology and Energetics, University of Pannonia, Egyetem u. 10, 8200 Veszprém, Hungary

[2]School of Civil and Environmental Engineering, Yonsei University, Seoul 38722, Republic of Korea

[3]Department of Environmental Energy Engineering, Kyonggi University, Suwon 16227, Republic of Korea

[*]Corresponding Author: Péter Bakonyi
Tel: +36 88 624385
Fax: +36 88 624292
E-mail: bakonyip@almos.uni-pannon.hu

Abstract

In this paper, the enrichment of methane by membrane technology was studied by employing (i) a model as well as (ii) a real biogas mixture produced on a laboratory-scale. Thereafter, the endurance of the process was tested at an existing biogas plant. The commercial gas separation module under investigation contained hollow fiber membranes with a polyimide selective layer. During the measurements, the effect of critical factors (including the permeate-to-feed pressure ratio and the splitting factor) was sought in terms of the (i) CH_4 content on the retentate-side and (ii) CH_4 recovery, which are important measures of biogas upgrading efficiency. The results indicated that a retentate with 93.8 vol.% of CH_4 – almost biomethane (>95 vol.% of CH_4) quality – could be obtained using the model gas (consisting of 80 vol.% of CH_4 and 20 vol.% of CO_2) along with 77.4 % CH_4 recovery in the single-stage permeation system. However, in the case of the real biogas mixture, ascribed primarily to inappropriate N_2/CH_4 separation, the peak methane concentration noted was only 80.7 vol.% with a corresponding 76 % CH_4 recovery. Besides, longer-term experiments revealed the adequate time-stability of membrane purification, suggesting such a process is feasible under industrial conditions for the improvement of biogas quality.

Keywords: biogas; biomethane; gas separation; membrane; polyimide; renewable energy

1. Introduction

Biogas is a mixture generated from organic matter via the process known as anaerobic digestion (Patinvoh et al., 2017; Pavi et al., 2017). Basically, it consists of methane, carbon dioxide and other (trace) compounds such as N_2, H_2S, water vapour, etc. (Weiland, 2010). Given its valuable CH_4 content, it has been widely applied to replace fossil fuels (such as natural gas) and contribute to sustainable energy, i.e. heat and electricity production (Ge et al., 2016). Though it can be utilized after partial purification, i.e. in Combined Heat and Power (CHP) systems, upgrading to biomethane is also an option. In this latter case, the sufficient separation of impurities is required, making the subsequent use of biomethane possible (i) in the transportation sector as a vehicle fuel or alternatively, (ii) it may be fed into the natural gas grid once quality requirements are met (Chen et al., 2015; Makaruk et al., 2010).

Biogas cleaning can rely on a range of physical, chemical and biological techniques that include, but are not limited to, (i) condensation, (ii) absorption based on components such as amines, ionic liquids (Albo et al., 2010), (iii) pressure swing adsorption (PSA), (iv) bio-scrubbing, i.e. for hydrogen sulfide elimination, and (v) membrane separation (Bauer et al., 2013; Ryckebosch et al., 2011). This latest option employing membrane contactors and polymerized membranes as permselective barriers has gained remarkable attention in recent years (Albo et al., 2014; Albo and Irabien, 2012). The several reasons behind are portability, relatively simple scalability, sufficient selectivity and stability of modules, advantageous energy requirements, etc. (Basu et al., 2010; Niesner et al., 2013). Although membrane gas separation is regarded as a mature technology and various modules are available on the market supplied by several companies, most of them were not originally intended for biogas-separation purposes but rather to process other gaseous mixtures, i.e. natural gas (Makaruk

et al., 2010). Thus, once such membrane has been adopted for biogas upgrading, however, careful assessment of their separation behaviour as well as optimization of operating conditions should be carried out, i.e. due to the different compositions of gas streams handled, to be able to meet biomethane specifications.

So far, various “membrane-powered” applications have been developed and thoroughly evaluated in terms of biogas enrichment, most of which are designed from polymeric membranes, i.e. cellulose acetate (CA), polydimethylsiloxane (PDMS), polysulfone (PSf) and polyimide (PI) (Scholz et al., 2013). A contemporary membrane system, in order to provide biomethane as a substitute for natural gas, should be capable of providing at least 95 % CH_4 purity with 90 % CH_4 recovery (Brunetti et al., 2015). Typically, the raw biogas that is subjected to purification contains approximately 50-70 % methane, 30-50 % carbon dioxide, lower quantities of nitrogen and water, and trace amounts of substances such as H_2S, depending on its source, e.g. a farm, sewage sludge digester, landfill, etc. (Rasi et al., 2007, 2011). In general, the performance of a given membrane system that deals with such gaseous streams will strongly depend on the operating conditions, namely the (i) pressure gradient across the membrane module (assisting the driving force), (ii) retentate (R) to feed (F) flow ratio (R/F) known as the splitting factor, (iii) separation temperature, and (iv) feed-gas composition, etc., which play a major role (Bakonyi et al., 2013ab).

Over the preceding years, our group has been conducting research into gaseous biofuels (hydrogen and methane) production as well as their subsequent separation. As a result, membrane bioreactors (MBR), as integrated approaches, have been designed (Bakonyi et al., 2017; Szentgyörgyi et al., 2010). Besides, ex-situ tests with regard to the evaluation of gas upgrading were performed as well (Bakonyi et al., 2013b). In the light of preliminary experiments, hollow fiber membranes (HFMs) made of PI are shown as applicable candidates

in terms of gas upgrading (Bakonyi et al., 2013b; Szentgyörgyi et al., 2010). Though previous information concerning biogas purification using certain PI membranes is available in the literature (Harasimowicz et al., 2007), an in-depth examination of the particular one employed in this study, to the best of our knowledge, has not been yet reported. Hence, in this work, the thorough evaluation of a commercialized membrane made of PI – a polymer with the potential to be utilized in CH_4/CO_2 separation (Baker and Low, 2014) – was aimed to study. The main scope of investigation was laid down to reveal the operating circumstances under which biomethane may be produced. Over the course of the assessment, model and real biogas mixtures were applied to determine how the composition affects the efficiency of purification. Afterwards, the time-stability of the gas permeation process was analysed over a series of longer-term experiments to obtain information concerning its applicability with regard to possible industrial implementation. To the best of our knowledge, such experimental results are not found in the literature for this PI membrane module and hence, this work is believed to exhibit added value and contribute to the development of anaerobic digestion technology.

2. Experimental setup

Biogas purification measurements were performed on a membrane module (UBE-CO5, Ube Industries, Ltd.) designed for natural gas separation. It contains composite hollow fibers membranes composed of a PI selective layer. Since a number of module features, i.e. the active surface area and thickness of the membrane are unknown, the gas permeability, measured in the recognised non-SI unit of Barrer, cannot be calculated to characterise the separation process. Therefore, an experimental, pressure-normalized volumetric gas flow rate is

reported according to **Eq. 2**. The module was installed into a high-pressure gas separation membrane system, referred to as GSMS (**Fig. 1**). The schematic drawing of the GSMS and its most essential technical details can be found in our earlier paper (Bakonyi et al., 2013b). The permeate and retentate were quantified by digital mass flow meters (Bronkhorst EL-FLOW® Select), which had undergone preliminary calibration. To obtain the exact flow rate of mixtures throughout the separation process, a correction factor was provided by Fluidat® (https://www.fluidat.com, Bronkhorst®). This took into account the exact composition of the permeate and retentate streams in terms of CH_4, CO_2 and N_2 as determined according to Section 3.

The gas separation experiments were carried out at a temperature of 30 ^{o}C unless otherwise stated, first by using a binary (model) mixture composed of 80 vol.% methane and 20 vol.% carbon dioxide (SIAD Hungary Kft., Hungary) (**Table 1**). Afterwards, real biogas – from a continuously operated anaerobic membrane bioreactor system – as documented by Szentgyörgyi et al. (2010) – was collected over a period of time, compressed into a gas cylinder and subsequently tested. Recently, together with our industrial partner, work has commenced on the valorization of landfill-deposited organic waste fractions, i.e. to generate biogas. As a part of that line of research, the assessment of methane purification by membrane technologies is a distinct goal. In accordance with a summary in the paper of Brunetti et al. (2015), the nitrogen content in biogas can vary considerably (1-17 vol.%). Hence, to simulate realistic conditions and typical compositions of landfill-derived biogas, enrichment of the real gaseous mixture (pressurized in the external tank, as noted above) by N_2 was conducted. As a result, the final composition was as follows: 70 vol.% CH_4, 19.8 vol.% CO_2, 9.2 vol.% N_2 and approx. 1 vol.% unidentified minor impurities.

As can be observed in **Tables 1 and 2**, the effect of the main membrane operating parameters – namely the (i) feed pressure to permate pressure ratio

(p^F/p^P) and (ii) the splitting factor (R/F) defined as the retentate flow rate relative to the total feed flow rate – on (i) methane concentration on the side of the retentate and (ii) methane recovery was sought (**Figs. 2-5**). All data presented in this work were obtained under steady-state permeation conditions, reflected by the properly stabilized volumetric flows and corresponding concentrations of gaseous substances, namely CH_4, CO_2 and N_2. In addition to the experimental runs listed in **Tables 1 and 2**, the membrane module was tested at a biogas plant located in Hungary in order to determine its behaviour in the longer-term and provide feedback concerning the stability of this time-dependent process, which could be useful as far as an envisaged industrial application is concerned. The respective permeation conditions are described in **Table 3**. Mass balance calculations, that took into account volumetric flow rates and respective concentrations of gases, thoroughly verified the reliability of such measurements. This indicated that the entire feed could only be extracted either as the retentate or permeate after separation had occurred. Repetitions (i.e. duplicates) under particular experimental settings were carried out occasionally, resulting in relative deviations < 5 %.

3. Analytical methods

Gas samples taken from the feed, permeate and retentate were analyzed by gas chromatography. On the one hand, the concentrations of CH_4 and N_2 could be determined from a Gow-Mac Series 600 gas chromatograph equipped with a molecular sieve packed column (filled with zeolite), a thermal conductivity detector (TCD), and He as a carrier gas. On the other hand, the concentration of CO_2 was analyzed by a Hewlett Packard HP 5890 Series II gas chromatograph equipped with a capillary column (GS-CarbonPLOT, Agilent Technologies), a TCD and N_2 as a carrier gas.

4. Calculations

CH_4 recovery ($Y_{methane}$) was defined (in the unit of %) according to **Eq. 1**:

$$Y_{methane} = 100 \frac{V_R\, C^R_{methane}}{V_F\, C^F_{methane}} \quad (1)$$

where V_R and V_F are the total volumetric flow rates of the retentate and feed ($dm^3\ min^{-1}$ at standard temperature (273 K) and pressure (1 bar) (STP)), respectively; while $C^R_{methane}$ and $C^F_{methane}$ stand for the CH_4 concentrations (vol.%) in these fractions, respectively (**Tables 1-3**).

The experimental, pressure-normalized volumetric gas flow rate (J_j) of a given component (*j*) in the mixture for the PI membrane module was computed (in the unit of $dm^3\ min^{-1}\ bar^{-1}$ at STP), as follows (**Eq. 2**):

$$J_j = \frac{V_P C^P_j}{\Delta p_{j,mean}} \quad (2)$$

where V_P is the total volumetric flow rate of the permeate ($dm^3\ min^{-1}$ at STP), C^P_j is the actual (measured) concentration of component (*j*) in the permeate (vol.%), and $\Delta p_{j,mean}$ (in the unit of bar) is the mean pressure gradient across the membrane capillaries (Asadi et al., 2016) or, in other words, the partial driving force of component (*j*), according to **Eq. 3**.

$$\Delta p_{j,mean} = \Delta p^{lumen}_{j,mean} - \Delta p^{shell}_{j,mean} \quad (3)$$

where $\Delta p_{j,mean}^{lumen}$ and $\Delta p_{j,mean}^{shell}$ are the average partial pressures for component (*j*) on the lumen-side (where the gas was fed) and the shell-side (where the permeate was collected), respectively according to Asadi et al. (2016), assuming in the calculation that the membrane permeate stream was under non-well-mixed conditions.

The permselectivity (α) for a certain gas pair was defined by **Eq. 4**.

$$\alpha = \frac{J_i}{J_j} \tag{4}$$

where J_i and J_j are the experimental, pressure-normalized volumetric gas flow rates of the rapidly and the slowly permeating compounds, (*i)* and (*j)*, respectively ($J_i > J_j$). In this work, the permselectivities for CO_2 and CH_4, as major constituents of biogas that need to be separated, were computed (**Tables 1-3**).

5. Methane enrichment and recovery from binary (model) and real biogas mixtures

In essence, the gas separation applying non-porous, polymeric materials e.g. in the case of UBE-CO5 requires the partial pressure difference of substances across the membrane (Mulder, 1996), where the rapidly permeating compound is enriched in the permeate, meanwhile, the slower (less-permeable) one is concentrated in the retentate. Accordingly, on the grounds of carbon dioxide enrichment on the permeate-side (**Tables 1 and 2**), it can be concluded that the membrane used in this investigation is CO_2-selective. This is primarily

attributed to the properties of PI, which act as the selective layer of composite hollow fibers membranes found in the module. This glassy polymer can provide a sufficient degree of CO_2/CH_4 selectivity given its high permeability of CO_2, which can be even an order of magnitude larger than that of CH_4 (Harasimowicz et al., 2007). The fact that the PI membrane is CH_4-rejective (**Tables 1 and 2**) leads to increased methane content in the retentate under upstream-side pressure conditions. This is quite advantageous, especially when the (i) upgraded biogas, namely biomethane, is to be injected into the distribution pipeline network (Brunetti et al., 2015) or (ii) when a sufficient level of biogas purification is not achieved in a single-stage, requiring further steps by means of additional processing to reach the defined gas (biomethane) quality.

With both the binary (model) as well as real biogas mixtures employed in this work, the achievable concentration of methane in the retentate seemed to be positively influenced by the greater difference between p^F and p^P, which made a particular contribution to the actual driving force (**Eq. 4**). This is reflected in **Figs. 2 and 4**, where the relationship between p^F/p^P and the CH_4 concentration on the retentate-side as well as the CO_2/CH_4 permselectivity can be regarded as directly proportional. In addition, the so-called splitting factor (R/F) had also been proven as a variable that exhibits a substantial impact on the performance of gas separation (Bakonyi et al., 2013b; Harasimowicz et al., 2007). Based on **Figs. 3 and 5**, regardless of the gas actually fed into the module, the lower R/F range should be preferred to attain a more significant degree of enrichment of methane in the retentate and maintain a larger permselectivity of CO_2/CH_4. This observation agrees well with the features generally described concerning the technique of gas separation by membranes (Baker, 2000). Overall, by comparing **Fig. 2** with **Fig. 4** and **Fig. 3** with **Fig. 5**, the results demonstrate that the composition of the gas used, either in terms of the model or real biogas, did not remarkably change the profile of response given by the membrane as a function

of various operating conditions, namely p^F/p^P and R/F. Consequently, the conclusion can be drawn that the process ought to be conducted by ensuring a larger driving force along with a smaller splitting factor to enhance the percentage of methane in the retentate. From the viewpoint of peak methane concentrations on the retentate side, it should be pointed out that the performance of the module (under comparable test conditions: p^F/p^P = 2.42-2.65, R/F = 0.66) was less attractive attributed to the higher degree of complexity, lower initial CH_4 content, etc. of real biogas (**Tables 1 and 2**).

As a matter of fact, in terms of the model gas, the highest enrichment of methane (93.8 vol.%) was accomplished with a corresponding recovery ($Y_{methane}$, Eq. 1) of 77.4 % (**Table 1**). In the case of real biogas, however, the best recorded methane concentration was 80.7 vol.% linked to 76 % of $Y_{methane}$ (**Table 2)**. Hence, these results indicate that a retentate of almost biomethane quality (93.8 vs. 95 vol.%) could be delivered in the case of the model gas mixture. Therefore, it can be presumed that following slight modifications of the process parameters, i.e. raising the driving force and/or lowering the splitting factor, the target value of 95 vol.% could be realistic. On the contrary, further study is required to achieve a similar degree of success with real biogas. As can be inferred from **Table 2**, the membrane was unable to efficiently deal with the substantial N_2 content of the feed (**Table 2**), making this compound of major concern. To understand why only marginal N_2/CH_4 separation could be realised, it should be kept in mind that the permselectivity is dependent on particular factors such as (i) diffusivity and (ii) solubility of the permeating compounds in the polymer material (Freeman, 1999). The variation in the former term contributes to the so-called mobility selectivity, while that of the latter parameter influences the commonly named sorption selectivity. Unfortunately, in many cases these two characteristics are opposed to each other when working with mixtures comprised of nitrogen as well as methane. Therefore, no effective separation of these two gases can be

accomplished (Lokhandwala et al., 2010). Consequently, the elimination of N_2 from the biogas stream is an objective of further research where membranes possessing better characteristics are developed. Moreover, provided that the overall technology undergoes careful optimization by reconsidering the number of purification stages and the possible application of cascades (Baker and Lokhandwala, 2008; Lokhandwala et al., 2010), additional benefits that enhance the process can be expected. For comparison of membrane performance with other materials/modules, data summarized in review articles such as Basu et al. (2010) and Scholz et al. (2013) can be referenced. Among commercialized polymer materials, permselectivity values for CO_2/CH_4 span 1.4-42.8 and hence, the respective values attained with the commercialized PI module in this work (**Tables 1-3**) fit well into this range.

6. Evaluation of the stability of the biogas upgrading process over longer-term measurements – implications of application in the field

Apart from the issues elaborated in Section 5, e.g. the N_2 content of the biogas, the time-stability of the process is also a crucial aspect that must be considered. In other words, to acquire a reasonable comprehension of the relevance of the membrane module in terms of an actual application in the field that attempts to improve the quality of the biogas, an adequate degree of process durability should be acquired. Therefore, performance of the PI membrane module was further analyzed over the longer-term by running permeation experiments with real biogas (generated by an anaerobic digestion plant located in the countryside of Hungary). Furthermore, implementation of the whole test rig in an industrial setting is accompanied with the advantage of a continuous gas supply and the availability of sufficient feed volumes, which would otherwise limit the exploitation of permeation capacities over a more extensive period of time.

As can be seen in **Table 3**, the biogas generated in the plant could be characterised as a clearly distinguishable quality compared to the one applied during laboratory tests (**Table 2**). This might be attributed to differences in the attributes of biotic and abiotic processes, i.e. in terms of the (i) composition of underlying microbial consortia, (ii) source and complexity of the feedstock to be utilized, (iii) operational settings of the fermenters, etc. During the permeation stability tests, separation conditions were constants (**Table 3**) for almost 9 hours during the experiment (**Figs. 6 and 7**). It should be noted that besides the clearly identifiable components, namely CH_4, CO_2 and N_2, the raw biogas, on average, contains a comparable amount of trace substances to the biogas evolved in the laboratory-scale bioreactor (**Table 2**). However, the similarities regarding the distribution (partial concentrations) of these components remain unknown and such an analysis could be a subject of a future study to elaborate on such related effects. Actually, based on the already published experiences in the existing literature, pro-longed operation of the biogas-upgrading membrane permeation system can require the pretreatment of raw fermenter off-gas to get rid of particular secondary components (i.e. ammonia, hydrogen sulfide and water vapor that may damage the membrane material over time) by drying, condesnation and desulphurization before conveying the biogas to the membrane purification technology (Miltner et al., 2010, 2009). Such an action can help to extend membrane lifetime and preserve its performance (Stern et al., 1998)

The time profiles of the qualities of the permeate and retentate are depicted in **Figs. 6 and 7**, respectively. It should be inferred that only slight changes in the compositions were recorded and, therefore, the purification performance could be considered quite stable throughout the test period. Similarly to the results of the other gas mixtures discussed above, a considerable degree of CH_4/CO_2 separation was achieved. However, the removal of nitrogen

gas seemed to be challenging, in accordance with statements made in Section 5. Under the circumstances mentioned in **Table 3**, a reasonable and steady level of CH_4 recovery ($Y_{methane}$ > 82 %) was accomplished with a corresponding methane concentration of 81-82 vol.% in the retentate. Overall, these research outcomes imply that the gas permeation process was able to function properly over an extended period of time without considerable variation in the separation efficiency. Thus, it can be deduced that the PI membrane employed may be a worthy candidate for further investigation and possible installation at biogas plants. However, the experiments conducted point to the fact that this particular module should be applied as one component of a multi-stage (sequential) membrane system, enriching the CH_4 content of the biogas to the desired level of biomethane quality (Makaruk et al., 2010). Such a system is supposed to manage the efficient separation of N_2 from CH_4 and attain large $Y_{methane}$ values to reduce losses in the permeate (increase product recovery) (Rautenbach and Welsch, 1993) and consequently, minimise the environmental impacts associated with the emission of methane. Many times, however, high methane purities may be attained only with compromises in methane recovery, when some methane is lost in the permeate (Sun et al., 2015). Under these conditions, for instance, the permeate with methane content can be recycled and burnt in gas engines at the biogas plant (Miltner et al., 2009).

7. Conclusions

In this paper, a polyimide gas separation membrane was investigated in terms of biogas purification. The results showed that the feed-to-permeate-pressure ratio as well as the splitting factor had a notable effect on the performance of the process. In fact, under actual operating circumstances, the

module provided biogas with methane content (93.8 vol.% along with 77.4 % recovery) via efficient removal of CO_2 in the case of the binary, model mixture. The CO_2/CH_4 permselectivity values were dependent on the experimental conditions and accordingly, could be as high as 11-12 in some cases. However, primarily due to the insufficient CH_4/N_2 separation capacity of the membrane, it was not possible to upgrade the real biogas in the same manner and additional research into the subject is encouraged. Nevertheless, tests revealed an adequate level of endurance of the membrane permeation process over the longer-term, leading to the conclusion that the process, based on the module that contains PI hollow fibers, is worthy of further elaboration under industrial conditions in the field. The appropriate design of the process, in particular the deployment of a membrane cascade purification system, could overcome the existing bottleneck observed with the single-stage application to deliver biomethane from biogas.

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Figure legends

Fig. 1 – Image of the gas separation membrane system (left-hand side) with the PI membrane module installed (right-hand side).

Fig. 2 – The effect of p_F/p_p on the methane concentration on the retentate side (diamond) and CO_2/CH_4 permselectivity (square) using the model biogas.

Fig. 3 – The effect of the splitting factor (R/F) on the methane concentration on the retentate side (diamond) and CO_2/CH_4 permselectivity (square) using the model biogas.

Fig. 4 – The effect of p_F/p_p on the methane concentration on the retentate side (diamond) and CO_2/CH_4 permselectivity (square) using the real biogas.

Fig. 5 – The effect of the splitting factor (R/F) on the methane concentration of the retentate side (diamond) and CO_2/CH_4 permselectivity (square) using the real biogas.

Fig. 6 – The time dependency of the composition of the permeate under the conditions listed in Table 3. Square: carbon dioxide; Diamond: methane; Triangle: nitrogen.

Fig. 7 – The time dependency of the composition of the retentate under the conditions listed in Table 3. Square: carbon dioxide; Diamond: methane; Triangle: nitrogen.

Table 1 – Experimental conditions and results using the binary gas mixture (80 vol.% CH_4, 20 vol.% CO_2)

p^F (bar)	p^F/p^P (-)	R/F (-)	Gas concentration (vol.%)				J (dm^3 min^{-1} bar^{-1} at STP)		CO_2/CH_4 Permselectivity (-)	$Y_{methane}$ (%)
			Permeate		Retentate		CH_4	CO_2		
			CH_4	CO_2	CH_4	CO_2				
7.0	1.78	0.89	64.9	35.1	81.9	18.1	5.53	15.43	2.79	90.8
11.8	2.33	0.65	62.6	37.4	89.3	10.7	2.81	17.31	6.17	72.7
12.3	2.42	0.66	53.2	46.8	93.8	6.2	4.85	34.08	7.03	77.4
13.5	1.76	0.73	55.7	44.3	89.1	10.9	9.00	53.54	5.95	81.0
13.6	1.77	0.73	69.5	30.5	83.9	16.1	1.96	10.35	5.27	76.4
14.5	1.40	0.81	74.6	25.4	81.3	18.7	2.11	7.64	3.63	81.9

Table 2 – Experimental conditions and results using the biogas mixture containing 70 vol.% CH_4, 19.8 vol.% CO_2, 9.2 vol.% N_2 and unknown trace substances to balance.

p^F (bar)	p^F/p^p (-)	R/F (-)	Gas concentration (vol.%)						J (dm^3 min^{-1} bar^{-1} at STP)		CO_2/CH_4 Permselectivity (-)	$Y_{methane}$ (%)
			Permeate			Retentate			CH_4	CO_2		
			CH_4	CO_2	N_2	CH_4	CO_2	N_2				
8.5	1.36	0.78	69.4	28.5	2.2	72.3	17.2	10.1	8.74	33.92	3.88	80.9
7.7	1.43	0.79	69.2	19.9	10.0	70.2	19.7	9.5	7.66	7.84	1.04	79.1
4.3	2.65	0.66	49.3	42.8	6.9	80.7	7.5	11.4	5.26	46.58	8.85	76.0
6.4	1.76	0.93	58.5	31.7	8.8	70.8	18.3	10.2	2.52	8.89	3.53	94.3

Table 3 – Average experimental conditions for the assessment of process stability during longer-term biogas (57.4 vol.% CH_4, 39 vol.% CO_2, 2.5 vol.% N_2 and unknown trace substances to balance) permeation conducted at 50 ^oC.

p^F (bar)	p^F/p^p (-)	R/F (-)	Gas concentration (vol.%)						J (dm^3 min^{-1} bar^{-1} at STP)		CO_2/CH_4 Permselectivity (-)	$Y_{methane}$ (%)
			Permeate			Retentate			CH_4	CO_2		
			CH_4	CO_2	N_2	CH_4	CO_2	N_2				
10.8	5.48	0.58	21.6	75.8	1.4	81.7	14.6	2.9	1.07	12.55	11.77	82.9

Fig. 1

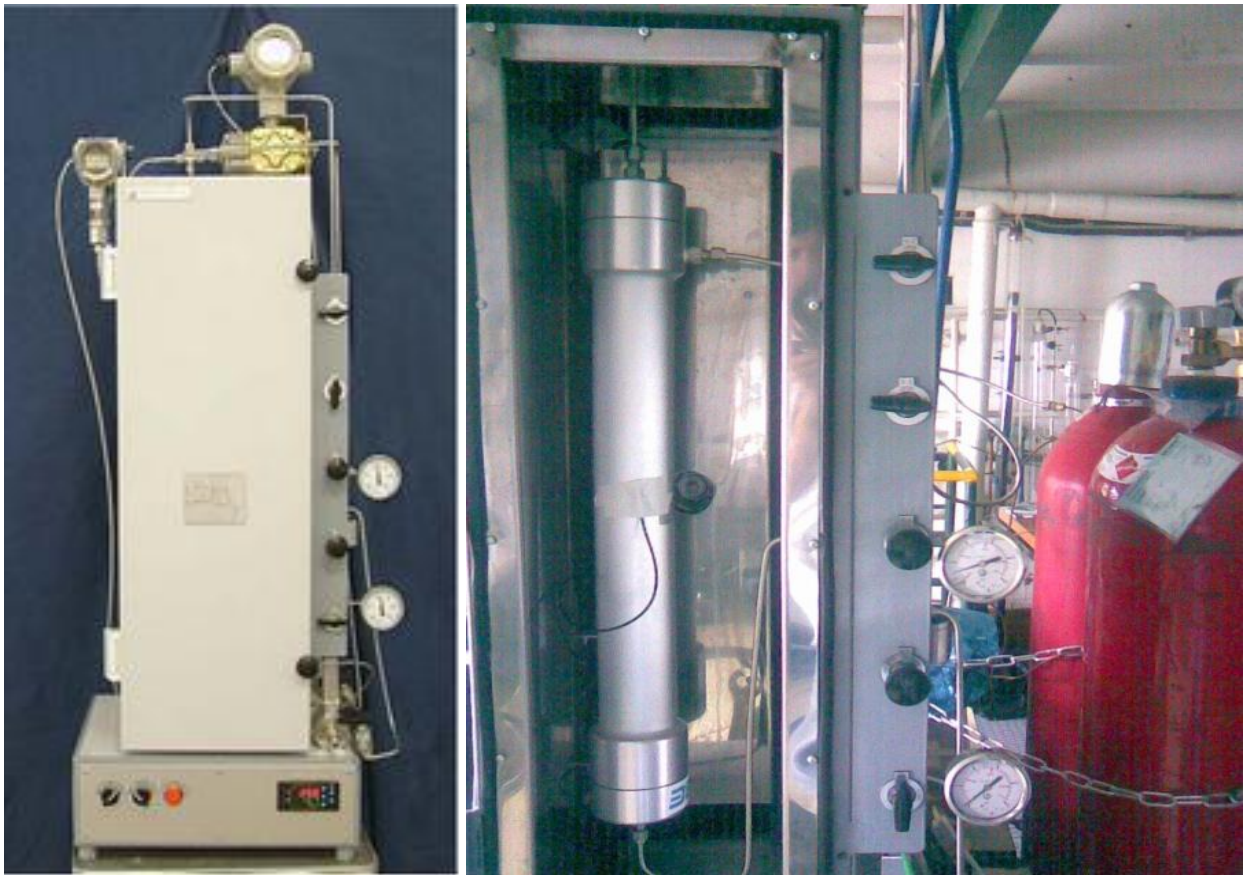
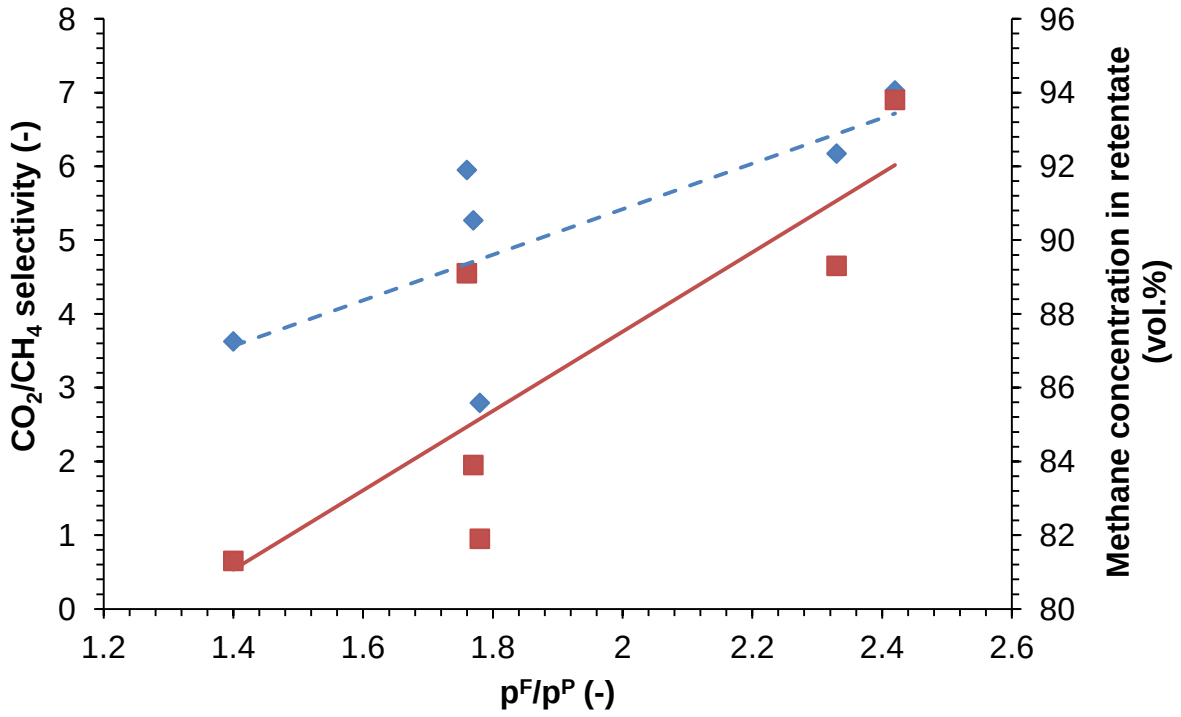


Fig. 2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1.6
1.8
2
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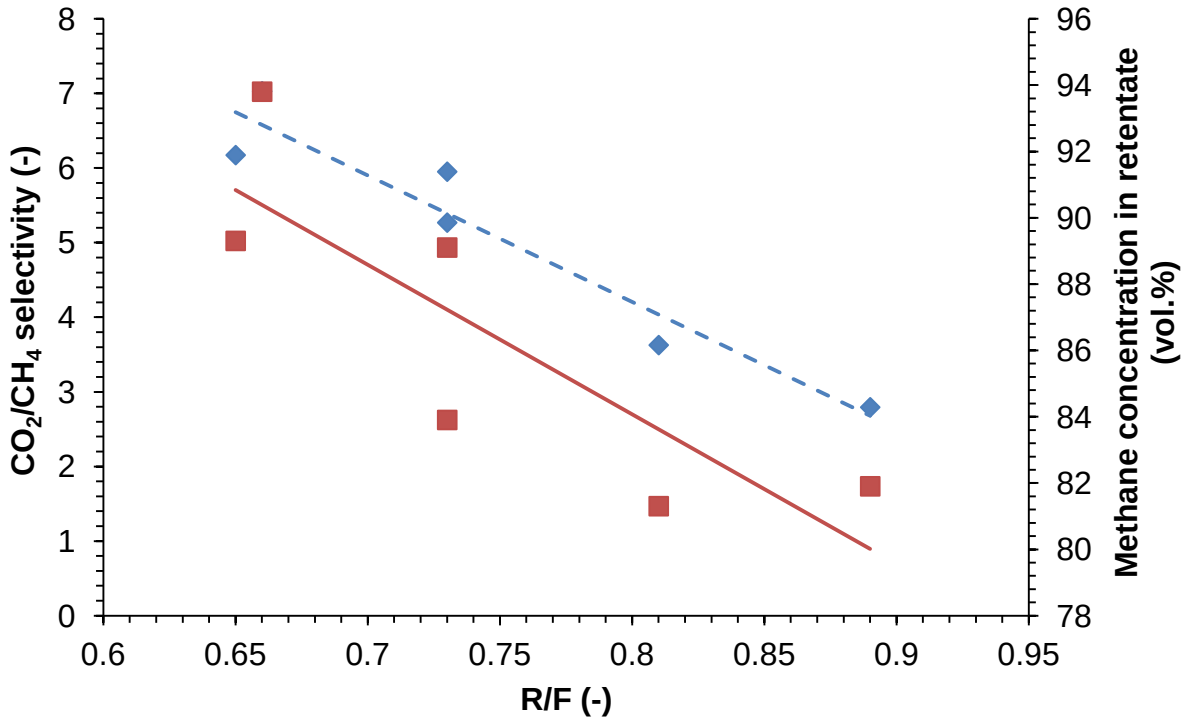
2.6
CO_2/CH_4 selectivity (-)
Methane concentration in retentate (vol.%)
p^F/p^P (-)

Fig. 3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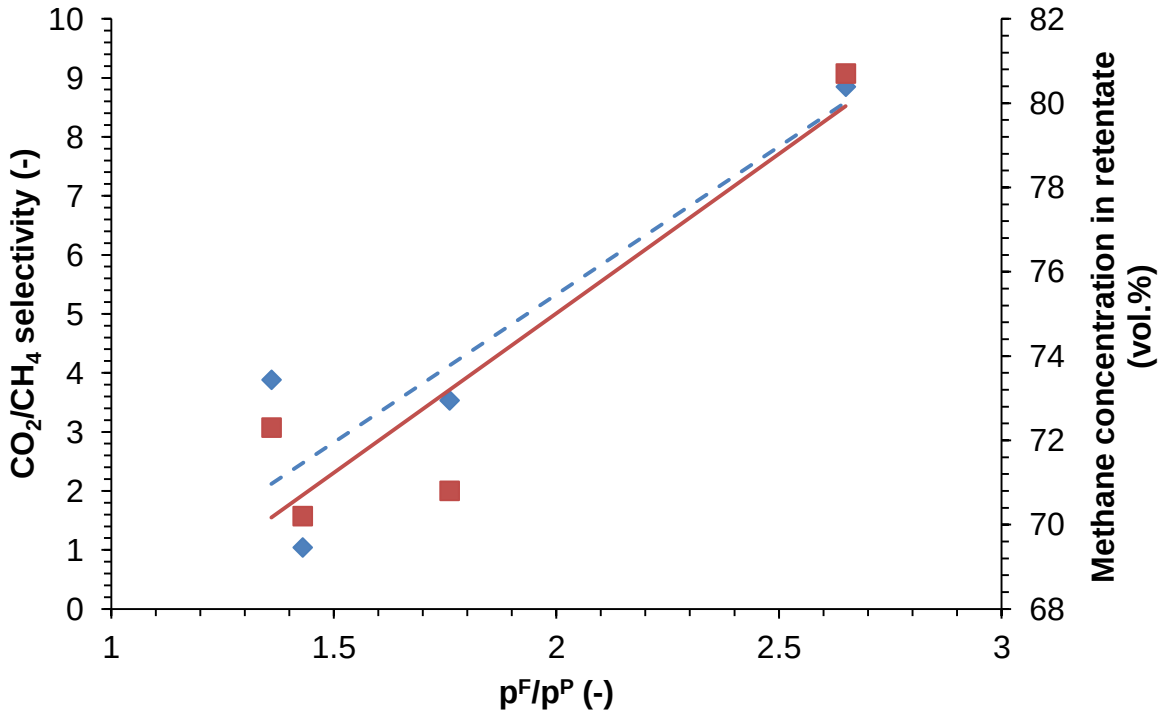
CO_2/CH_4 selectivity (-)
96
94
92
90
88
86
84
82
80
78
Methane concentration in retentate (vol.%)
0.6
0.65
0.7
0.75
0.8
0.85
0.9
0.95
R/F (-)

Fig. 4


10
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2
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CO2/CH4 selectivity (-)
82
80
78
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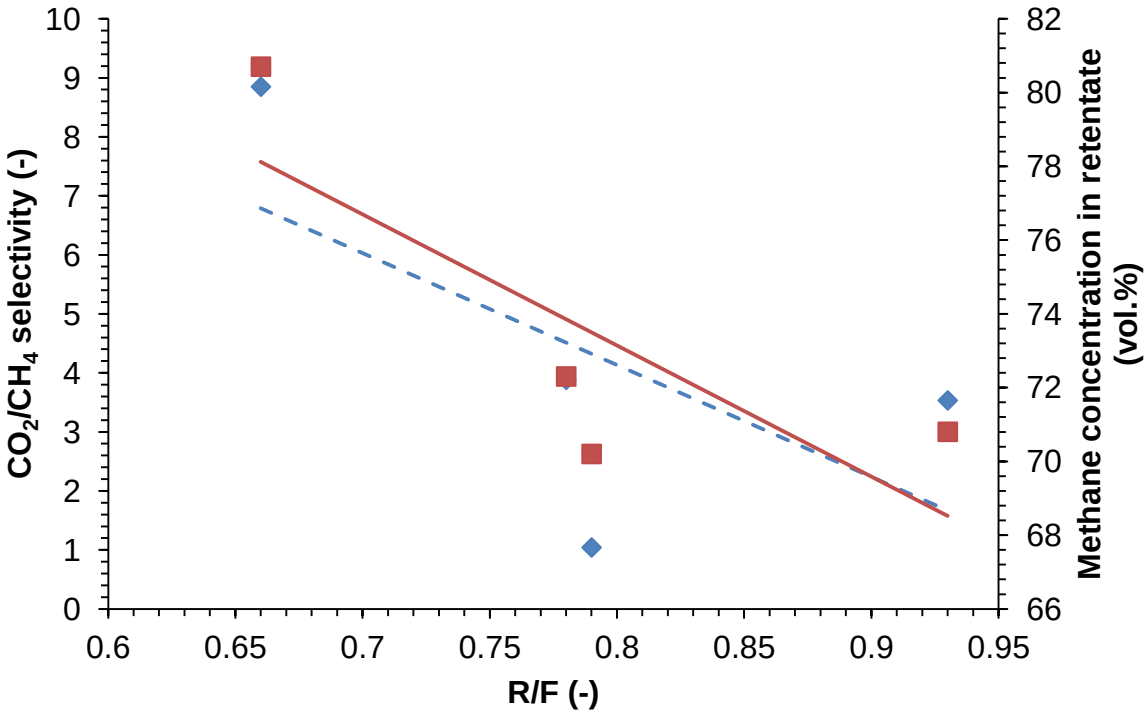
74
72
70
68
Methane concentration in retentate (vol.%)
1
1.5
2
2.5
3
pF/pP (-)

Fig. 5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CO_2/CH_4 selectivity (-)
82
80
78
76
74
72
70
68
66
Methane concentration in retentate (vol.%)
0.6
0.65
0.7
0.75
0.8
0.85
0.9
0.95
R/F (-)

Fig. 6

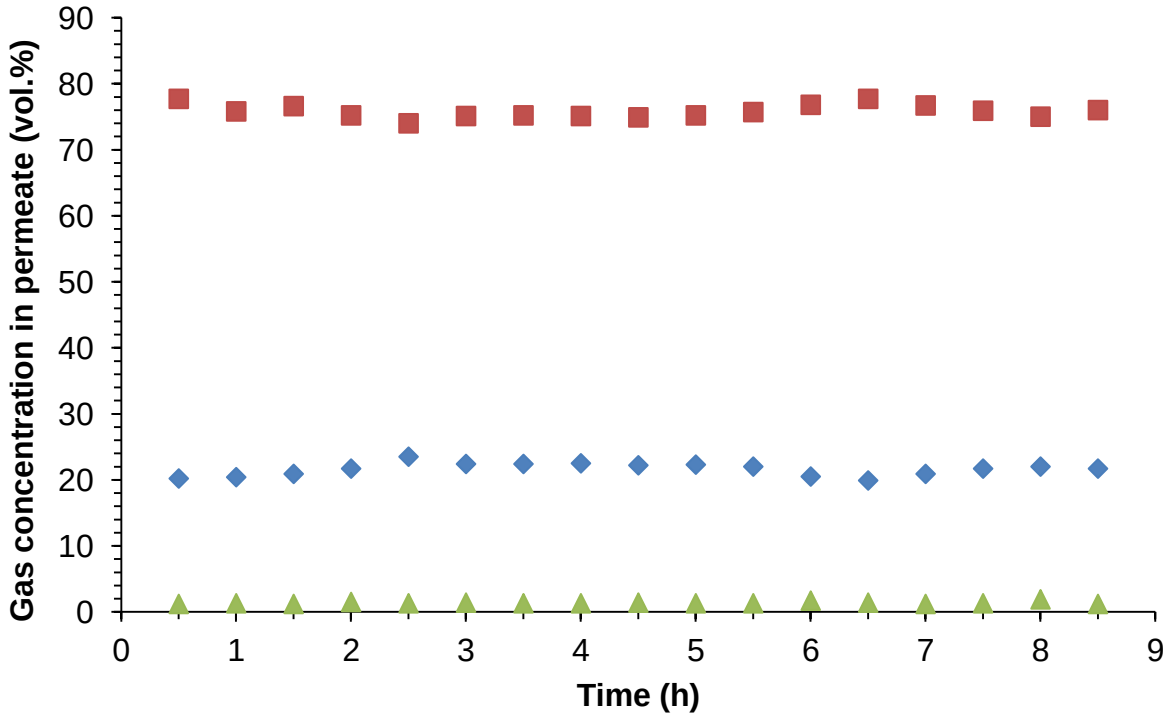
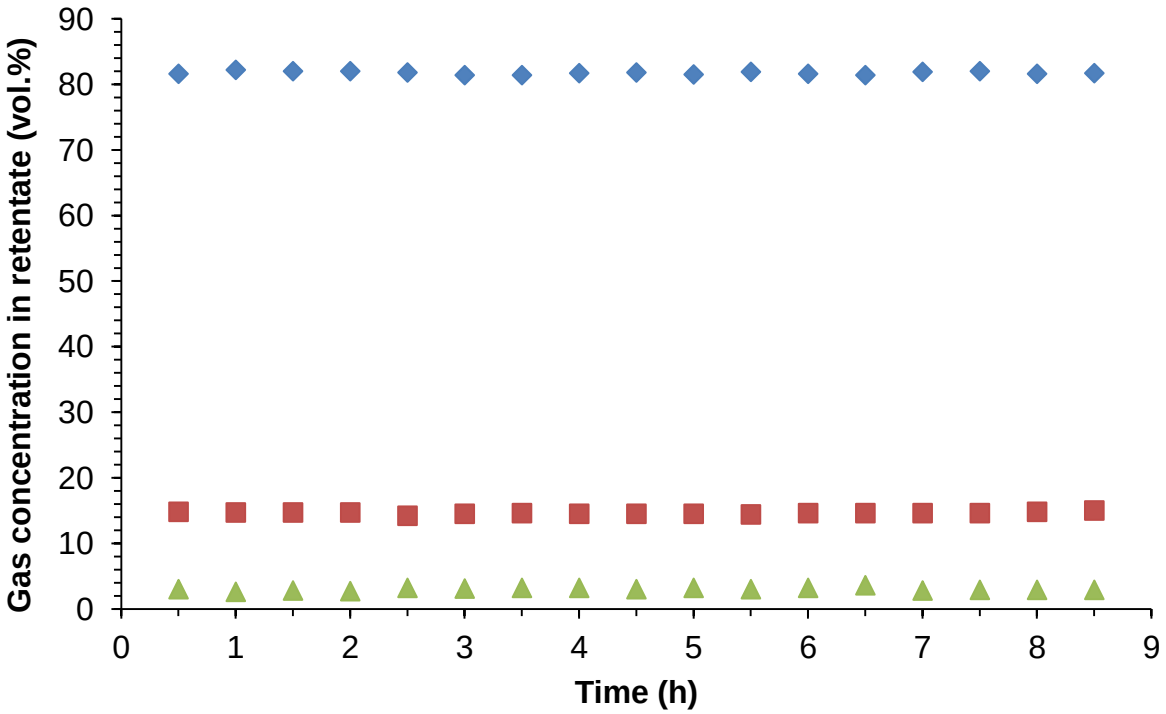

Gas concentration in permeate (vol.%)
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
9
Time (h)

Fig. 7


Gas concentration in retentate (vol.%)
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
9
Time (h)

(Word count: 5488)

Evaluation of a membrane permeation system for biogas upgrading using model and real gaseous mixtures: The effect of operating conditions on separation behaviour, methane recovery and process stability

Nándor Nemestóthy[1], Péter Bakonyi[1,*], Eszter Szentgyörgyi[1], Gopalakrishnan Kumar[2], Dinh Duc Nguyen[3], Soon Woong Chang[3], Sang-Hyoun Kim[2], Katalin Bélafi-Bakó[1]

[1]Research Institute of Bioengineering, Membrane Technology and Energetics, University of Pannonia, Egyetem u. 10, 8200 Veszprém, Hungary

[2]School of Civil and Environmental Engineering, Yonsei University, Seoul 38722, Republic of Korea

[3]Department of Environmental Energy Engineering, Kyonggi University, Suwon 16227, Republic of Korea

[*]Corresponding Author: Péter Bakonyi
Tel: +36 88 624385
Fax: +36 88 624292
E-mail: bakonyip@almos.uni-pannon.hu

Abstract

In this paper, the enrichment of methane by membrane technology was studied by employing (i) a model as well as (ii) a real biogas mixture produced on a laboratory-scale. Thereafter, the endurance of the process was tested at an existing biogas plant. The commercial gas separation module under investigation contained hollow fiber membranes with a polyimide selective layer. During the measurements, the effect of critical factors (including the permeate-to-feed pressure ratio and the splitting factor) was sought in terms of the (i) CH_4 content on the retentate-side and (ii) CH_4 recovery, which are important measures of biogas upgrading efficiency. The results indicated that a retentate with 93.8 vol.% of CH_4 – almost biomethane (>95 vol.% of CH_4) quality – could be obtained using the model gas (consisting of 80 vol.% of CH_4 and 20 vol.% of CO_2) along with 77.4 % CH_4 recovery in the single-stage permeation system. However, in the case of the real biogas mixture, ascribed primarily to inappropriate N_2/CH_4 separation, the peak methane concentration noted was only 80.7 vol.% with a corresponding 76 % CH_4 recovery. Besides, longer-term experiments revealed the adequate time-stability of membrane purification, suggesting such a process is feasible under industrial conditions for the improvement of biogas quality.

Keywords: biogas; biomethane; gas separation; membrane; polyimide; renewable energy

1. Introduction

Biogas is a mixture generated from organic matter via the process known as anaerobic digestion (Patinvoh et al., 2017; Pavi et al., 2017). Basically, it consists of methane, carbon dioxide and other (trace) compounds such as N_2, H_2S, water vapour, etc. (Weiland, 2010). Given its valuable CH_4 content, it has been widely applied to replace fossil fuels (such as natural gas) and contribute to sustainable energy, i.e. heat and electricity production (Ge et al., 2016). Though it can be utilized after partial purification, i.e. in Combined Heat and Power (CHP) systems, upgrading to biomethane is also an option. In this latter case, the sufficient separation of impurities is required, making the subsequent use of biomethane possible (i) in the transportation sector as a vehicle fuel or alternatively, (ii) it may be fed into the natural gas grid once quality requirements are met (Chen et al., 2015; Makaruk et al., 2010).

Biogas cleaning can rely on a range of physical, chemical and biological techniques that include, but are not limited to, (i) condensation, (ii) absorption based on components such as amines, ionic liquids (Albo et al., 2010), (iii) pressure swing adsorption (PSA), (iv) bio-scrubbing, i.e. for hydrogen sulfide elimination, and (v) membrane separation (Bauer et al., 2013; Ryckebosch et al., 2011). This latest option employing membrane contactors and polymerized membranes as permselective barriers has gained remarkable attention in recent years (Albo et al., 2014; Albo and Irabien, 2012). The several reasons behind are portability, relatively simple scalability, sufficient selectivity and stability of modules, advantageous energy requirements, etc. (Basu et al., 2010; Niesner et al., 2013). Although membrane gas separation is regarded as a mature technology and various modules are available on the market supplied by several companies, most of them were not originally intended for biogas-separation purposes but rather to process other gaseous mixtures, i.e. natural gas (Makaruk

et al., 2010). Thus, once such membrane has been adopted for biogas upgrading, however, careful assessment of their separation behaviour as well as optimization of operating conditions should be carried out, i.e. due to the different compositions of gas streams handled, to be able to meet biomethane specifications.

So far, various “membrane-powered” applications have been developed and thoroughly evaluated in terms of biogas enrichment, most of which are designed from polymeric membranes, i.e. cellulose acetate (CA), polydimethylsiloxane (PDMS), polysulfone (PSf) and polyimide (PI) (Scholz et al., 2013). A contemporary membrane system, in order to provide biomethane as a substitute for natural gas, should be capable of providing at least 95 % CH_4 purity with 90 % CH_4 recovery (Brunetti et al., 2015). Typically, the raw biogas that is subjected to purification contains approximately 50-70 % methane, 30-50 % carbon dioxide, lower quantities of nitrogen and water, and trace amounts of substances such as H_2S, depending on its source, e.g. a farm, sewage sludge digester, landfill, etc. (Rasi et al., 2007, 2011). In general, the performance of a given membrane system that deals with such gaseous streams will strongly depend on the operating conditions, namely the (i) pressure gradient across the membrane module (assisting the driving force), (ii) retentate (R) to feed (F) flow ratio (R/F) known as the splitting factor, (iii) separation temperature, and (iv) feed-gas composition, etc., which play a major role (Bakonyi et al., 2013ab).

Over the preceding years, our group has been conducting research into gaseous biofuels (hydrogen and methane) production as well as their subsequent separation. As a result, membrane bioreactors (MBR), as integrated approaches, have been designed (Bakonyi et al., 2017; Szentgyörgyi et al., 2010). Besides, ex-situ tests with regard to the evaluation of gas upgrading were performed as well (Bakonyi et al., 2013b). In the light of preliminary experiments, hollow fiber membranes (HFMs) made of PI are shown as applicable candidates

in terms of gas upgrading (Bakonyi et al., 2013b; Szentgyörgyi et al., 2010). Though previous information concerning biogas purification using certain PI membranes is available in the literature (Harasimowicz et al., 2007), an in-depth examination of the particular one employed in this study, to the best of our knowledge, has not been yet reported. Hence, in this work, the thorough evaluation of a commercialized membrane made of PI – a polymer with the potential to be utilized in CH_4/CO_2 separation (Baker and Low, 2014) – was aimed to study. The main scope of investigation was laid down to reveal the operating circumstances under which biomethane may be produced. Over the course of the assessment, model and real biogas mixtures were applied to determine how the composition affects the efficiency of purification. Afterwards, the time-stability of the gas permeation process was analysed over a series of longer-term experiments to obtain information concerning its applicability with regard to possible industrial implementation. To the best of our knowledge, such experimental results are not found in the literature for this PI membrane module and hence, this work is believed to exhibit added value and contribute to the development of anaerobic digestion technology.

2. Experimental setup

Biogas purification measurements were performed on a membrane module (UBE-CO5, Ube Industries, Ltd.) designed for natural gas separation. It contains composite hollow fibers membranes composed of a PI selective layer. Since a number of module features, i.e. the active surface area and thickness of the membrane are unknown, the gas permeability, measured in the recognised non-SI unit of Barrer, cannot be calculated to characterise the separation process. Therefore, an experimental, pressure-normalized volumetric gas flow rate is

reported according to **Eq. 2**. The module was installed into a high-pressure gas separation membrane system, referred to as GSMS (**Fig. 1**). The schematic drawing of the GSMS and its most essential technical details can be found in our earlier paper (Bakonyi et al., 2013b). The permeate and retentate were quantified by digital mass flow meters (Bronkhorst EL-FLOW® Select), which had undergone preliminary calibration. To obtain the exact flow rate of mixtures throughout the separation process, a correction factor was provided by Fluidat® (https://www.fluidat.com, Bronkhorst®). This took into account the exact composition of the permeate and retentate streams in terms of CH_4, CO_2 and N_2 as determined according to Section 3.

The gas separation experiments were carried out at a temperature of 30 ^{o}C unless otherwise stated, first by using a binary (model) mixture composed of 80 vol.% methane and 20 vol.% carbon dioxide (SIAD Hungary Kft., Hungary) (**Table 1**). Afterwards, real biogas – from a continuously operated anaerobic membrane bioreactor system – as documented by Szentgyörgyi et al. (2010) – was collected over a period of time, compressed into a gas cylinder and subsequently tested. Recently, together with our industrial partner, work has commenced on the valorization of landfill-deposited organic waste fractions, i.e. to generate biogas. As a part of that line of research, the assessment of methane purification by membrane technologies is a distinct goal. In accordance with a summary in the paper of Brunetti et al. (2015), the nitrogen content in biogas can vary considerably (1-17 vol.%). Hence, to simulate realistic conditions and typical compositions of landfill-derived biogas, enrichment of the real gaseous mixture (pressurized in the external tank, as noted above) by N_2 was conducted. As a result, the final composition was as follows: 70 vol.% CH_4, 19.8 vol.% CO_2, 9.2 vol.% N_2 and approx. 1 vol.% unidentified minor impurities.

As can be observed in **Tables 1 and 2**, the effect of the main membrane operating parameters – namely the (i) feed pressure to permate pressure ratio

(p^F/p^P) and (ii) the splitting factor (R/F) defined as the retentate flow rate relative to the total feed flow rate – on (i) methane concentration on the side of the retentate and (ii) methane recovery was sought (**Figs. 2-5**). All data presented in this work were obtained under steady-state permeation conditions, reflected by the properly stabilized volumetric flows and corresponding concentrations of gaseous substances, namely CH_4, CO_2 and N_2. In addition to the experimental runs listed in **Tables 1 and 2**, the membrane module was tested at a biogas plant located in Hungary in order to determine its behaviour in the longer-term and provide feedback concerning the stability of this time-dependent process, which could be useful as far as an envisaged industrial application is concerned. The respective permeation conditions are described in **Table 3**. Mass balance calculations, that took into account volumetric flow rates and respective concentrations of gases, thoroughly verified the reliability of such measurements. This indicated that the entire feed could only be extracted either as the retentate or permeate after separation had occurred. Repetitions (i.e. duplicates) under particular experimental settings were carried out occasionally, resulting in relative deviations < 5 %.

3. Analytical methods

Gas samples taken from the feed, permeate and retentate were analyzed by gas chromatography. On the one hand, the concentrations of CH_4 and N_2 could be determined from a Gow-Mac Series 600 gas chromatograph equipped with a molecular sieve packed column (filled with zeolite), a thermal conductivity detector (TCD), and He as a carrier gas. On the other hand, the concentration of CO_2 was analyzed by a Hewlett Packard HP 5890 Series II gas chromatograph equipped with a capillary column (GS-CarbonPLOT, Agilent Technologies), a TCD and N_2 as a carrier gas.

4. Calculations

CH_4 recovery ($Y_{methane}$) was defined (in the unit of %) according to **Eq. 1**:

$$Y_{methane} = 100\ \frac{V_R\, C^R_{methane}}{V_F\, C^F_{methane}} \qquad (1)$$

where V_R and V_F are the total volumetric flow rates of the retentate and feed ($dm^3\ min^{-1}$ at standard temperature (273 K) and pressure (1 bar) (STP)), respectively; while $C^R_{methane}$ and $C^F_{methane}$ stand for the CH_4 concentrations (vol.%) in these fractions, respectively (**Tables 1-3**).

The experimental, pressure-normalized volumetric gas flow rate (J_j) of a given component (*j)* in the mixture for the PI membrane module was computed (in the unit of $dm^3\ min^{-1}\ bar^{-1}$ at STP), as follows (**Eq. 2**):

$$J_j = \frac{V_P C^P_j}{\Delta p_{j,mean}} \qquad (2)$$

where V_P is the total volumetric flow rate of the permeate ($dm^3\ min^{-1}$ at STP), C^P_j is the actual (measured) concentration of component (*j*) in the permeate (vol.%), and $\Delta p_{j,mean}$ (in the unit of bar) is the mean pressure gradient across the membrane capillaries (Asadi et al., 2016) or, in other words, the partial driving force of component (*j*), according to **Eq. 3**.

$$\Delta p_{j,mean} = \Delta p^{lumen}_{j,mean} - \Delta p^{shell}_{j,mean} \qquad (3)$$

where $\Delta p_{j,mean}^{lumen}$ and $\Delta p_{j,mean}^{shell}$ are the average partial pressures for component (*j*) on the lumen-side (where the gas was fed) and the shell-side (where the permeate was collected), respectively according to Asadi et al. (2016), assuming in the calculation that the membrane permeate stream was under non-well-mixed conditions.

The permselectivity (α) for a certain gas pair was defined by **Eq. 4**.

$$\alpha = \frac{J_i}{J_j} \tag{4}$$

where J_i and J_j are the experimental, pressure-normalized volumetric gas flow rates of the rapidly and the slowly permeating compounds, (*i)* and (*j)*, respectively ($J_i > J_j$). In this work, the permselectivities for CO_2 and CH_4, as major constituents of biogas that need to be separated, were computed (**Tables 1-3**).

5. Methane enrichment and recovery from binary (model) and real biogas mixtures

In essence, the gas separation applying non-porous, polymeric materials e.g. in the case of UBE-CO5 requires the partial pressure difference of substances across the membrane (Mulder, 1996), where the rapidly permeating compound is enriched in the permeate, meanwhile, the slower (less-permeable) one is concentrated in the retentate. Accordingly, on the grounds of carbon dioxide enrichment on the permeate-side (**Tables 1 and 2**), it can be concluded that the membrane used in this investigation is CO_2-selective. This is primarily

attributed to the properties of PI, which act as the selective layer of composite hollow fibers membranes found in the module. This glassy polymer can provide a sufficient degree of CO_2/CH_4 selectivity given its high permeability of CO_2, which can be even an order of magnitude larger than that of CH_4 (Harasimowicz et al., 2007). The fact that the PI membrane is CH_4-rejective (**Tables 1 and 2**) leads to increased methane content in the retentate under upstream-side pressure conditions. This is quite advantageous, especially when the (i) upgraded biogas, namely biomethane, is to be injected into the distribution pipeline network (Brunetti et al., 2015) or (ii) when a sufficient level of biogas purification is not achieved in a single-stage, requiring further steps by means of additional processing to reach the defined gas (biomethane) quality.

With both the binary (model) as well as real biogas mixtures employed in this work, the achievable concentration of methane in the retentate seemed to be positively influenced by the greater difference between p^F and p^P, which made a particular contribution to the actual driving force (**Eq. 4**). This is reflected in **Figs. 2 and 4**, where the relationship between p^F/p^P and the CH_4 concentration on the retentate-side as well as the CO_2/CH_4 permselectivity can be regarded as directly proportional. In addition, the so-called splitting factor (R/F) had also been proven as a variable that exhibits a substantial impact on the performance of gas separation (Bakonyi et al., 2013b; Harasimowicz et al., 2007). Based on **Figs. 3 and 5**, regardless of the gas actually fed into the module, the lower R/F range should be preferred to attain a more significant degree of enrichment of methane in the retentate and maintain a larger permselectivity of CO_2/CH_4. This observation agrees well with the features generally described concerning the technique of gas separation by membranes (Baker, 2000). Overall, by comparing **Fig. 2** with **Fig. 4** and **Fig. 3** with **Fig. 5**, the results demonstrate that the composition of the gas used, either in terms of the model or real biogas, did not remarkably change the profile of response given by the membrane as a function

of various operating conditions, namely p^F/p^P and R/F. Consequently, the conclusion can be drawn that the process ought to be conducted by ensuring a larger driving force along with a smaller splitting factor to enhance the percentage of methane in the retentate. From the viewpoint of peak methane concentrations on the retentate side, it should be pointed out that the performance of the module (under comparable test conditions: p^F/p^P = 2.42-2.65, R/F = 0.66) was less attractive attributed to the higher degree of complexity, lower initial CH_4 content, etc. of real biogas (**Tables 1 and 2**).

As a matter of fact, in terms of the model gas, the highest enrichment of methane (93.8 vol.%) was accomplished with a corresponding recovery ($Y_{methane}$, Eq. 1) of 77.4 % (**Table 1**). In the case of real biogas, however, the best recorded methane concentration was 80.7 vol.% linked to 76 % of $Y_{methane}$ (**Table 2)**. Hence, these results indicate that a retentate of almost biomethane quality (93.8 vs. 95 vol.%) could be delivered in the case of the model gas mixture. Therefore, it can be presumed that following slight modifications of the process parameters, i.e. raising the driving force and/or lowering the splitting factor, the target value of 95 vol.% could be realistic. On the contrary, further study is required to achieve a similar degree of success with real biogas. As can be inferred from **Table 2**, the membrane was unable to efficiently deal with the substantial N_2 content of the feed (**Table 2**), making this compound of major concern. To understand why only marginal N_2/CH_4 separation could be realised, it should be kept in mind that the permselectivity is dependent on particular factors such as (i) diffusivity and (ii) solubility of the permeating compounds in the polymer material (Freeman, 1999). The variation in the former term contributes to the so-called mobility selectivity, while that of the latter parameter influences the commonly named sorption selectivity. Unfortunately, in many cases these two characteristics are opposed to each other when working with mixtures comprised of nitrogen as well as methane. Therefore, no effective separation of these two gases can be

accomplished (Lokhandwala et al., 2010). Consequently, the elimination of N_2 from the biogas stream is an objective of further research where membranes possessing better characteristics are developed. Moreover, provided that the overall technology undergoes careful optimization by reconsidering the number of purification stages and the possible application of cascades (Baker and Lokhandwala, 2008; Lokhandwala et al., 2010), additional benefits that enhance the process can be expected. For comparison of membrane performance with other materials/modules, data summarized in review articles such as Basu et al. (2010) and Scholz et al. (2013) can be referenced. Among commercialized polymer materials, permselectivity values for CO_2/CH_4 span 1.4-42.8 and hence, the respective values attained with the commercialized PI module in this work (**Tables 1-3**) fit well into this range.

6. Evaluation of the stability of the biogas upgrading process over longer-term measurements – implications of application in the field

Apart from the issues elaborated in Section 5, e.g. the N_2 content of the biogas, the time-stability of the process is also a crucial aspect that must be considered. In other words, to acquire a reasonable comprehension of the relevance of the membrane module in terms of an actual application in the field that attempts to improve the quality of the biogas, an adequate degree of process durability should be acquired. Therefore, performance of the PI membrane module was further analyzed over the longer-term by running permeation experiments with real biogas (generated by an anaerobic digestion plant located in the countryside of Hungary). Furthermore, implementation of the whole test rig in an industrial setting is accompanied with the advantage of a continuous gas supply and the availability of sufficient feed volumes, which would otherwise limit the exploitation of permeation capacities over a more extensive period of time.

As can be seen in **Table 3**, the biogas generated in the plant could be characterised as a clearly distinguishable quality compared to the one applied during laboratory tests (**Table 2**). This might be attributed to differences in the attributes of biotic and abiotic processes, i.e. in terms of the (i) composition of underlying microbial consortia, (ii) source and complexity of the feedstock to be utilized, (iii) operational settings of the fermenters, etc. During the permeation stability tests, separation conditions were constants (**Table 3**) for almost 9 hours during the experiment (**Figs. 6 and 7**). It should be noted that besides the clearly identifiable components, namely CH_4, CO_2 and N_2, the raw biogas, on average, contains a comparable amount of trace substances to the biogas evolved in the laboratory-scale bioreactor (**Table 2**). However, the similarities regarding the distribution (partial concentrations) of these components remain unknown and such an analysis could be a subject of a future study to elaborate on such related effects. Actually, based on the already published experiences in the existing literature, pro-longed operation of the biogas-upgrading membrane permeation system can require the pretreatment of raw fermenter off-gas to get rid of particular secondary components (i.e. ammonia, hydrogen sulfide and water vapor that may damage the membrane material over time) by drying, condesnation and desulphurization before conveying the biogas to the membrane purification technology (Miltner et al., 2010, 2009). Such an action can help to extend membrane lifetime and preserve its performance (Stern et al., 1998)

The time profiles of the qualities of the permeate and retentate are depicted in **Figs. 6 and 7**, respectively. It should be inferred that only slight changes in the compositions were recorded and, therefore, the purification performance could be considered quite stable throughout the test period. Similarly to the results of the other gas mixtures discussed above, a considerable degree of CH_4/CO_2 separation was achieved. However, the removal of nitrogen

gas seemed to be challenging, in accordance with statements made in Section 5. Under the circumstances mentioned in **Table 3**, a reasonable and steady level of CH_4 recovery ($Y_{methane}$ > 82 %) was accomplished with a corresponding methane concentration of 81-82 vol.% in the retentate. Overall, these research outcomes imply that the gas permeation process was able to function properly over an extended period of time without considerable variation in the separation efficiency. Thus, it can be deduced that the PI membrane employed may be a worthy candidate for further investigation and possible installation at biogas plants. However, the experiments conducted point to the fact that this particular module should be applied as one component of a multi-stage (sequential) membrane system, enriching the CH_4 content of the biogas to the desired level of biomethane quality (Makaruk et al., 2010). Such a system is supposed to manage the efficient separation of N_2 from CH_4 and attain large $Y_{methane}$ values to reduce losses in the permeate (increase product recovery) (Rautenbach and Welsch, 1993) and consequently, minimise the environmental impacts associated with the emission of methane. Many times, however, high methane purities may be attained only with compromises in methane recovery, when some methane is lost in the permeate (Sun et al., 2015). Under these conditions, for instance, the permeate with methane content can be recycled and burnt in gas engines at the biogas plant (Miltner et al., 2009).

7. Conclusions

In this paper, a polyimide gas separation membrane was investigated in terms of biogas purification. The results showed that the feed-to-permeate-pressure ratio as well as the splitting factor had a notable effect on the performance of the process. In fact, under actual operating circumstances, the

module provided biogas with methane content (93.8 vol.% along with 77.4 % recovery) via efficient removal of CO_2 in the case of the binary, model mixture. The CO_2/CH_4 permselectivity values were dependent on the experimental conditions and accordingly, could be as high as 11-12 in some cases. However, primarily due to the insufficient CH_4/N_2 separation capacity of the membrane, it was not possible to upgrade the real biogas in the same manner and additional research into the subject is encouraged. Nevertheless, tests revealed an adequate level of endurance of the membrane permeation process over the longer-term, leading to the conclusion that the process, based on the module that contains PI hollow fibers, is worthy of further elaboration under industrial conditions in the field. The appropriate design of the process, in particular the deployment of a membrane cascade purification system, could overcome the existing bottleneck observed with the single-stage application to deliver biomethane from biogas.

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Figure legends

Fig. 1 – Image of the gas separation membrane system (left-hand side) with the PI membrane module installed (right-hand side).

Fig. 2 – The effect of p_F/p_p on the methane concentration on the retentate side (diamond) and CO_2/CH_4 permselectivity (square) using the model biogas.

Fig. 3 – The effect of the splitting factor (R/F) on the methane concentration on the retentate side (diamond) and CO_2/CH_4 permselectivity (square) using the model biogas.

Fig. 4 – The effect of p_F/p_p on the methane concentration on the retentate side (diamond) and CO_2/CH_4 permselectivity (square) using the real biogas.

Fig. 5 – The effect of the splitting factor (R/F) on the methane concentration of the retentate side (diamond) and CO_2/CH_4 permselectivity (square) using the real biogas.

Fig. 6 – The time dependency of the composition of the permeate under the conditions listed in Table 3. Square: carbon dioxide; Diamond: methane; Triangle: nitrogen.

Fig. 7 – The time dependency of the composition of the retentate under the conditions listed in Table 3. Square: carbon dioxide; Diamond: methane; Triangle: nitrogen.

Table 1 – Experimental conditions and results using the binary gas mixture (80 vol.% CH_4, 20 vol.% CO_2)

p^F (bar)	p^F/p^P (-)	R/F (-)	Gas concentration (vol.%)				J (dm^3 min^{-1} bar^{-1} at STP)		CO_2/CH_4 Permselectivity (-)	$Y_{methane}$ (%)
			Permeate		Retentate		CH_4	CO_2		
			CH_4	CO_2	CH_4	CO_2				
7.0	1.78	0.89	64.9	35.1	81.9	18.1	5.53	15.43	2.79	90.8
11.8	2.33	0.65	62.6	37.4	89.3	10.7	2.81	17.31	6.17	72.7
12.3	2.42	0.66	53.2	46.8	93.8	6.2	4.85	34.08	7.03	77.4
13.5	1.76	0.73	55.7	44.3	89.1	10.9	9.00	53.54	5.95	81.0
13.6	1.77	0.73	69.5	30.5	83.9	16.1	1.96	10.35	5.27	76.4
14.5	1.40	0.81	74.6	25.4	81.3	18.7	2.11	7.64	3.63	81.9

Table 2 – Experimental conditions and results using the biogas mixture containing 70 vol.% CH_4, 19.8 vol.% CO_2, 9.2 vol.% N_2 and unknown trace substances to balance.

p^F (bar)	p^F/p^p (-)	R/F (-)	Gas concentration (vol.%)						J (dm^3 min^{-1} bar^{-1} at STP)		CO_2/CH_4 Permselectivity (-)	$Y_{methane}$ (%)
			Permeate			Retentate			CH_4	CO_2		
			CH_4	CO_2	N_2	CH_4	CO_2	N_2				
8.5	1.36	0.78	69.4	28.5	2.2	72.3	17.2	10.1	8.74	33.92	3.88	80.9
7.7	1.43	0.79	69.2	19.9	10.0	70.2	19.7	9.5	7.66	7.84	1.04	79.1
4.3	2.65	0.66	49.3	42.8	6.9	80.7	7.5	11.4	5.26	46.58	8.85	76.0
6.4	1.76	0.93	58.5	31.7	8.8	70.8	18.3	10.2	2.52	8.89	3.53	94.3

Table 3 – Average experimental conditions for the assessment of process stability during longer-term biogas (57.4 vol.% CH_4, 39 vol.% CO_2, 2.5 vol.% N_2 and unknown trace substances to balance) permeation conducted at 50 ^{o}C.

p^F (bar)	p^F/p^p (-)	R/F (-)	Gas concentration (vol.%)						J (dm^3 min^{-1} bar^{-1} at STP)		CO_2/CH_4 Permselectivity (-)	$Y_{methane}$ (%)
			Permeate			Retentate			CH_4	CO_2		
			CH_4	CO_2	N_2	CH_4	CO_2	N_2				
10.8	5.48	0.58	21.6	75.8	1.4	81.7	14.6	2.9	1.07	12.55	11.77	82.9

Fig. 1

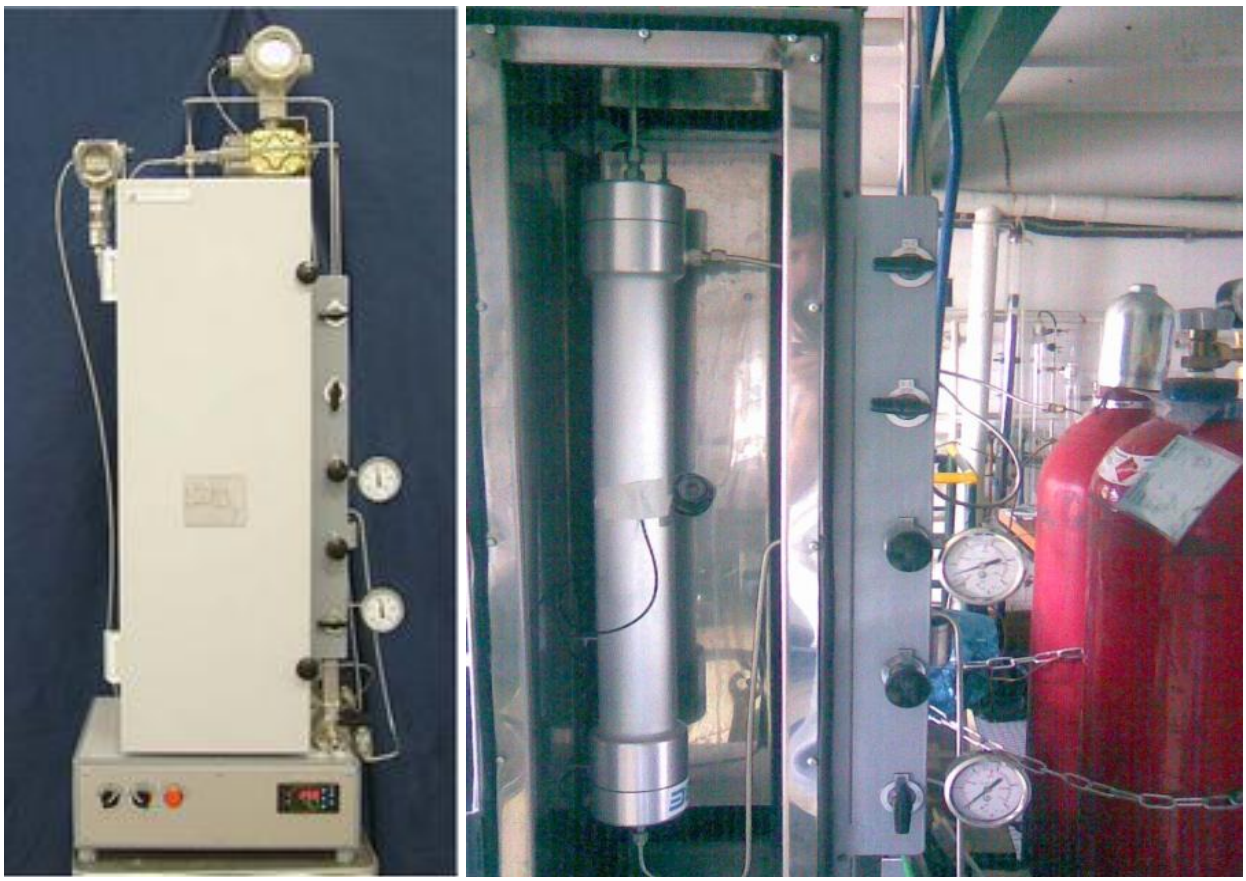
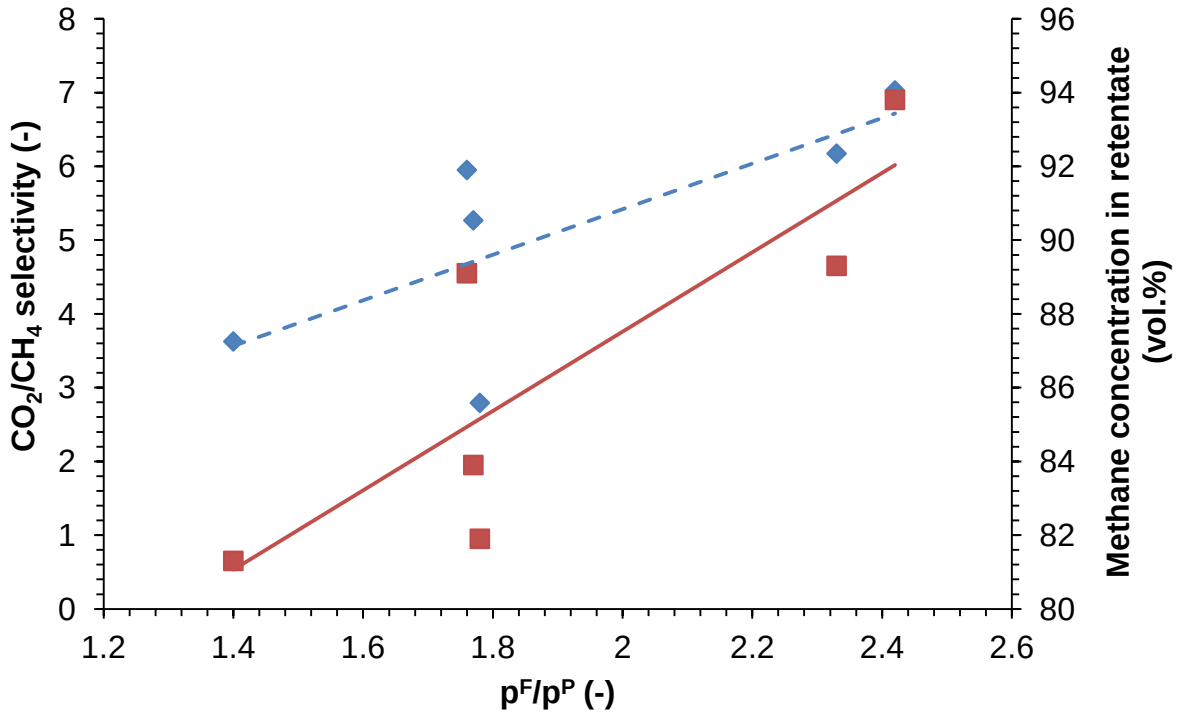


Fig. 2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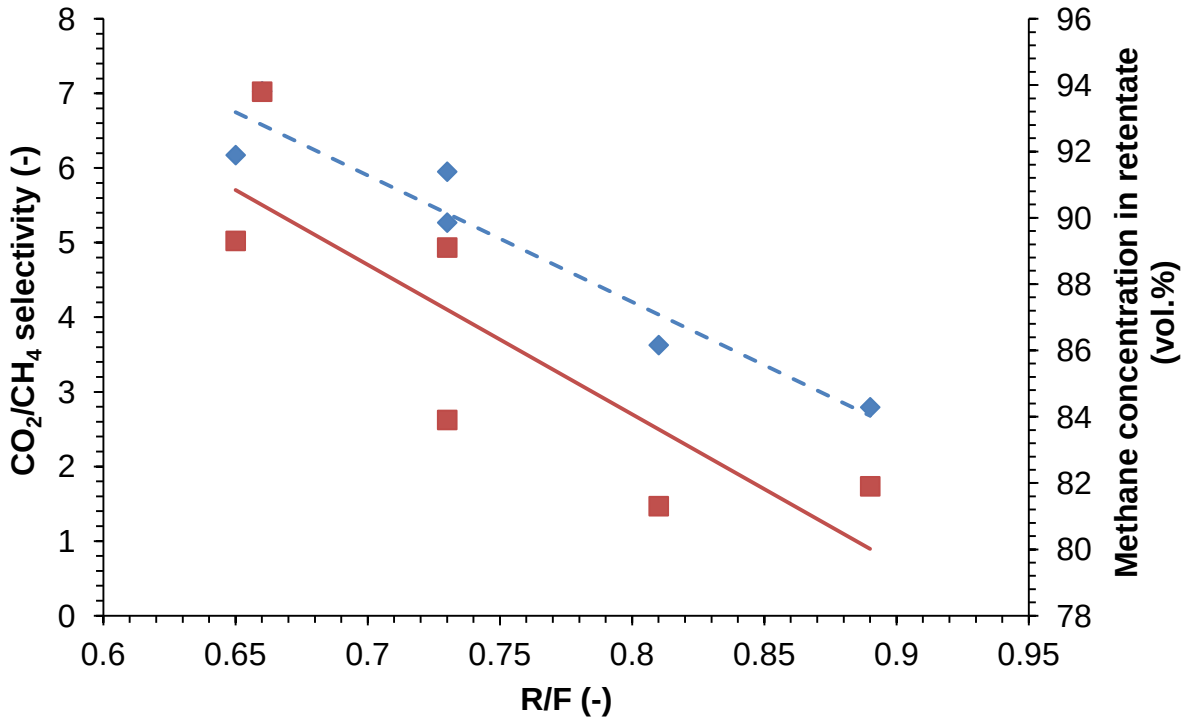
1.2
1.4
1.6
1.8
2
2.2
2.4
2.6
CO_2/CH_4 selectivity (-)
Methane concentration in retentate (vol.%)
p^F/p^P (-)

Fig. 3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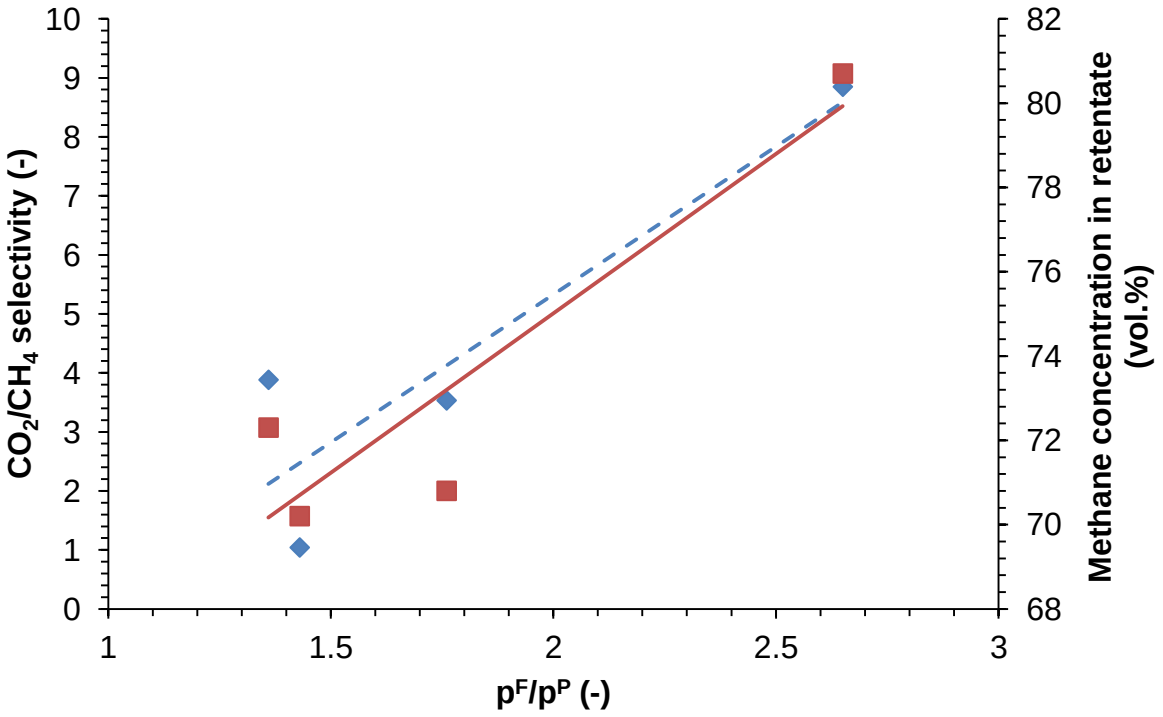
R/F (-)
CO2/CH4 selectivity (-)
Methane concentration in retentate (vol.%)

Fig. 4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7
6
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3
2
1
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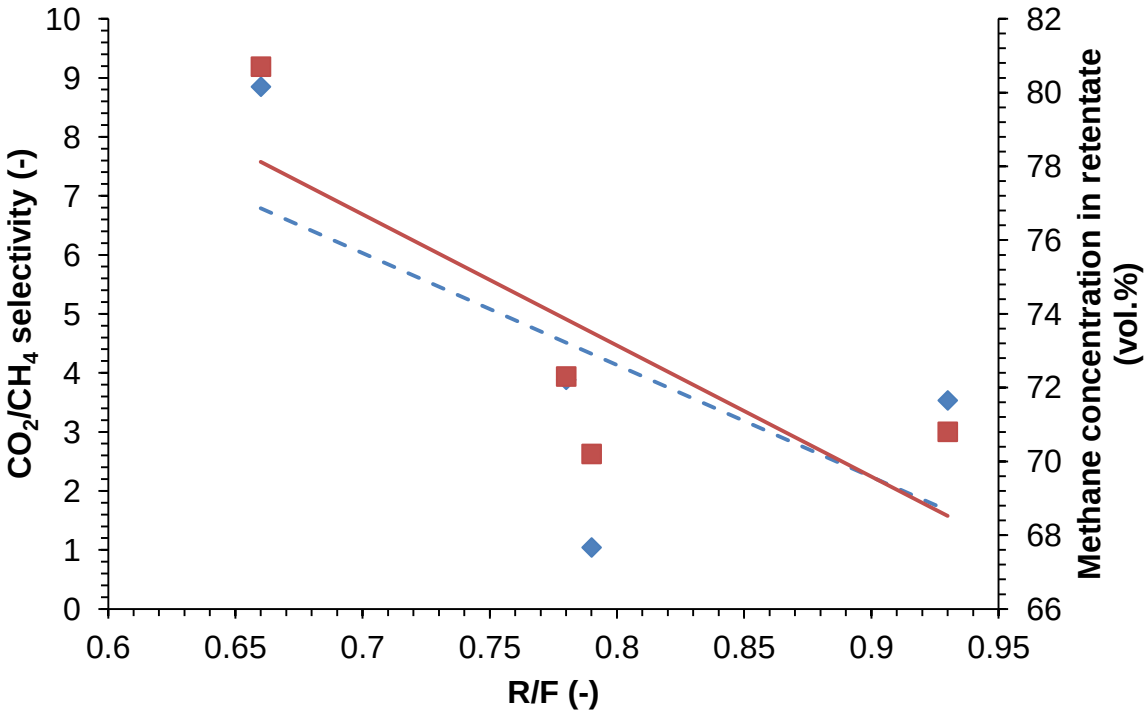
CO_2/CH_4 selectivity (-)
82
80
78
76
74
72
70
68
Methane concentration in retentate (vol.%)
1
1.5
2
2.5
3
p^F/p^P (-)

Fig. 5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0.65
0.7
0.75
0.8
0.85
0.9
0.95
R/F (-)
CO2/CH4 selectivity (-)
Methane concentration in retentate (vol.%)

Fig. 6

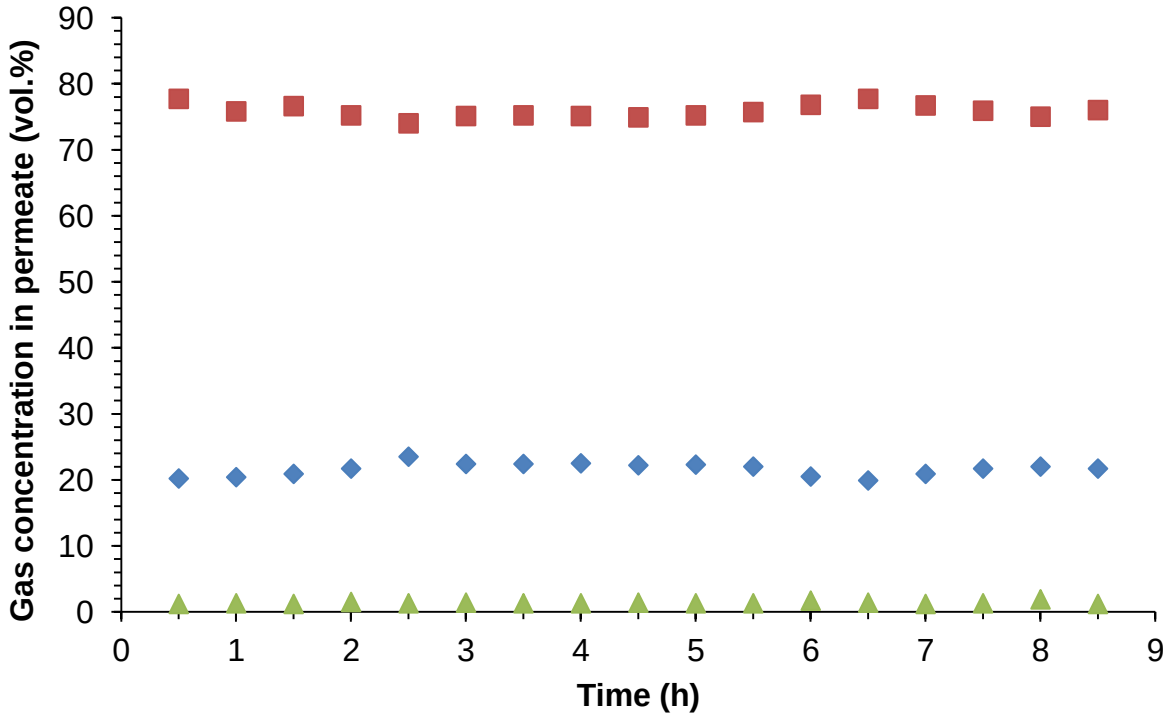
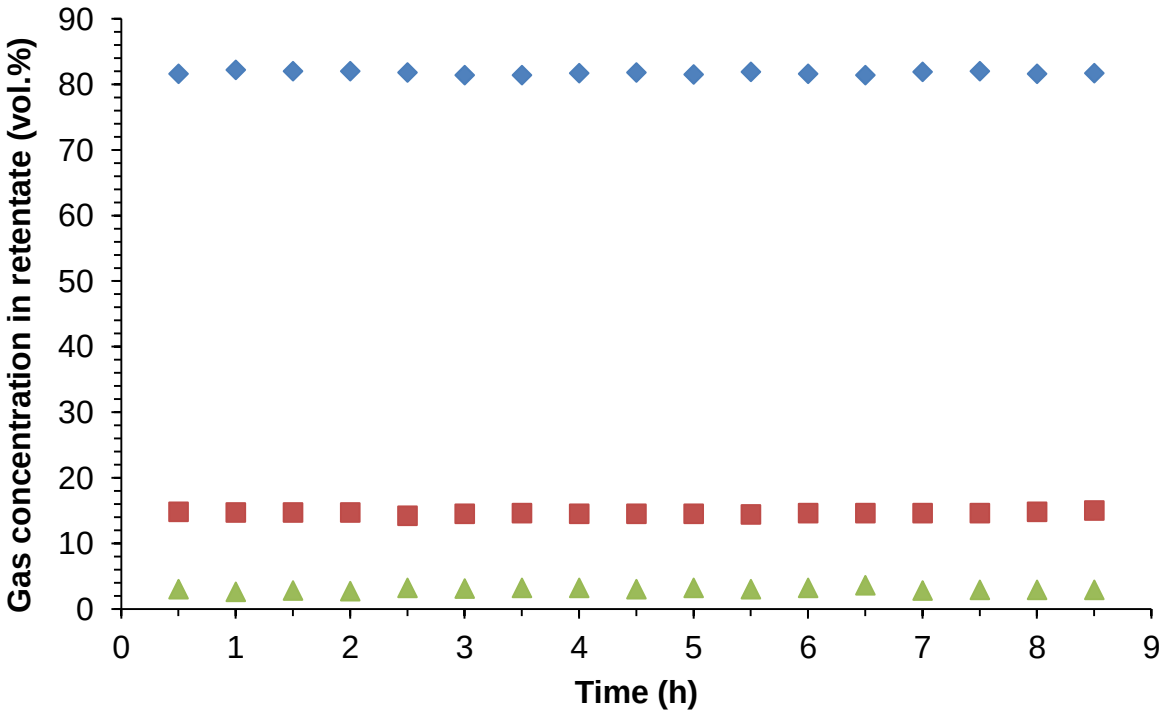

Gas concentration in permeate (vol.%)
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
9
Time (h)

Fig. 7


Gas concentration in retentate (vol.%)
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
9
Time (h)