

1 (Word count: 5488)

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

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6 Nándor Nemestóthy¹, Péter Bakonyi^{1,*}, Eszter Szentgyörgyi¹, Gopalakrishnan
7 Kumar², Dinh Duc Nguyen³, Soon Woong Chang³, Sang-Hyoun Kim², Katalin
8 Bélafi-Bakó¹

9
10 ¹Research Institute of Bioengineering, Membrane Technology and Energetics,
11 University of Pannonia, Egyetem u. 10, 8200 Veszprém, Hungary

12 ²School of Civil and Environmental Engineering, Yonsei University, Seoul 38722,
13 Republic of Korea

14 ³Department of Environmental Energy Engineering, Kyonggi University, Suwon
15 16227, Republic of Korea

16
17 *Corresponding Author: Péter Bakonyi

18 Tel: +36 88 624385

19 Fax: +36 88 624292

20 E-mail: bakonyip@almos.uni-pannon.hu

21

22 **Abstract**

23

24 In this paper, the enrichment of methane by membrane technology was
25 studied by employing (i) a model as well as (ii) a real biogas mixture produced on
26 a laboratory-scale. Thereafter, the endurance of the process was tested at an
27 existing biogas plant. The commercial gas separation module under investigation
28 contained hollow fiber membranes with a polyimide selective layer. During the
29 measurements, the effect of **critical** factors (including the permeate-to-feed
30 pressure ratio and the splitting factor) was sought in terms of the (i) CH₄ content
31 on the retentate-side and (ii) CH₄ recovery, **which are important measures of**
32 **biogas upgrading efficiency**. The results indicated that a retentate with 93.8 vol.%
33 of CH₄ – almost biomethane (>95 vol.% of CH₄) quality – could be obtained using
34 the model gas (consisting of 80 vol.% of CH₄ and 20 vol.% of CO₂) along with
35 77.4 % CH₄ recovery in the single-stage permeation system. However, in the
36 case of the real biogas mixture, ascribed primarily to inappropriate N₂/CH₄
37 separation, the peak methane concentration noted was only 80.7 vol.% with a
38 corresponding 76 % CH₄ recovery. Besides, longer-term experiments revealed
39 the adequate time-stability of membrane purification, suggesting such a process
40 is feasible under industrial conditions for the improvement of biogas quality.

41

42 **Keywords:** biogas; biomethane; gas separation; membrane; polyimide;
43 renewable energy

44

45 1. Introduction

46

47 Biogas is a mixture generated from organic matter via the process known
48 as anaerobic digestion (Patinvoh et al., 2017; Pavi et al., 2017). Basically, it
49 consists of methane, carbon dioxide and other (trace) compounds such as N₂,
50 H₂S, water vapour, etc. (Weiland, 2010). Given its valuable CH₄ content, it has
51 been widely applied to replace fossil fuels (such as natural gas) and contribute to
52 sustainable energy, i.e. heat and electricity production (Ge et al., 2016). Though
53 it can be utilized after partial purification, i.e. in Combined Heat and Power (CHP)
54 systems, upgrading to biomethane is also an option. In this latter case, the
55 sufficient separation of impurities is required, making the subsequent use of
56 biomethane possible (i) in the transportation sector as a vehicle fuel or
57 alternatively, (ii) it may be fed into the natural gas grid once quality requirements
58 are met (Chen et al., 2015; Makaruk et al., 2010).

59 Biogas cleaning can rely on a range of physical, chemical and biological
60 techniques that include, but are not limited to, (i) condensation, (ii) absorption
61 based on components such as amines, ionic liquids (Albo et al., 2010), (iii)
62 pressure swing adsorption (PSA), (iv) bio-scrubbing, i.e. for hydrogen sulfide
63 elimination, and (v) membrane separation (Bauer et al., 2013; Ryckebosch et al.,
64 2011). This latest option employing membrane contactors and polymerized
65 membranes as permselective barriers has gained remarkable attention in recent
66 years (Albo et al., 2014; Albo and Irabien, 2012). The several reasons behind are
67 portability, relatively simple scalability, sufficient selectivity and stability of
68 modules, advantageous energy requirements, etc. (Basu et al., 2010; Niesner et
69 al., 2013). Although membrane gas separation is regarded as a mature
70 technology and various modules are available on the market supplied by several
71 companies, most of them were not originally intended for biogas-separation
72 purposes but rather to process other gaseous mixtures, i.e. natural gas (Makaruk

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

78 So far, various “membrane-powered” applications have been developed
79 and thoroughly evaluated in terms of biogas enrichment, most of which are
80 designed from polymeric membranes, i.e. cellulose acetate (CA),
81 polydimethylsiloxane (PDMS), polysulfone (PSf) and polyimide (PI) (Scholz et al.,
82 2013). A contemporary membrane system, in order to provide biomethane as a
83 substitute for natural gas, should be capable of providing at least 95 % CH₄ purity
84 with 90 % CH₄ recovery (Brunetti et al., 2015). Typically, the raw biogas that is
85 subjected to purification contains approximately 50-70 % methane, 30-50 %
86 carbon dioxide, lower quantities of nitrogen and water, and trace amounts of
87 substances such as H₂S, depending on its source, e.g. a farm, sewage sludge
88 digester, landfill, etc. (Rasi et al., 2007, 2011). In general, the performance of a
89 given membrane system that deals with such gaseous streams will strongly
90 depend on the operating conditions, namely the (i) pressure gradient across the
91 membrane module (assisting the driving force), (ii) retentate (R) to feed (F) flow
92 ratio (R/F) known as the splitting factor, (iii) separation temperature, and (iv)
93 feed-gas composition, etc., which play a major role (Bakonyi et al., 2013ab).

94 Over the preceding years, our group has been conducting research into
95 gaseous biofuels (hydrogen and methane) production as well as their
96 subsequent separation. As a result, membrane bioreactors (MBR), as integrated
97 approaches, have been designed (Bakonyi et al., 2017; Szentgyörgyi et al.,
98 2010). Besides, ex-situ tests with regard to the evaluation of gas upgrading were
99 performed as well (Bakonyi et al., 2013b). In the light of preliminary experiments,
100 hollow fiber membranes (HFMs) made of PI are shown as applicable candidates

101 in terms of gas upgrading (Bakonyi et al., 2013b; Szentgyörgyi et al., 2010).
102 Though previous information concerning biogas purification using certain PI
103 membranes is available in the literature (Harasimowicz et al., 2007), an in-depth
104 examination of the particular one employed in this study, to the best of our
105 knowledge, has not been yet reported. Hence, in this work, the thorough
106 evaluation of a commercialized membrane made of PI – a polymer with the
107 potential to be utilized in CH₄/CO₂ separation (Baker and Low, 2014) – was
108 aimed to study. The main scope of investigation was laid down to reveal the
109 operating circumstances under which biomethane may be produced. Over the
110 course of the assessment, model and real biogas mixtures were applied to
111 determine how the composition affects the efficiency of purification. Afterwards,
112 the time-stability of the gas permeation process was analysed over a series of
113 longer-term experiments to obtain information concerning its applicability with
114 regard to possible industrial implementation. To the best of our knowledge, such
115 experimental results are not found in the literature for this PI membrane module
116 and hence, this work is believed to exhibit added value and contribute to the
117 development of anaerobic digestion technology.

118

119 2. Experimental setup

120

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

128 reported according to Eq. 2. The module was installed into a high-pressure gas
129 separation membrane system, referred to as GSMS (Fig. 1). The schematic
130 drawing of the GSMS and its most essential technical details can be found in our
131 earlier paper (Bakonyi et al., 2013b). The permeate and retentate were quantified
132 by digital mass flow meters (Bronkhorst EL-FLOW[®] Select), which had
133 undergone preliminary calibration. To obtain the exact flow rate of mixtures
134 throughout the separation process, a correction factor was provided by Fluidat[®]
135 (<https://www.fluidat.com>, Bronkhorst[®]). This took into account the exact
136 composition of the permeate and retentate streams in terms of CH₄, CO₂ and N₂
137 as determined according to Section 3.

138 The gas separation experiments were carried out at a temperature of 30 °C
139 unless otherwise stated, first by using a binary (model) mixture composed of 80
140 vol.% methane and 20 vol.% carbon dioxide (SIAD Hungary Kft., Hungary)
141 (Table 1). Afterwards, real biogas – from a continuously operated anaerobic
142 membrane bioreactor system – as documented by Szentgyörgyi et al. (2010) –
143 was collected over a period of time, compressed into a gas cylinder and
144 subsequently tested. Recently, together with our industrial partner, work has
145 commenced on the valorization of landfill-deposited organic waste fractions, i.e.
146 to generate biogas. As a part of that line of research, the assessment of methane
147 purification by membrane technologies is a distinct goal. In accordance with a
148 summary in the paper of Brunetti et al. (2015), the nitrogen content in biogas can
149 vary considerably (1-17 vol.%). Hence, to simulate realistic conditions and typical
150 compositions of landfill-derived biogas, enrichment of the real gaseous mixture
151 (pressurized in the external tank, as noted above) by N₂ was conducted. As a
152 result, the final composition was as follows: 70 vol.% CH₄, 19.8 vol.% CO₂, 9.2
153 vol.% N₂ and approx. 1 vol.% unidentified minor impurities.

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

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

173

174 **3. Analytical methods**

175

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

4. Calculations

CH₄ recovery (Y_{methane}) was defined (in the unit of %) according to Eq. 1:

$$Y_{\text{methane}} = 100 \frac{V_R C_{\text{methane}}^R}{V_F C_{\text{methane}}^F} \quad (1)$$

where V_R and V_F are the total volumetric flow rates of the retentate and feed ($\text{dm}^3 \text{min}^{-1}$ at standard temperature (273 K) and pressure (1 bar) (STP)), respectively; while C_{methane}^R and C_{methane}^F stand for the CH₄ 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 $\text{dm}^3 \text{min}^{-1} \text{bar}^{-1}$ at STP), as follows (Eq. 2):

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

where V_P is the total volumetric flow rate of the permeate ($\text{dm}^3 \text{min}^{-1}$ at STP), C_j^P 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.

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

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

212

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

214

$$215 \quad \alpha = \frac{J_i}{J_j} \quad (4)$$

216

217 where J_i and J_j are the **experimental, pressure-normalized volumetric gas flow**
218 **rates** of the rapidly and the slowly permeating compounds, (i) and (j), respectively
219 ($J_i > J_j$). In this work, the permselectivities for CO₂ and CH₄, as major
220 constituents of biogas that need to be separated, were computed (**Tables 1-3**).

221

222 **5. Methane enrichment and recovery from binary (model) and real** 223 **biogas mixtures**

224

225 In essence, the gas separation applying non-porous, polymeric materials
226 e.g. in the case of UBE-CO5 requires the partial pressure difference of
227 substances across the membrane (Mulder, 1996), where the rapidly permeating
228 compound is enriched in the permeate, meanwhile, the slower (less-permeable)
229 one is concentrated in the retentate. Accordingly, on the grounds of carbon
230 dioxide enrichment on the permeate-side (**Tables 1 and 2**), it can be concluded
231 that the membrane used in this investigation is CO₂-selective. This is primarily

232 attributed to the properties of PI, which act as the selective layer of composite
233 hollow fibers membranes found in the module. This glassy polymer can provide a
234 sufficient degree of CO₂/CH₄ selectivity given its high permeability of CO₂, which
235 can be even an order of magnitude larger than that of CH₄ (Harasimowicz et al.,
236 2007). The fact that the PI membrane is CH₄-rejective (**Tables 1 and 2**) leads to
237 increased methane content in the retentate under upstream-side pressure
238 conditions. This is quite advantageous, especially when the (i) upgraded biogas,
239 namely biomethane, is to be injected into the distribution pipeline network
240 (Brunetti et al., 2015) or (ii) when a sufficient level of biogas purification is not
241 achieved in a single-stage, requiring further steps by means of additional
242 processing to reach the defined gas (biomethane) quality.

243 With both the binary (model) as well as real biogas mixtures employed in
244 this work, the achievable concentration of methane in the retentate seemed to be
245 positively influenced by the greater difference between p^F and p^P , which made a
246 particular contribution to the actual driving force (**Eq. 4**). This is reflected in **Figs.**
247 **2 and 4**, where the relationship between p^F/p^P and the CH₄ concentration on the
248 retentate-side as well as the CO₂/CH₄ permselectivity can be regarded as directly
249 proportional. In addition, the so-called splitting factor (R/F) had also been proven
250 as a variable that exhibits a substantial impact on the performance of gas
251 separation (Bakonyi et al., 2013b; Harasimowicz et al., 2007). Based on **Figs. 3**
252 **and 5**, regardless of the gas actually fed into the module, the lower R/F range
253 should be preferred to attain a more significant degree of enrichment of methane
254 in the retentate and maintain a larger permselectivity of CO₂/CH₄. This
255 observation agrees well with the features generally described concerning the
256 technique of gas separation by membranes (Baker, 2000). Overall, by comparing
257 **Fig. 2** with **Fig. 4** and **Fig. 3** with **Fig. 5**, the results demonstrate that the
258 composition of the gas used, either in terms of the model or real biogas, did not
259 remarkably change the profile of response given by the membrane as a function

260 of various operating conditions, namely p^F/p^P and R/F. Consequently, the
261 conclusion can be drawn that the process ought to be conducted by ensuring a
262 larger driving force along with a smaller splitting factor to enhance the
263 percentage of methane in the retentate. From the viewpoint of peak methane
264 concentrations on the retentate side, it should be pointed out that the
265 performance of the module (under comparable test conditions: $p^F/p^P = 2.42-2.65$,
266 R/F = 0.66) was less attractive attributed to the higher degree of complexity,
267 lower initial CH₄ content, etc. of real biogas (**Tables 1 and 2**).

268 As a matter of fact, in terms of the model gas, the highest enrichment of
269 methane (93.8 vol.%) was accomplished with a corresponding recovery (Y_{methane} ,
270 Eq. 1) of 77.4 % (**Table 1**). In the case of real biogas, however, the best recorded
271 methane concentration was 80.7 vol.% linked to 76 % of Y_{methane} (**Table 2**).
272 Hence, these results indicate that a retentate of almost biomethane quality (93.8
273 vs. 95 vol.%) could be delivered in the case of the model gas mixture. Therefore,
274 it can be presumed that following slight modifications of the process parameters,
275 i.e. raising the driving force and/or lowering the splitting factor, the target value of
276 95 vol.% could be realistic. On the contrary, further study is required to achieve a
277 similar degree of success with real biogas. As can be inferred from **Table 2**, the
278 membrane was unable to efficiently deal with the substantial N₂ content of the
279 feed (**Table 2**), making this compound of major concern. To understand why only
280 marginal N₂/CH₄ separation could be realised, it should be kept in mind that the
281 permselectivity is dependent on particular factors such as (i) diffusivity and (ii)
282 solubility of the permeating compounds in the polymer material (Freeman, 1999).
283 The variation in the former term contributes to the so-called mobility selectivity,
284 while that of the latter parameter influences the commonly named sorption
285 selectivity. Unfortunately, in many cases these two characteristics are opposed to
286 each other when working with mixtures comprised of nitrogen as well as
287 methane. Therefore, no effective separation of these two gases can be

288 accomplished (Lokhandwala et al., 2010). Consequently, the elimination of N₂
289 from the biogas stream is an objective of further research where membranes
290 possessing better characteristics are developed. Moreover, provided that the
291 overall technology undergoes careful optimization by reconsidering the number
292 of purification stages and the possible application of cascades (Baker and
293 Lokhandwala, 2008; Lokhandwala et al., 2010), additional benefits that enhance
294 the process can be expected. For comparison of membrane performance with
295 other materials/modules, data summarized in review articles such as Basu et al.
296 (2010) and Scholz et al. (2013) can be referenced. Among commercialized
297 polymer materials, permselectivity values for CO₂/CH₄ span 1.4-42.8 and hence,
298 the respective values attained with the commercialized PI module in this work
299 (Tables 1-3) fit well into this range.

300

301 **6. Evaluation of the stability of the biogas upgrading process over** 302 **longer-term measurements – implications of application in the field**

303

304 Apart from the issues elaborated in Section 5, e.g. the N₂ content of the
305 biogas, the time-stability of the process is also a crucial aspect that must be
306 considered. In other words, to acquire a reasonable comprehension of the
307 relevance of the membrane module in terms of an actual application in the field
308 that attempts to improve the quality of the biogas, an adequate degree of process
309 durability should be acquired. Therefore, performance of the PI membrane
310 module was further analyzed over the longer-term by running permeation
311 experiments with real biogas (generated by an anaerobic digestion plant located
312 in the countryside of Hungary). Furthermore, implementation of the whole test rig
313 in an industrial setting is accompanied with the advantage of a continuous gas
314 supply and the availability of sufficient feed volumes, which would otherwise limit
315 the exploitation of permeation capacities over a more extensive period of time.

316 As can be seen in **Table 3**, the biogas generated in the plant could be
317 characterised as a clearly distinguishable quality compared to the one applied
318 during laboratory tests (**Table 2**). This might be attributed to differences in the
319 attributes of biotic and abiotic processes, i.e. in terms of the (i) composition of
320 underlying microbial consortia, (ii) source and complexity of the feedstock to be
321 utilized, (iii) operational settings of the fermenters, etc. During the permeation
322 stability tests, separation conditions were constants (**Table 3**) for almost 9 hours
323 during the experiment (**Figs. 6 and 7**). It should be noted that besides the clearly
324 identifiable components, namely CH₄, CO₂ and N₂, the raw biogas, on average,
325 contains a comparable amount of trace substances to the biogas evolved in the
326 laboratory-scale bioreactor (**Table 2**). However, the similarities regarding the
327 distribution (partial concentrations) of these components remain unknown and
328 such an analysis could be a subject of a future study to elaborate on such related
329 effects. Actually, based on the already published experiences in the existing
330 literature, pro-longed operation of the biogas-upgrading membrane permeation
331 system can require the pretreatment of raw fermenter off-gas to get rid of
332 particular secondary components (i.e. ammonia, hydrogen sulfide and water
333 vapor that may damage the membrane material over time) by drying,
334 condensation and desulphurization before conveying the biogas to the
335 membrane purification technology (Miltner et al., 2010, 2009). Such an action
336 can help to extend membrane lifetime and preserve its performance (Stern et al.,
337 1998)

338 The time profiles of the qualities of the permeate and retentate are
339 depicted in **Figs. 6 and 7**, respectively. It should be inferred that only slight
340 changes in the compositions were recorded and, therefore, the purification
341 performance could be considered quite stable throughout the test period.
342 Similarly to the results of the other gas mixtures discussed above, a considerable
343 degree of CH₄/CO₂ separation was achieved. However, the removal of nitrogen

344 gas seemed to be challenging, in accordance with statements made in Section 5.
345 Under the circumstances mentioned in **Table 3**, a reasonable and steady level of
346 CH₄ recovery ($Y_{\text{methane}} > 82 \%$) was accomplished with a corresponding methane
347 concentration of 81-82 vol.% in the retentate. Overall, these research outcomes
348 imply that the gas permeation process was able to function properly over an
349 extended period of time without considerable variation in the separation
350 efficiency. Thus, it can be deduced that the PI membrane employed may be a
351 worthy candidate for further investigation and possible installation at biogas
352 plants. However, the experiments conducted point to the fact that this particular
353 module should be applied as one component of a multi-stage (sequential)
354 membrane system, enriching the CH₄ content of the biogas to the desired level of
355 biomethane quality (Makaruk et al., 2010). Such a system is supposed to
356 manage the efficient separation of N₂ from CH₄ and attain large Y_{methane} values to
357 reduce losses in the permeate (increase product recovery) (Rautenbach and
358 Welsch, 1993) and consequently, minimise the environmental impacts
359 associated with the emission of methane. Many times, however, high methane
360 purities may be attained only with compromises in methane recovery, when
361 some methane is lost in the permeate (Sun et al., 2015). Under these conditions,
362 for instance, the permeate with methane content can be recycled and burnt in
363 gas engines at the biogas plant (Miltner et al., 2009).

364

365 **7. Conclusions**

366

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

371 module provided biogas with methane content (93.8 vol.% along with 77.4 %
372 recovery) via efficient removal of CO₂ in the case of the binary, model mixture.
373 The CO₂/CH₄ permselectivity values were dependent on the experimental
374 conditions and accordingly, could be as high as 11-12 in some cases. However,
375 primarily due to the insufficient CH₄/N₂ separation capacity of the membrane, it
376 was not possible to upgrade the real biogas in the same manner and additional
377 research into the subject is encouraged. Nevertheless, tests revealed an
378 adequate level of endurance of the membrane permeation process over the
379 longer-term, leading to the conclusion that the process, based on the module that
380 contains PI hollow fibers, is worthy of further elaboration under industrial
381 conditions in the field. The appropriate design of the process, in particular the
382 deployment of a membrane cascade purification system, could overcome the
383 existing bottleneck observed with the single-stage application to deliver
384 biomethane from biogas.

385

386 **Acknowledgement**

387

388 The authors would like to express their gratitude for the financial support
389 provided by the Széchenyi 2020 Programme under the project EFOP-3.6.1-16-
390 2016-00015, and by the Excellence of Strategic R+D Workshops under the
391 project GINOP-2.3.2-15 (which encompasses the development of modular,
392 mobile water treatment systems and wastewater treatment technologies based at
393 the University of Pannonia to enhance growing dynamic exportation from
394 Hungary between 2016 and 2020). The János Bolyai Research Scholarship of
395 the Hungarian Academy of Sciences is duly acknowledged for the support. This
396 work was supported by the Korea Research Fellowship Program through the
397 National Research Foundation of Korea (NRF) funded by the Ministry of Science

398 and ICT (Grant No: 2016H1D3A1908953). This work was supported by the New
399 & Renewable Energy Core Technology Program of the Korea Institute of Energy
400 Technology Evaluation and Planning (KETEP) granted financial resource from
401 the Ministry of Trade, Industry & Energy, Republic of Korea (No.
402 20173010092470).

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Figure legends

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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.% CH₄, 20 vol.% CO₂)

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.% CH₄, 19.8 vol.% CO₂, 9.2 vol.% N₂ and unknown trace substances to balance.

p ^F (bar)	p ^F /p ^D (-)	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.% CH₄, 39 vol.% CO₂, 2.5 vol.% N₂ and unknown trace substances to balance) permeation conducted at 50 °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

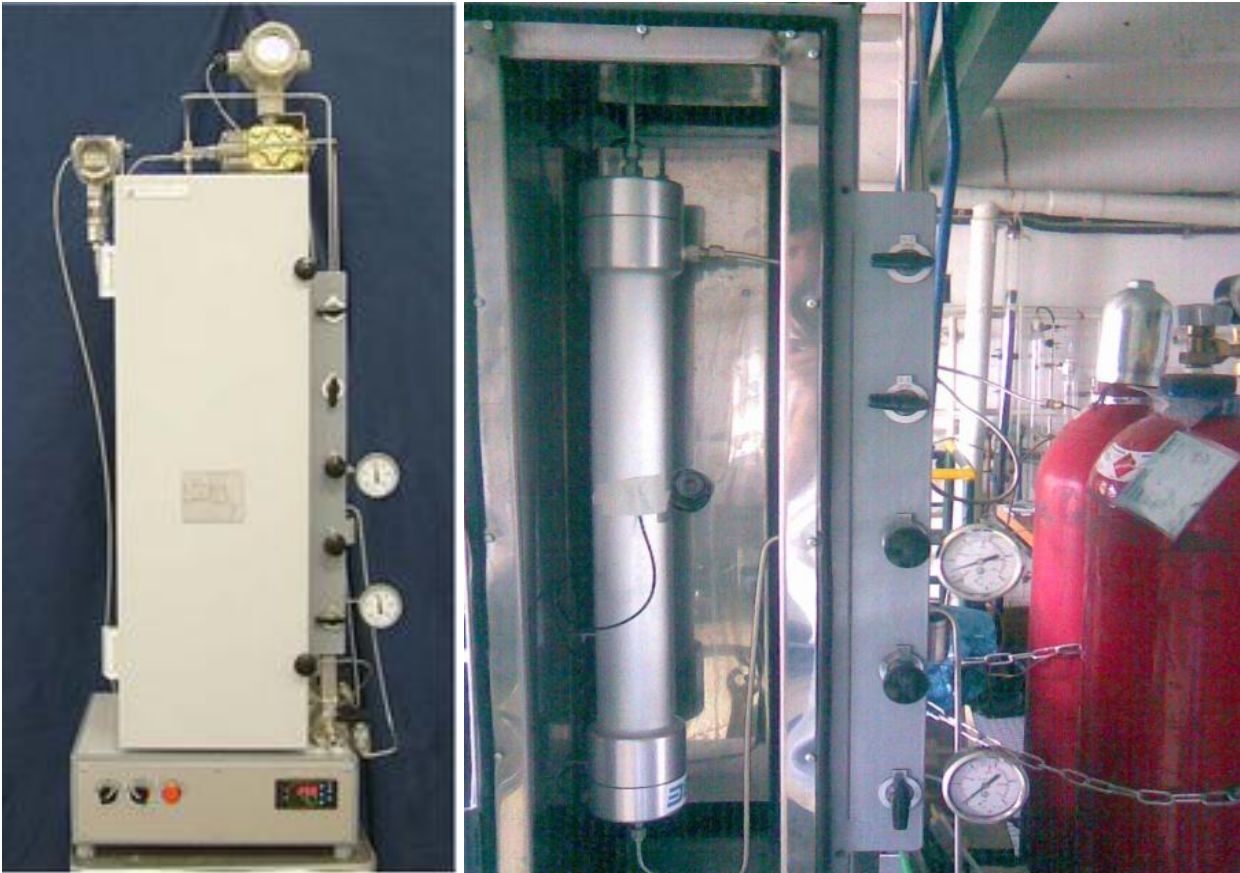


Fig. 2

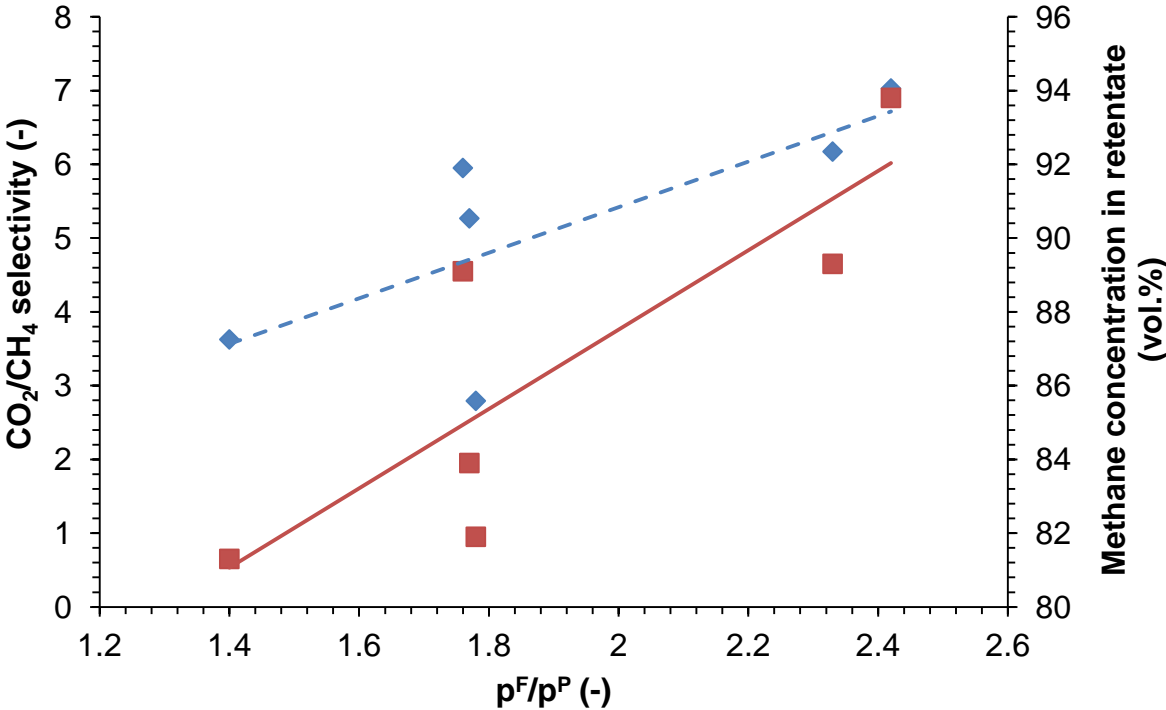


Fig. 3

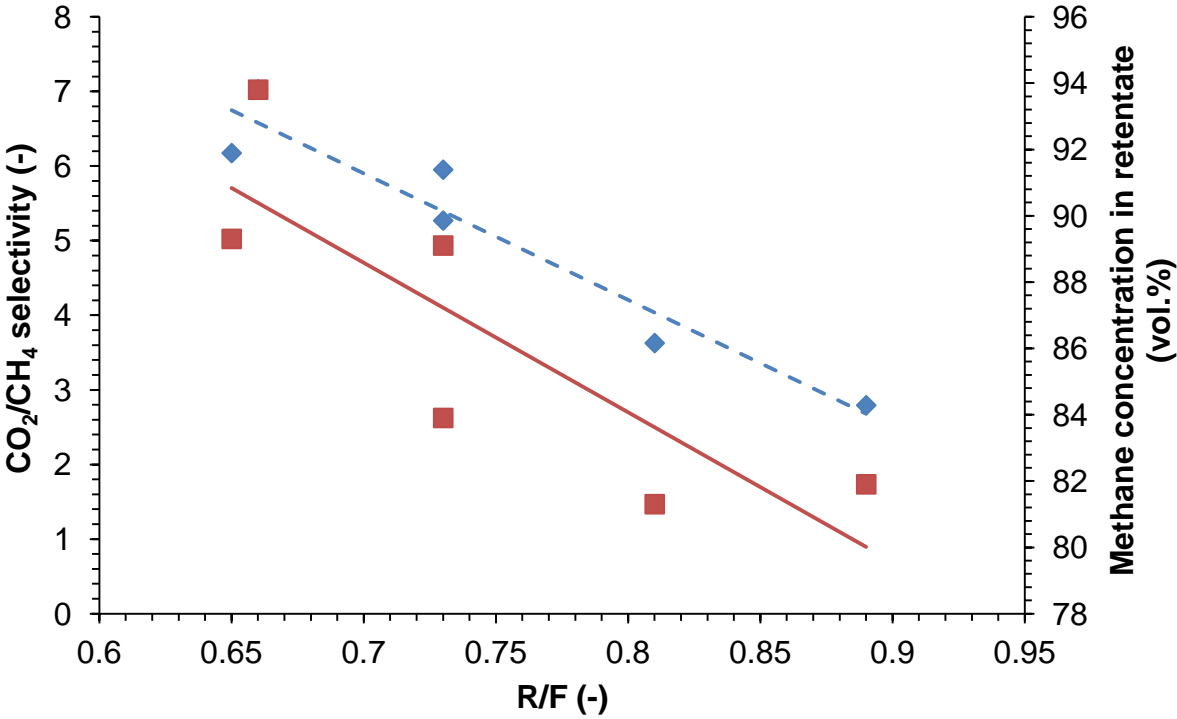


Fig. 4

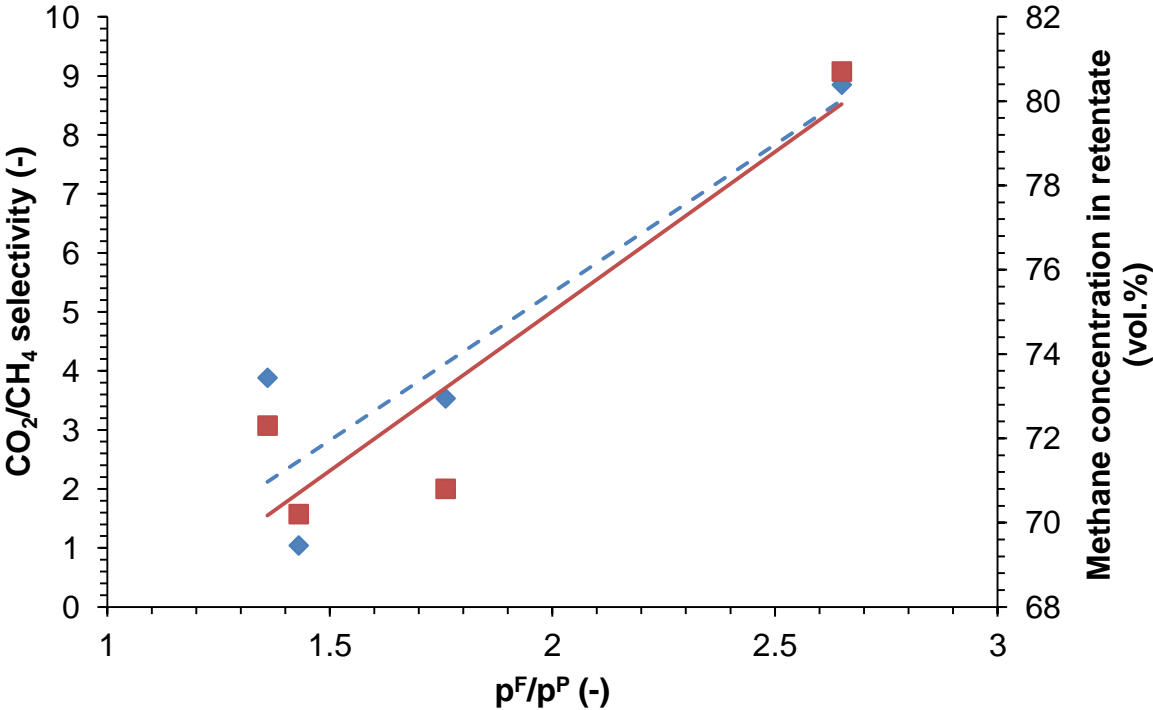


Fig. 5

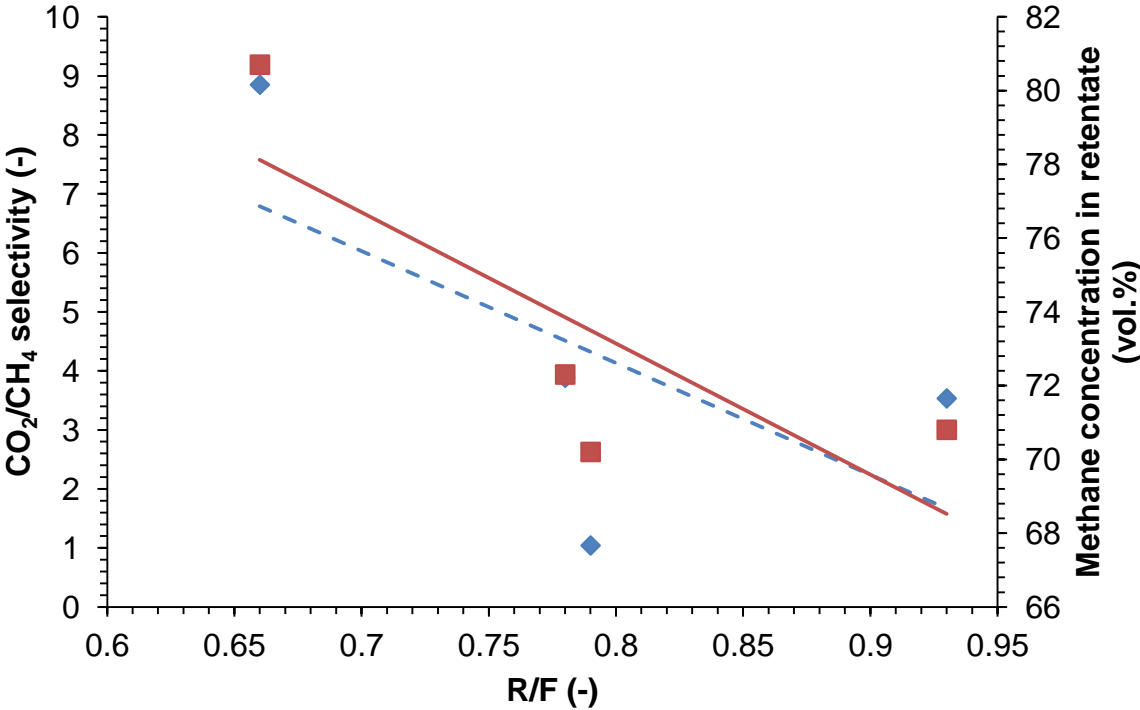


Fig. 6

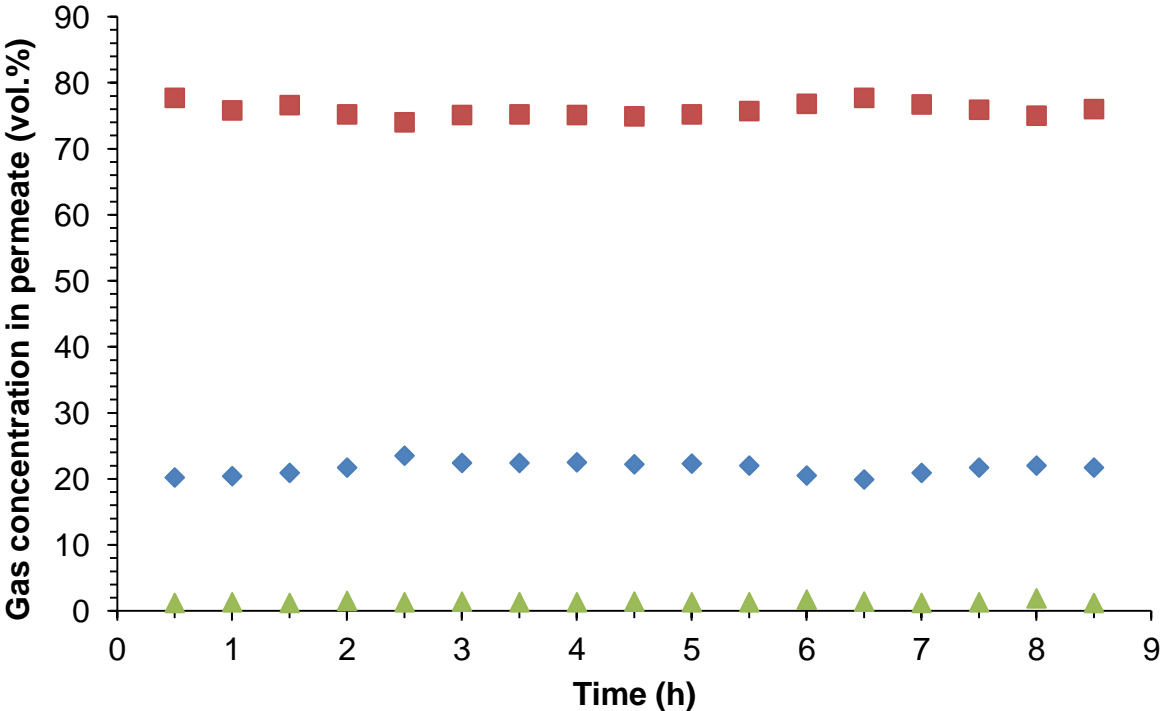
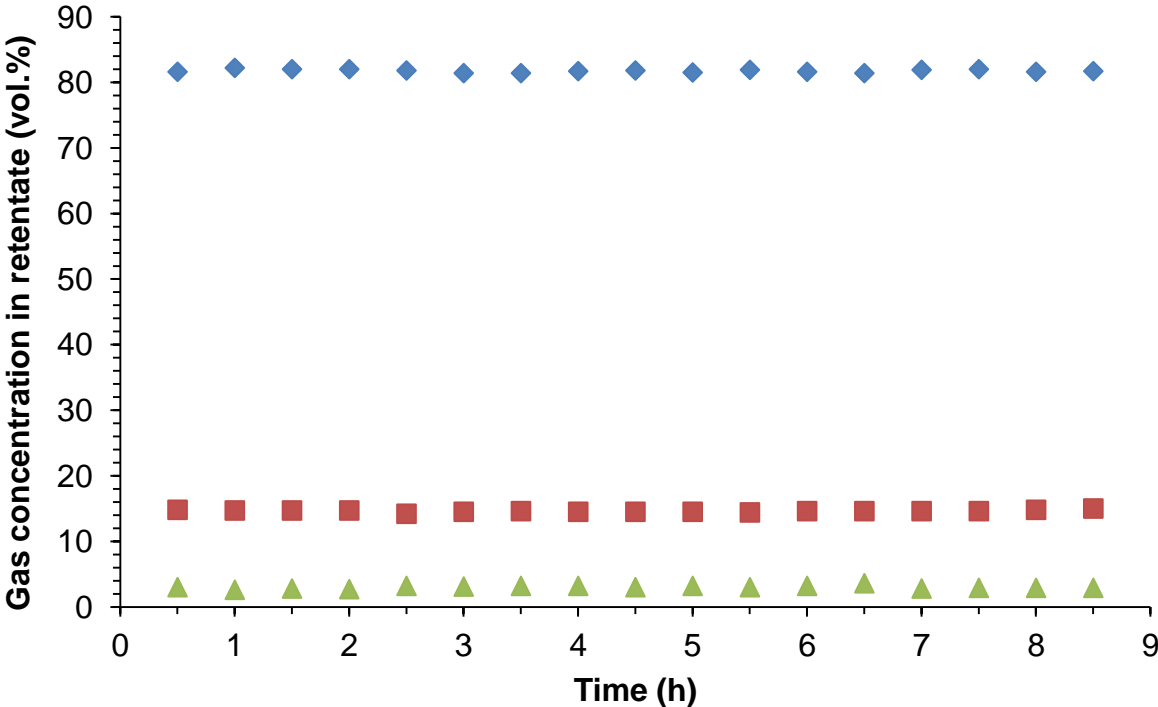


Fig. 7



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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 Nemestóthy¹, Péter Bakonyi^{1,*}, Eszter Szentgyörgyi¹, Gopalakrishnan Kumar², Dinh Duc Nguyen³, Soon Woong Chang³, Sang-Hyoun Kim², Katalin Bélafi-Bakó¹

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

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

³Department 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

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22 **Abstract**

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24 In this paper, the enrichment of methane by membrane technology was
25 studied by employing (i) a model as well as (ii) a real biogas mixture produced on
26 a laboratory-scale. Thereafter, the endurance of the process was tested at an
27 existing biogas plant. The commercial gas separation module under investigation
28 contained hollow fiber membranes with a polyimide selective layer. During the
29 measurements, the effect of critical factors (including the permeate-to-feed
30 pressure ratio and the splitting factor) was sought in terms of the (i) CH₄ content
31 on the retentate-side and (ii) CH₄ recovery, which are important measures of
32 biogas upgrading efficiency. The results indicated that a retentate with 93.8 vol.%
33 of CH₄ – almost biomethane (>95 vol.% of CH₄) quality – could be obtained using
34 the model gas (consisting of 80 vol.% of CH₄ and 20 vol.% of CO₂) along with
35 77.4 % CH₄ recovery in the single-stage permeation system. However, in the
36 case of the real biogas mixture, ascribed primarily to inappropriate N₂/CH₄
37 separation, the peak methane concentration noted was only 80.7 vol.% with a
38 corresponding 76 % CH₄ recovery. Besides, longer-term experiments revealed
39 the adequate time-stability of membrane purification, suggesting such a process
40 is feasible under industrial conditions for the improvement of biogas quality.

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42 **Keywords:** biogas; biomethane; gas separation; membrane; polyimide;
43 renewable energy

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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

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

78 So far, various “membrane-powered” applications have been developed
79 and thoroughly evaluated in terms of biogas enrichment, most of which are
80 designed from polymeric membranes, i.e. cellulose acetate (CA),
81 polydimethylsiloxane (PDMS), polysulfone (PSf) and polyimide (PI) (Scholz et al.,
82 2013). A contemporary membrane system, in order to provide biomethane as a
83 substitute for natural gas, should be capable of providing at least 95 % CH₄ purity
84 with 90 % CH₄ recovery (Brunetti et al., 2015). Typically, the raw biogas that is
85 subjected to purification contains approximately 50-70 % methane, 30-50 %
86 carbon dioxide, lower quantities of nitrogen and water, and trace amounts of
87 substances such as H₂S, depending on its source, e.g. a farm, sewage sludge
88 digester, landfill, etc. (Rasi et al., 2007, 2011). In general, the performance of a
89 given membrane system that deals with such gaseous streams will strongly
90 depend on the operating conditions, namely the (i) pressure gradient across the
91 membrane module (assisting the driving force), (ii) retentate (R) to feed (F) flow
92 ratio (R/F) known as the splitting factor, (iii) separation temperature, and (iv)
93 feed-gas composition, etc., which play a major role (Bakonyi et al., 2013ab).

94 Over the preceding years, our group has been conducting research into
95 gaseous biofuels (hydrogen and methane) production as well as their
96 subsequent separation. As a result, membrane bioreactors (MBR), as integrated
97 approaches, have been designed (Bakonyi et al., 2017; Szentgyörgyi et al.,
98 2010). Besides, ex-situ tests with regard to the evaluation of gas upgrading were
99 performed as well (Bakonyi et al., 2013b). In the light of preliminary experiments,
100 hollow fiber membranes (HFMs) made of PI are shown as applicable candidates

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4 101 in terms of gas upgrading (Bakonyi et al., 2013b; Szentgyörgyi et al., 2010).
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6 102 Though previous information concerning biogas purification using certain PI
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8 103 membranes is available in the literature (Harasimowicz et al., 2007), an in-depth
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10 104 examination of the particular one employed in this study, to the best of our
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12 105 knowledge, has not been yet reported. Hence, in this work, the thorough
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14 106 evaluation of a commercialized membrane made of PI – a polymer with the
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16 107 potential to be utilized in CH₄/CO₂ separation (Baker and Low, 2014) – was
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18 108 aimed to study. The main scope of investigation was laid down to reveal the
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20 109 operating circumstances under which biomethane may be produced. Over the
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22 110 course of the assessment, model and real biogas mixtures were applied to
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24 111 determine how the composition affects the efficiency of purification. Afterwards,
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26 112 the time-stability of the gas permeation process was analysed over a series of
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28 113 longer-term experiments to obtain information concerning its applicability with
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30 114 regard to possible industrial implementation. To the best of our knowledge, such
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32 115 experimental results are not found in the literature for this PI membrane module
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34 116 and hence, this work is believed to exhibit added value and contribute to the
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36 117 development of anaerobic digestion technology.
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40 41 119 **2. Experimental setup** 42 43

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46 121 Biogas purification measurements were performed on a membrane module
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48 122 (UBE-CO5, Ube Industries, Ltd.) designed for natural gas separation. It contains
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50 123 composite hollow fibers membranes composed of a PI selective layer. Since a
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52 124 number of module features, i.e. the active surface area and thickness of the
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54 125 membrane are unknown, the gas permeability, measured in the recognised non-
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56 126 SI unit of Barrer, cannot be calculated to characterise the separation process.
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58 127 Therefore, an experimental, pressure-normalized volumetric gas flow rate is
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4 128 reported according to **Eq. 2**. The module was installed into a high-pressure gas
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6 129 separation membrane system, referred to as GSMS (**Fig. 1**). The schematic
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8 130 drawing of the GSMS and its most essential technical details can be found in our
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10 131 earlier paper (Bakonyi et al., 2013b). The permeate and retentate were quantified
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12 132 by digital mass flow meters (Bronkhorst EL-FLOW[®] Select), which had
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14 133 undergone preliminary calibration. To obtain the exact flow rate of mixtures
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16 134 throughout the separation process, a correction factor was provided by Fluidat[®]
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18 135 (<https://www.fluidat.com>, Bronkhorst[®]). This took into account the exact
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20 136 composition of the permeate and retentate streams in terms of CH₄, CO₂ and N₂
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22 137 as determined according to Section 3.

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25 138 The gas separation experiments were carried out at a temperature of 30 °C
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27 139 unless otherwise stated, first by using a binary (model) mixture composed of 80
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29 140 vol.% methane and 20 vol.% carbon dioxide (SIAD Hungary Kft., Hungary)
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31 141 (**Table 1**). Afterwards, real biogas – from a continuously operated anaerobic
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33 142 membrane bioreactor system – as documented by Szentgyörgyi et al. (2010) –
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35 143 was collected over a period of time, compressed into a gas cylinder and
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37 144 subsequently tested. Recently, together with our industrial partner, work has
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39 145 commenced on the valorization of landfill-deposited organic waste fractions, i.e.
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41 146 to generate biogas. As a part of that line of research, the assessment of methane
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43 147 purification by membrane technologies is a distinct goal. In accordance with a
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45 148 summary in the paper of Brunetti et al. (2015), the nitrogen content in biogas can
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47 149 vary considerably (1-17 vol.%). Hence, to simulate realistic conditions and typical
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49 150 compositions of landfill-derived biogas, enrichment of the real gaseous mixture
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51 151 (pressurized in the external tank, as noted above) by N₂ was conducted. As a
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53 152 result, the final composition was as follows: 70 vol.% CH₄, 19.8 vol.% CO₂, 9.2
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55 153 vol.% N₂ and approx. 1 vol.% unidentified minor impurities.

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57 154 As can be observed in **Tables 1 and 2**, the effect of the main membrane
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59 155 operating parameters – namely the (i) feed pressure to permeate pressure ratio

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6 157 to the total feed flow rate – on (i) methane concentration on the side of the
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8 158 retentate and (ii) methane recovery was sought (**Figs. 2-5**). All data presented in
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10 159 this work were obtained under steady-state permeation conditions, reflected by
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12 160 the properly stabilized volumetric flows and corresponding concentrations of
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14 161 gaseous substances, namely CH_4 , CO_2 and N_2 . In addition to the experimental
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16 162 runs listed in **Tables 1 and 2**, the membrane module was tested at a biogas
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18 163 plant located in Hungary in order to determine its behaviour in the longer-term
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20 164 and provide feedback concerning the stability of this time-dependent process,
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22 165 which could be useful as far as an envisaged industrial application is concerned.
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24 166 The respective permeation conditions are described in **Table 3**. Mass balance
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26 167 calculations, that took into account volumetric flow rates and respective
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28 168 concentrations of gases, thoroughly verified the reliability of such measurements.
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30 169 This indicated that the entire feed could only be extracted either as the retentate
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32 170 or permeate after separation had occurred. Repetitions (i.e. duplicates) under
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34 171 particular experimental settings were carried out occasionally, resulting in relative
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36 172 deviations $< 5\%$.

3. Analytical methods

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46 176 Gas samples taken from the feed, permeate and retentate were analyzed
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48 177 by gas chromatography. On the one hand, the concentrations of CH_4 and N_2
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50 178 could be determined from a Gow-Mac Series 600 gas chromatograph equipped
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52 179 with a molecular sieve packed column (filled with zeolite), a thermal conductivity
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54 180 detector (TCD), and He as a carrier gas. On the other hand, the concentration of
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56 181 CO_2 was analyzed by a Hewlett Packard HP 5890 Series II gas chromatograph
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58 182 equipped with a capillary column (GS-CarbonPLOT, Agilent Technologies), a
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60 183 TCD and N_2 as a carrier gas.

4. Calculations

CH₄ recovery (Y_{methane}) was defined (in the unit of %) according to **Eq. 1**:

$$Y_{\text{methane}} = 100 \frac{V_R C_{\text{methane}}^R}{V_F C_{\text{methane}}^F} \quad (1)$$

where V_R and V_F are the total volumetric flow rates of the retentate and feed ($\text{dm}^3 \text{min}^{-1}$ at standard temperature (273 K) and pressure (1 bar) (STP)), respectively; while C_{methane}^R and C_{methane}^F stand for the CH₄ 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 $\text{dm}^3 \text{min}^{-1} \text{bar}^{-1}$ at STP), as follows (**Eq. 2**):

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

where V_p is the total volumetric flow rate of the permeate ($\text{dm}^3 \text{min}^{-1}$ at STP), C_j^P 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**.

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

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4 207 where $\Delta p_{j,mean}^{lumen}$ and $\Delta p_{j,mean}^{shell}$ are the average partial pressures for component (*j*)
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6 208 on the lumen-side (where the gas was fed) and the shell-side (where the
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8 209 permeate was collected), respectively according to Asadi et al. (2016), assuming
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10 210 in the calculation that the membrane permeate stream was under non-well-mixed
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12 211 conditions.
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17 213 The permselectivity (α) for a certain gas pair was defined by **Eq. 4**.
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$$\alpha = \frac{J_i}{J_j} \tag{4}$$

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28 217 where J_i and J_j are the experimental, pressure-normalized volumetric gas flow
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30 218 rates of the rapidly and the slowly permeating compounds, (*i*) and (*j*), respectively
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32 219 ($J_i > J_j$). In this work, the permselectivities for CO₂ and CH₄, as major
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34 220 constituents of biogas that need to be separated, were computed (**Tables 1-3**).
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40 222 **5. Methane enrichment and recovery from binary (model) and real**
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42 223 **biogas mixtures**
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47 225 In essence, the gas separation applying non-porous, polymeric materials
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49 226 e.g. in the case of UBE-CO5 requires the partial pressure difference of
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51 227 substances across the membrane (Mulder, 1996), where the rapidly permeating
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53 228 compound is enriched in the permeate, meanwhile, the slower (less-permeable)
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55 229 one is concentrated in the retentate. Accordingly, on the grounds of carbon
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57 230 dioxide enrichment on the permeate-side (**Tables 1 and 2**), it can be concluded
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59 231 that the membrane used in this investigation is CO₂-selective. This is primarily
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4 232 attributed to the properties of PI, which act as the selective layer of composite
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6 233 hollow fibers membranes found in the module. This glassy polymer can provide a
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8 234 sufficient degree of CO₂/CH₄ selectivity given its high permeability of CO₂, which
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10 235 can be even an order of magnitude larger than that of CH₄ (Harasimowicz et al.,
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12 236 2007). The fact that the PI membrane is CH₄-rejective (**Tables 1 and 2**) leads to
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14 237 increased methane content in the retentate under upstream-side pressure
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16 238 conditions. This is quite advantageous, especially when the (i) upgraded biogas,
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18 239 namely biomethane, is to be injected into the distribution pipeline network
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20 240 (Brunetti et al., 2015) or (ii) when a sufficient level of biogas purification is not
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22 241 achieved in a single-stage, requiring further steps by means of additional
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24 242 processing to reach the defined gas (biomethane) quality.

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26 243 With both the binary (model) as well as real biogas mixtures employed in
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28 244 this work, the achievable concentration of methane in the retentate seemed to be
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30 245 positively influenced by the greater difference between p^F and p^P , which made a
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32 246 particular contribution to the actual driving force (**Eq. 4**). This is reflected in **Figs.**
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34 247 **2 and 4**, where the relationship between p^F/p^P and the CH₄ concentration on the
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36 248 retentate-side as well as the CO₂/CH₄ permselectivity can be regarded as directly
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38 249 proportional. In addition, the so-called splitting factor (R/F) had also been proven
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40 250 as a variable that exhibits a substantial impact on the performance of gas
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42 251 separation (Bakonyi et al., 2013b; Harasimowicz et al., 2007). Based on **Figs. 3**
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44 252 **and 5**, regardless of the gas actually fed into the module, the lower R/F range
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46 253 should be preferred to attain a more significant degree of enrichment of methane
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48 254 in the retentate and maintain a larger permselectivity of CO₂/CH₄. This
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50 255 observation agrees well with the features generally described concerning the
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52 256 technique of gas separation by membranes (Baker, 2000). Overall, by comparing
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54 257 **Fig. 2** with **Fig. 4** and **Fig. 3** with **Fig. 5**, the results demonstrate that the
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56 258 composition of the gas used, either in terms of the model or real biogas, did not
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58 259 remarkably change the profile of response given by the membrane as a function
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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 CH₄ 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 N₂ content of the feed (**Table 2**), making this compound of major concern. To understand why only marginal N₂/CH₄ 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

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288 accomplished (Lokhandwala et al., 2010). Consequently, the elimination of N₂
289 from the biogas stream is an objective of further research where membranes
290 possessing better characteristics are developed. Moreover, provided that the
291 overall technology undergoes careful optimization by reconsidering the number
292 of purification stages and the possible application of cascades (Baker and
293 Lokhandwala, 2008; Lokhandwala et al., 2010), additional benefits that enhance
294 the process can be expected. For comparison of membrane performance with
295 other materials/modules, data summarized in review articles such as Basu et al.
296 (2010) and Scholz et al. (2013) can be referenced. Among commercialized
297 polymer materials, permselectivity values for CO₂/CH₄ span 1.4-42.8 and hence,
298 the respective values attained with the commercialized PI module in this work
299 (**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

304 Apart from the issues elaborated in Section 5, e.g. the N₂ content of the
305 biogas, the time-stability of the process is also a crucial aspect that must be
306 considered. In other words, to acquire a reasonable comprehension of the
307 relevance of the membrane module in terms of an actual application in the field
308 that attempts to improve the quality of the biogas, an adequate degree of process
309 durability should be acquired. Therefore, performance of the PI membrane
310 module was further analyzed over the longer-term by running permeation
311 experiments with real biogas (generated by an anaerobic digestion plant located
312 in the countryside of Hungary). Furthermore, implementation of the whole test rig
313 in an industrial setting is accompanied with the advantage of a continuous gas
314 supply and the availability of sufficient feed volumes, which would otherwise limit
315 the exploitation of permeation capacities over a more extensive period of time.

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4 316 As can be seen in **Table 3**, the biogas generated in the plant could be
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6 317 characterised as a clearly distinguishable quality compared to the one applied
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8 318 during laboratory tests (**Table 2**). This might be attributed to differences in the
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10 319 attributes of biotic and abiotic processes, i.e. in terms of the (i) composition of
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12 320 underlying microbial consortia, (ii) source and complexity of the feedstock to be
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14 321 utilized, (iii) operational settings of the fermenters, etc. During the permeation
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16 322 stability tests, separation conditions were constants (**Table 3**) for almost 9 hours
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18 323 during the experiment (**Figs. 6 and 7**). It should be noted that besides the clearly
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20 324 identifiable components, namely CH₄, CO₂ and N₂, the raw biogas, on average,
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22 325 contains a comparable amount of trace substances to the biogas evolved in the
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24 326 laboratory-scale bioreactor (**Table 2**). However, the similarities regarding the
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26 327 distribution (partial concentrations) of these components remain unknown and
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28 328 such an analysis could be a subject of a future study to elaborate on such related
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30 329 effects. Actually, based on the already published experiences in the existing
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32 330 literature, pro-longed operation of the biogas-upgrading membrane permeation
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34 331 system can require the pretreatment of raw fermenter off-gas to get rid of
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36 332 particular secondary components (i.e. ammonia, hydrogen sulfide and water
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38 333 vapor that may damage the membrane material over time) by drying,
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40 334 condensation and desulphurization before conveying the biogas to the
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42 335 membrane purification technology (Miltner et al., 2010, 2009). Such an action
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44 336 can help to extend membrane lifetime and preserve its performance (Stern et al.,
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46 337 1998)

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48 338 The time profiles of the qualities of the permeate and retentate are
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50 339 depicted in **Figs. 6 and 7**, respectively. It should be inferred that only slight
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52 340 changes in the compositions were recorded and, therefore, the purification
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54 341 performance could be considered quite stable throughout the test period.
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56 342 Similarly to the results of the other gas mixtures discussed above, a considerable
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58 343 degree of CH₄/CO₂ separation was achieved. However, the removal of nitrogen
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4 344 gas seemed to be challenging, in accordance with statements made in Section 5.
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6 345 Under the circumstances mentioned in **Table 3**, a reasonable and steady level of
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8 346 CH₄ recovery ($Y_{\text{methane}} > 82 \%$) was accomplished with a corresponding methane
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10 347 concentration of 81-82 vol.% in the retentate. Overall, these research outcomes
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12 348 imply that the gas permeation process was able to function properly over an
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14 349 extended period of time without considerable variation in the separation
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16 350 efficiency. Thus, it can be deduced that the PI membrane employed may be a
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18 351 worthy candidate for further investigation and possible installation at biogas
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20 352 plants. However, the experiments conducted point to the fact that this particular
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22 353 module should be applied as one component of a multi-stage (sequential)
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24 354 membrane system, enriching the CH₄ content of the biogas to the desired level of
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26 355 biomethane quality (Makaruk et al., 2010). Such a system is supposed to
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28 356 manage the efficient separation of N₂ from CH₄ and attain large Y_{methane} values to
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30 357 reduce losses in the permeate (increase product recovery) (Rautenbach and
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32 358 Welsch, 1993) and consequently, minimise the environmental impacts
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34 359 associated with the emission of methane. Many times, however, high methane
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36 360 purities may be attained only with compromises in methane recovery, when
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38 361 some methane is lost in the permeate (Sun et al., 2015). Under these conditions,
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40 362 for instance, the permeate with methane content can be recycled and burnt in
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42 363 gas engines at the biogas plant (Miltner et al., 2009).
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47 365 **7. Conclusions**

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52 367 In this paper, a polyimide gas separation membrane was investigated in
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54 368 terms of biogas purification. The results showed that the feed-to-permeate-
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56 369 pressure ratio as well as the splitting factor had a notable effect on the
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58 370 performance of the process. In fact, under actual operating circumstances, the
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371 module provided biogas with methane content (93.8 vol.% along with 77.4 %
372 recovery) via efficient removal of CO₂ in the case of the binary, model mixture.
373 The CO₂/CH₄ permselectivity values were dependent on the experimental
374 conditions and accordingly, could be as high as 11-12 in some cases. However,
375 primarily due to the insufficient CH₄/N₂ separation capacity of the membrane, it
376 was not possible to upgrade the real biogas in the same manner and additional
377 research into the subject is encouraged. Nevertheless, tests revealed an
378 adequate level of endurance of the membrane permeation process over the
379 longer-term, leading to the conclusion that the process, based on the module that
380 contains PI hollow fibers, is worthy of further elaboration under industrial
381 conditions in the field. The appropriate design of the process, in particular the
382 deployment of a membrane cascade purification system, could overcome the
383 existing bottleneck observed with the single-stage application to deliver
384 biomethane from biogas.

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Acknowledgement

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388 The authors would like to express their gratitude for the financial support
389 provided by the Széchenyi 2020 Programme under the project EFOP-3.6.1-16-
390 2016-00015, and by the Excellence of Strategic R+D Workshops under the
391 project GINOP-2.3.2-15 (which encompasses the development of modular,
392 mobile water treatment systems and wastewater treatment technologies based at
393 the University of Pannonia to enhance growing dynamic exportation from
394 Hungary between 2016 and 2020). The János Bolyai Research Scholarship of
395 the Hungarian Academy of Sciences is duly acknowledged for the support. This
396 work was supported by the Korea Research Fellowship Program through the
397 National Research Foundation of Korea (NRF) funded by the Ministry of Science

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398 and ICT (Grant No: 2016H1D3A1908953).This work was supported by the New
399 & Renewable Energy Core Technology Program of the Korea Institute of Energy
400 Technology Evaluation and Planning (KETEP) granted financial resource from
401 the Ministry of Trade, Industry & Energy, Republic of Korea (No.
402 20173010092470).

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4 513 **Figure legends**
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10 515 **Fig. 1 – Image of the gas separation membrane system (left-hand side) with**
11 516 **the PI membrane module installed (right-hand side).**

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14 517 **Fig. 2 – The effect of p_F/p_p on the methane concentration on the retentate**
15 518 **side (diamond) and CO_2/CH_4 permselectivity (square) using the model**
16 519 **biogas.**

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20 520 **Fig. 3 – The effect of the splitting factor (R/F) on the methane concentration**
21 521 **on the retentate side (diamond) and CO_2/CH_4 permselectivity (square) using**
22 522 **the model biogas.**

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24 523 **Fig. 4 – The effect of p_F/p_p on the methane concentration on the retentate**
25 524 **side (diamond) and CO_2/CH_4 permselectivity (square) using the real biogas.**

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27 525 **Fig. 5 – The effect of the splitting factor (R/F) on the methane concentration**
28 526 **of the retentate side (diamond) and CO_2/CH_4 permselectivity (square) using**
29 527 **the real biogas.**

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31 528 **Fig. 6 – The time dependency of the composition of the permeate under the**
32 529 **conditions listed in Table 3. Square: carbon dioxide; Diamond: methane;**
33 530 **Triangle: nitrogen.**

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35 531 **Fig. 7 – The time dependency of the composition of the retentate under the**
36 532 **conditions listed in Table 3. Square: carbon dioxide; Diamond: methane;**
37 533 **Triangle: nitrogen.**

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Table 1 – Experimental conditions and results using the binary gas mixture (80 vol.% CH₄, 20 vol.% CO₂)

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

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Table 2 – Experimental conditions and results using the biogas mixture containing 70 vol.% CH₄, 19.8 vol.% CO₂, 9.2 vol.% N₂ and unknown trace substances to balance.

p ^F (bar)	p ^F /p ^D (-)	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

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Table 3 – Average experimental conditions for the assessment of process stability during longer-term biogas (57.4 vol.% CH₄, 39 vol.% CO₂, 2.5 vol.% N₂ and unknown trace substances to balance) permeation conducted at 50 °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

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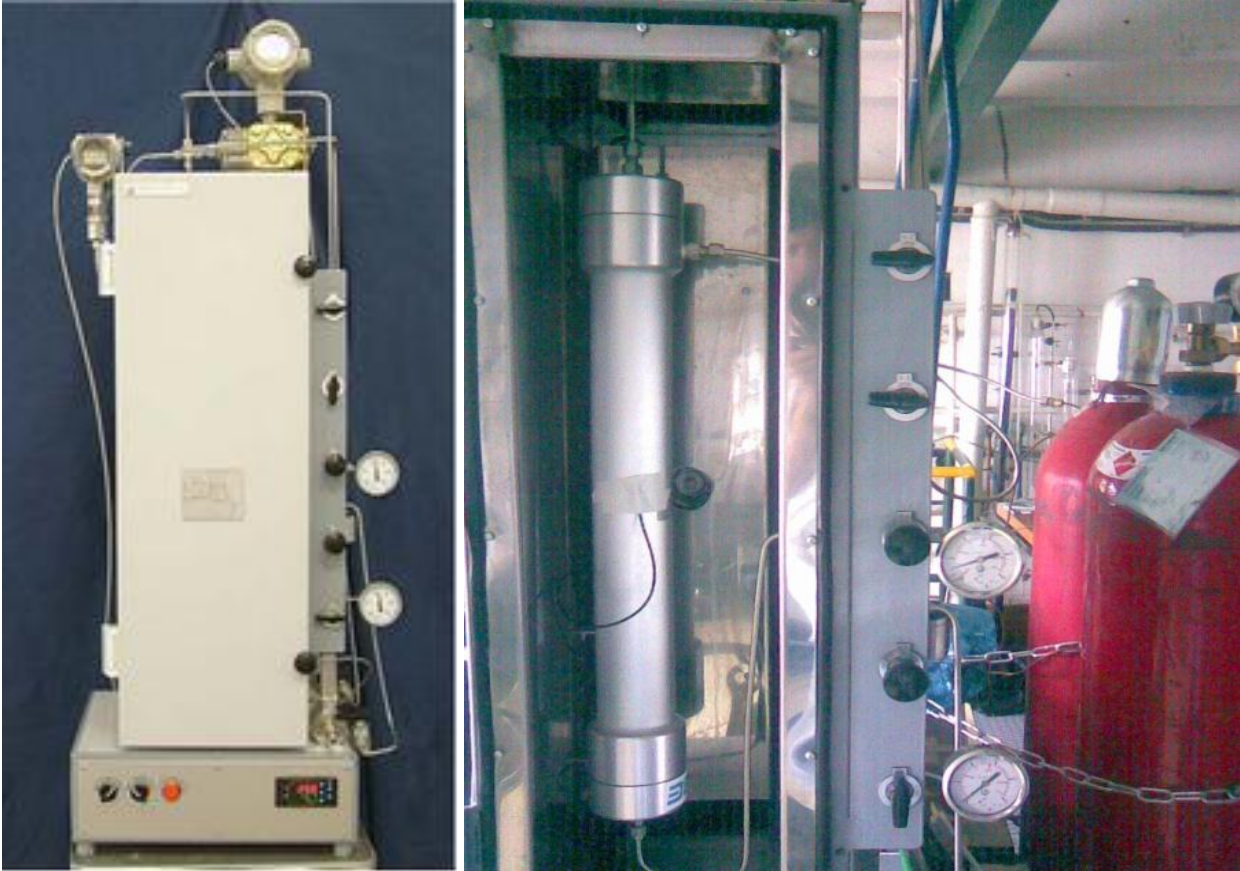


Fig. 2

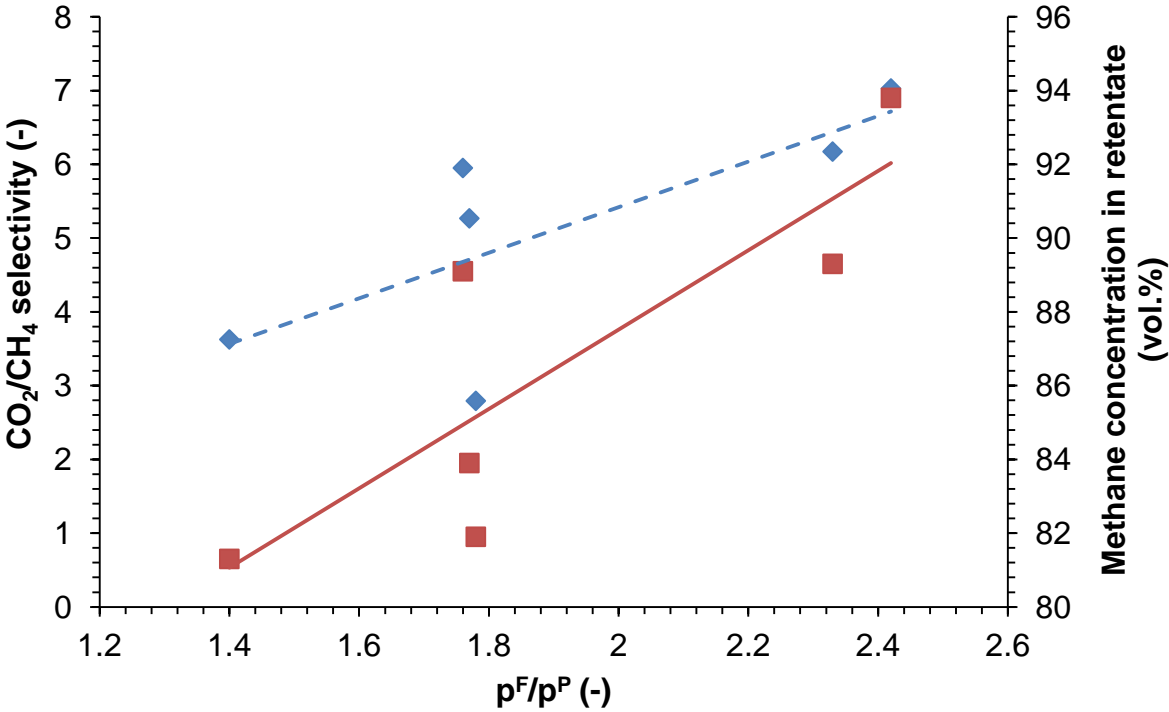
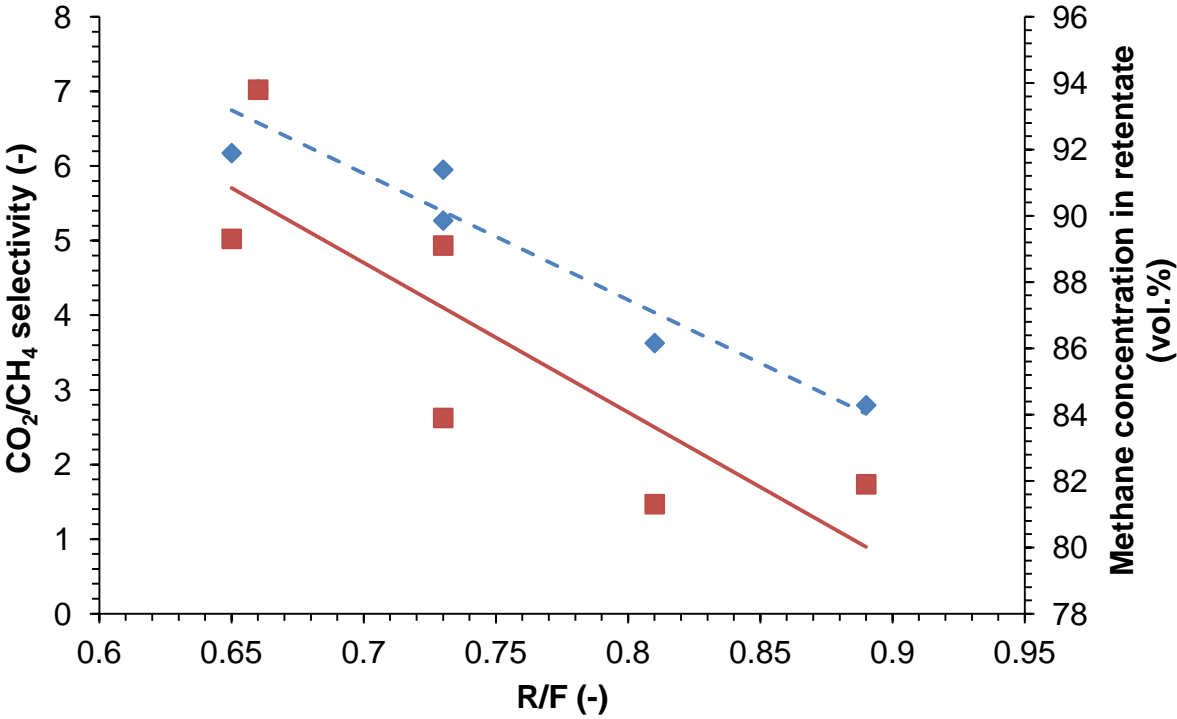
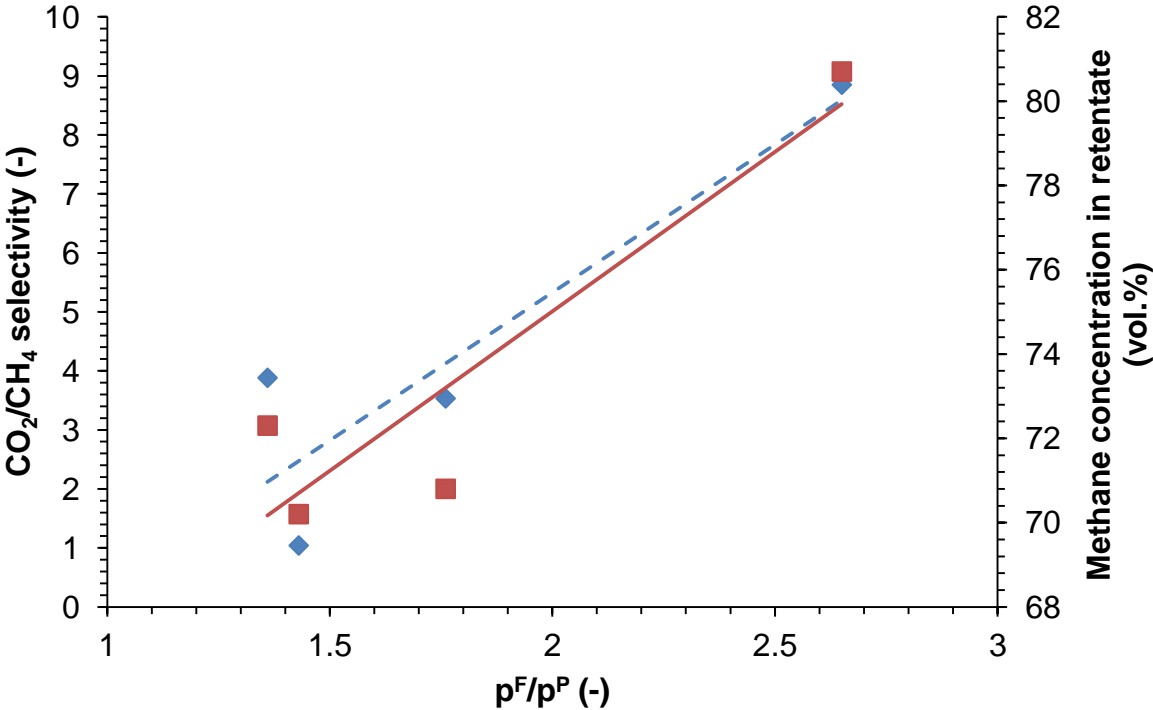


Fig. 3



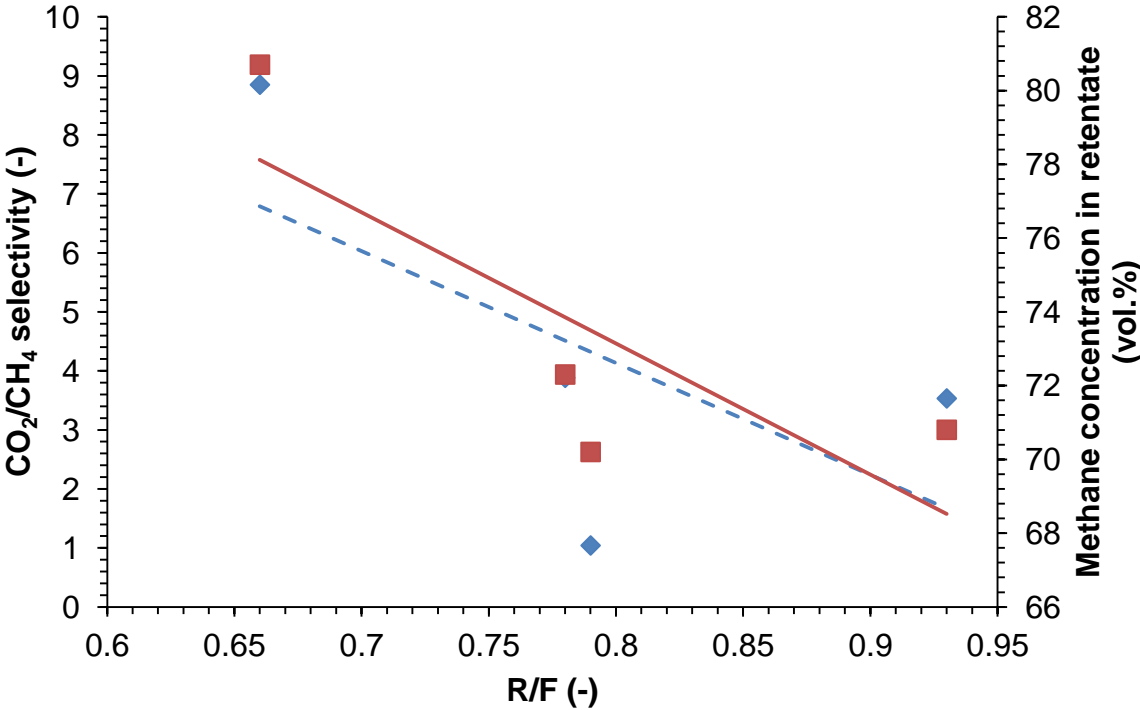
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Fig. 4



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Fig. 5



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Fig. 6

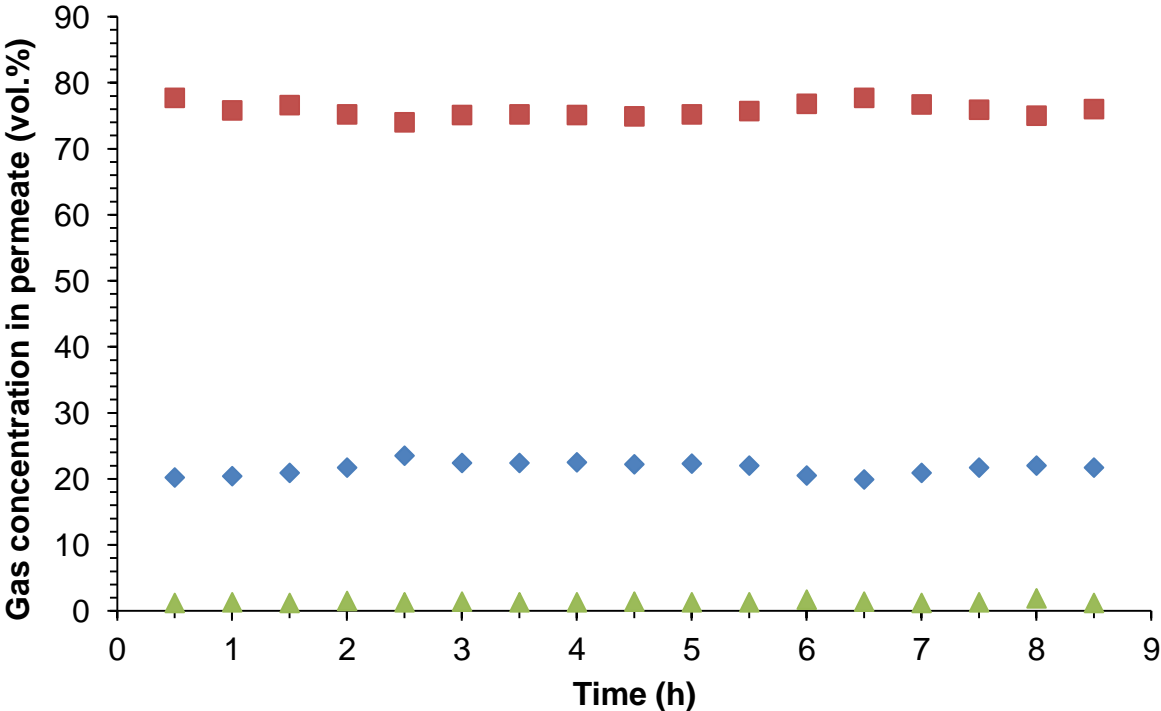
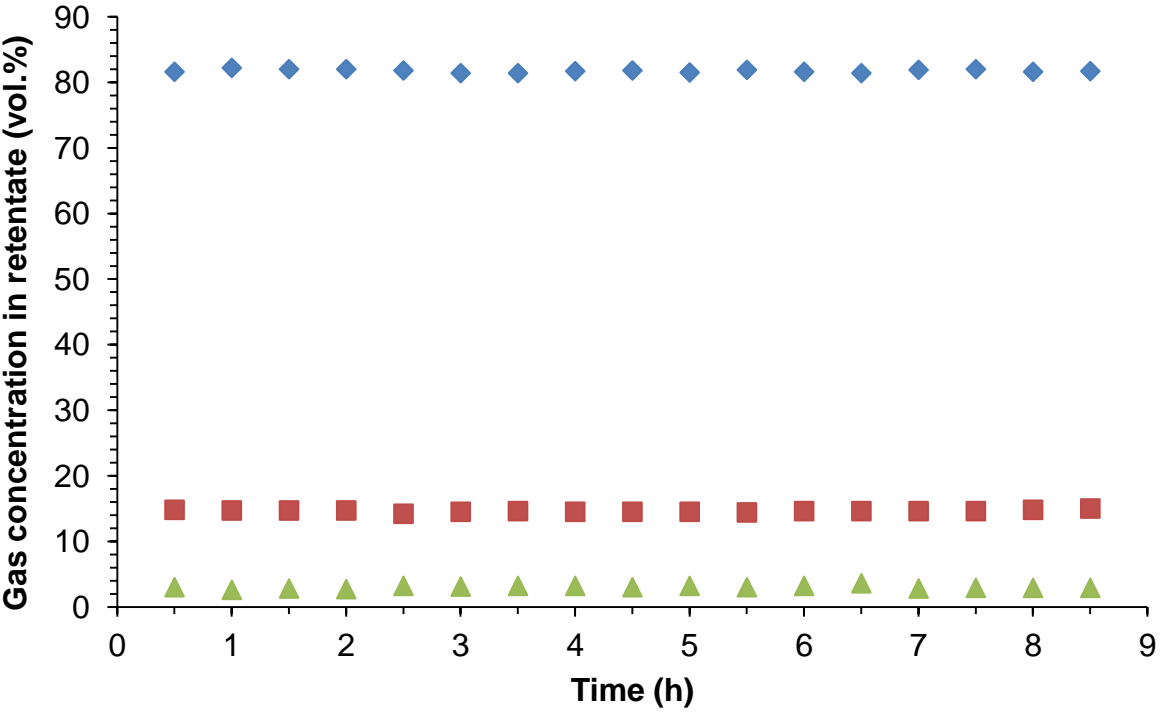


Fig. 7



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