

Application of polyimide membranes for biogas purification and enrichment

M. Harasimowicz^a, P. Orluk^b, G. Zakrzewska-Trznadel^a, A.G. Chmielewski^{a,b,*}

^a Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland

^b Faculty of Chemical and Process Engineering, Warsaw University of Technology, Waryńskiego 1, 00-645 Warsaw, Poland

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Abstract

Biogas is a clean environment friendly fuel that is produced by bacterial conversion of organic matter under anaerobic (oxygen-free) conditions. Raw biogas contains about 55–65% methane (CH₄), 30–45% carbon dioxide (CO₂), traces of hydrogen sulphide (H₂S) and fractions of water vapour. Pure methane has a calorific value of 9100 kcal/m³ at 15.5 °C and 1 atm; the calorific value of biogas varies from 4800 to 6900 kcal/m³. To achieve the standard composition of the biogas and calorific value of 5500 kcal/m³ the treatment techniques like absorption or membrane separation should be applied.

In the paper the results of the tests of the CH₄ enrichment in simulated biogas mixture consisted of methane, carbon dioxide and hydrogen sulphide were presented. It was showed that using the capillary module with polyimide membranes it was possible to achieve the enrichment of CH₄ from the concentrations of 55–85% up to 91–94.4%. The membrane material was resistant to the small concentrations of sour gases and assured the reduction of H₂S and water vapour concentrations, as well. The required enrichment was achieved in the single module, however to prevent CH₄ losses the multistage or hybrid systems should be used to improve process efficiency.

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1. Introduction

Off-gas from anaerobic digestion and landfills has significant potential as an alternative energy source. At present it can be used only at the place where it is produced, most often for steam generation. Biogas purified and enriched in methane can be used for household applications, automobile fuel (liquefied) or electricity generation. There is a great need to make biogas transportable. This can be done by compressing the gas in cylinders, what is possible only after removing CO₂, H₂S and water vapour. There is a lot of potential if biogas could be made viable as a transport vehicle fuel like CNG, by compressing and filling the cylinders in it after scrubbing and drying [1].

Enrichment of methane in biogas to have fuel of higher calorific value can be achieved by removal of carbon dioxide. Elimination of carbon dioxide from the flue gas helps to increase its calorific value as well as to eliminate the greenhouse gas. The

carbon dioxide thus generated can be utilised as an effective refrigerant. Current technologies to purify off-gas and increase its calorific value have been primarily limited to physicochemical methods such as chemical separation, membrane separation, cryogenic separation as well as adsorption. Chemical methods are based on absorption under elevated pressure (in water, 30% solution of potassium carbonate, solution of monoethyloamine, etc.). Other methods are based on adsorption in which a vital role plays suitable adsorbent material [2].

A very important stage of the biogas upgrading is its purification from H₂S traces. The biogas desulphurisation is based on a chemical reaction of H₂S with a suitable substance, such as quicklime, slaked lime in solid form, or slaked lime in liquid form. High concentration of CO₂ which is present in biogas makes the satisfactory removal of H₂S difficult; the CO₂ also reacts with the quick and slaked lime and uses it up quickly. The Ca(HCO₃)₂ formed reacts with Ca(SH)₂ which is generated by the reaction of H₂S with Ca(OH)₂ thus resulting in the recurrence of H₂S.

The membrane or hybrid processes have been studied for many years, however just recently, developments in membrane technology made this process more feasible from economical

* Corresponding author at: Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland.

E-mail address: a.chmielewski@ichtj.waw.pl (A.G. Chmielewski).

Nomenclature

c_m	average methane concentration along the capillary
c_{mF}	methane concentration in feed
c_{mP}	methane concentration in permeate
c_{mR}	methane concentration in retentate
F	parameter related to feed stream
k_S	splitting factor (cut parameter)
p_F	pressure at feed side
p_R	pressure at retentate side
P	parameter related to permeate stream
Q_F	feed flow rate
Q_P	permeate flow rate
Q_R	retentate flow rate
R	parameter related to retentate stream
T	temperature
x_i	mole fraction of i -component
x_j	mole fraction of j -component

Greek symbols

$\alpha_{i,j}$	separation factor of (i, j) components
α_{CH_4/CO_2}	separation factor of CH_4/CO_2 mixture

and technical points of view. Gas permeation seems to offer an economic alternative to absorption and adsorption for treatment of biogas.

Various membrane materials of different composition were tested for their permeability to CH_4 , CO_2 and H_2S [3], among them hollow-fiber-contained liquid membrane separator with polypropylene membranes, for both passive and facilitated transports [4]. The other paper analyses flow pattern in gas permeation modules and module arrangements. The optimal module arrangements for two important cases, enrichment of oxygen from air and production of methane from biogas, are one- or two-stage cascades. The question whether the application of vacuum at the permeate side is economical or not, for methane production from biogas has been discussed [5].

An internally staged membrane separator of bench-scale type has been employed in a study of methane enrichment from biogas. The separator contains two membranes of the same type; therefore, the overall driving force between feed and permeate side in the separator is divided into two parts by these membranes. Theoretical studies were conducted by use of mathematical models based on perfect mixing and co-current flow patterns. The experimental results from bench-scale studies agree well with theoretical predictions based on perfect mixing model. Simulation results show that the optimal performance of the separator can be obtained by proper selection of the stage cut parameter and stage pressure parameter, which are functions of individual stage cut and intermediate pressure, respectively. A comparative studies between the internally staged and conventional single-staged separators indicate that under the same energy consumption, the former offers higher product recovery, but requires much larger membrane area [6].

A bench-scale membrane pilot plant for upgrading biogas generated at municipal wastewater treatment plant was constructed and operated. It was showed that upgraded biogas containing over 90 mol% CH_4 produced in the plant could be used for generation of electricity. At the same time, the permeate (waste stream) would contain over 15 mol% CH_4 and could be used for heating applications [7].

The exploitation of landfill gas for energy purposes was initiated in the U.S.A. around 1975 and later in Europe. It was demonstrated that it is possible to upgrade the landfill gas to a methane content of nearly 100%, and then to distribute with natural gas. There are several landfill gas treatment plants in the U.S.A. [8]. By means of PRISM® separators it will be possible to recover methane by separating the carbon dioxide. The product is high methane gas which can be used as a natural gas. Due to new developed gas separation technology, namely PRISM® separators, a landfill owner is able to sell the methane-rich gas to gas distributors [9].

An alternative hybrid, membrane/biological method that increases the methane content with the use of a chemotrophic methanogen (*Methanobacterium thermoautotrophicum*), has been proposed [10].

Recent research on chemical and physical structure of the membrane, its separation properties, as well as optimisation of membrane manufacturing process led to the development of new membranes with the specific separation properties, suitable for the gas mixtures separation. A study of new type membranes for biogas enrichment and purification is presented in the paper.

2. Theory

Three types of processes can be considered depending on the membrane structure and permeation mechanism: Knudsen's diffusion through microporous barriers, molecular sieving with ultra-microporous membranes and diffusion through nonporous, dense membranes based on solubility-diffusion mechanism.

In accordance with the kinetic theory of gases, the Knudsen's diffusion separation occurs in the pores, which diameter is smaller than the mean free path of gas molecules. In this case the separation factor is rather low; for O_2/N_2 system is equal to 1.07 and for the system studied in this work – CH_4/CO_2 – only 1.05. To get high enrichment, the process has to be run in multistage cascade and it is applied exclusively in nuclear technology for uranium isotopes separation (as gaseous UF_6). The most important for gaseous mixture separation at normal conditions are nonporous membranes. When these membranes are used in a composite membrane where a dense top layer is supported by a porous structure, Knudsen flow may contribute to the total flow depending on the pore sizes in the sub-layer.

Gas separation through dense nonporous membranes depends on differences in the permeabilities of various gases through an appropriate membrane. For two-component mixture (i, j) $\alpha_{i,j}$ is defined by the formula:

$$\alpha_{i,j} = \frac{(x_i/x_j)_P}{(x_i/x_j)_F} \quad (1)$$

where x_i , x_j is the mole fractions in the feed stream (F) and permeate stream (P), respectively.

3. Experimental

3.1. Membrane and module selection

Application of polyimides that is formed by aromatic rings and functional groups of big volume, which act like molecular sieves, as a material for membranes used for gas separation is reasonable. Due to high glass transition temperature and low solubility of polymer, it is possible to apply polyimide in a wide range of temperatures and pressures. Moreover, the polymer is characterized by high selectivity and permeability to the gases in comparison to the others. Membranes based on specific compositions of polyimides (Table 1) have permeability higher than 400 Barrers for CO₂ and their selectivity for CO₂/CH₄ system is higher than 15. Other polymers have even higher selectivity for CO₂/CH₄ gas mixture; however the gas permeabilities obtained for them are two orders lower in comparison with polyimide membrane. With application of polyimide membranes CH₄ enrichment in a single stage is possible, what makes that type of membrane very attractive from technical and economical points of view.

In the case of gas separation, membrane fouling which is an onerous phenomenon observed in liquid separation does not occur. Therefore, gas separation (GS) modules can have high packing density, i.e. high area-to-volume ratio (m²/m³). The most appropriate are hollow fibers, since they have high mechanical strength, what is important when inside or outside the membrane capillary high pressure of gas is applied. In the case when raw gas pressure is higher than 2 MPa, the gas is fed from outside since the hollow fibers are more resistant to the compression than to the stretching. In the case when gas pressure is low the feed is introduced inside the micro-pipe. Presently manufactured hollow fibers are composed of nonporous separation layers (placed on outer or inner side of the fiber or capillary) and porous support.

In this work the tests were performed by use of the hollow fiber module, A-2 type (UBE) supplied by UBE Europa GmbH, with the productivity equal to 0.2 N m³/h for the feed pressure 0.6 MPa, retentate pressure 0.58 MPa, permeate at atmospheric pressure and Q_P/Q_R ratio 1:1, in the temperature range 10–60 °C.

Table 2

Separation of the CH₄ (50%) + CO₂ (50%) gas mixture with a A-2 membrane module

	Feed	Retentate	Permeate
Flow rate (N dm ³ /h)	100	50	50
Pressure (MPa)	0.60	0.58	0
Temperature (°C)	40	40	40
Gas mixture composition (mol%)			
CH ₄	50.0	89.5	10.5
CO ₂	50.0	10.5	89.5

3.2. Test rig

The test rig is shown in Fig. 1. It consisted of A-2 capillary module with polyimide membranes, two gas cylinders B1 and B2, TM feed temperature control system, two rotameters R1 and R2, two gas meters LG1 and LG2, Pi monometers, T thermometer, WAG-1 gas analyzer, Z1–Z13 valves and VR1 and VR2 distribution valves. In Fig. 1—F, R and P denote the feed, retentate and permeate streams, respectively.

4. Results and discussions

The separation efficiency of CO₂ and CH₄ gases was tested with apparatus presented in Fig. 1 and the influence of process parameters on methane enrichment was evaluated.

Two gas mixtures were used in experiments:

1. CH₄ (50%) + CO₂ (50%), $Q_P:Q_R = 50:50$.
2. CH₄ (68%) + CO₂ (30%) + H₂S (2%), $Q_P:Q_R = 50:50$.

In time of experiments the flow rates of the feed, permeate and retentate were measured and the composition of the gas streams was analysed with WAG-1 analyzer. Permeate and retentate flow rates ratio was kept as 50:50. The feed pressure was adjusted at 0.6 MPa, and temperature at 40 °C. The results of the experiments were presented in Tables 2 and 3. For both gas mixtures the enrichment of the retentate in CH₄ was high. At higher concentrations of methane in the feed, the higher concentrations in the retentate were reached, but the losses of CH₄ in permeate were high, as well. At 68 mol% CH₄ concentration in the feed gas, the 93.45 mol% content of CH₄ was achieved, what corresponds with G2-50 standard gas concentration. The experiments showed that it was rather difficult to remove H₂S from the gas

Table 1
Separation and selectivity parameters for different polymers used for manufacturing of membranes for CO₂ separation from N₂–CH₄–CO₂ mixture

Polymer	Permeability (Barrer)			Selectivity		
	N ₂	CO ₂	CH ₄	CH ₄ /N ₂	CO ₂ /N ₂	CO ₂ /CH ₄
Poly(4-methyl,1-penten)	6.7	84.6	14.9	2.22	12.6	5.68
PolyimideTMPA-6FDA	35.6	440	28.2	0.79	12.4	15.6
PPO	3.53	65.5	4.10	1.17	18.7	16.0
Polysulphone	0.20	4.90	0.21	1.05	24.5	23.3
Tri-bromodi-phenylopolycarbonate A	0.18	4.23	0.12	0.69	23.3	33.6

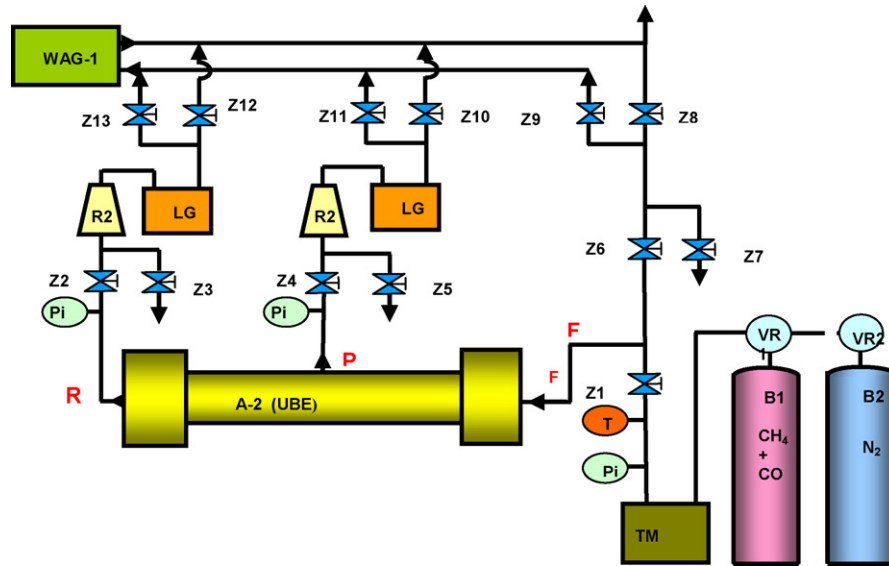


Fig. 1. A scheme of the test rig.

Table 3
Separation of the CH₄ (68%) + CO₂ (30%) + H₂S (2%) gas mixture with a A-2 membrane module

	Feed	Retentate	Permeate
Flow rate (N dm ³ /h)	100	56	44
Pressure (MPa)	0.60	0.58	0
Temperature (°C)	40	40	40
Gas mixture composition (mol%)			
CH ₄	68.0	93.45	35.75
CO ₂	30.0	5.65	61.0
H ₂ S	2.0	0.95	3.35

stream completely; however the concentration of 2 mol% in the feed used in experiment was higher as common H₂S content in biogas.

In Fig. 2 the variation of the flow rates of the process streams with CH₄ concentration— c_{mF} , is presented. The pressures were kept at 0.60/0.58 MPa as in previous experiment, at temperature 40 °C. The flow rate of the retentate was adjusted at the stable value— $Q_R = 50 \pm 0.01$ N dm³/h with free permeate outlet (to the atmosphere). Both, Q_F and Q_P flow rates decreased with c_{mF}

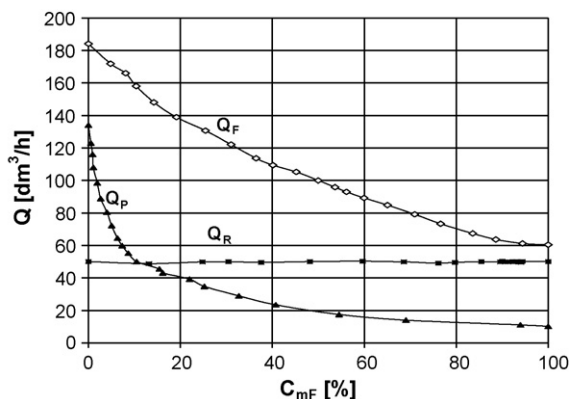


Fig. 2. Q_F , Q_P , and Q_R flow rates vs. CH₄ concentration in the feed— c_{mF} .

increase. In higher methane concentration the flow rate through the membrane was reduced, and lower flow rates of feed were necessary to keep retentate flow rate constant. In parallel, the increase of CH₄ concentration in both, retentate and permeate streams was observed.

Fig. 3 shows the variation of the methane concentration with splitting factor k_S (cut parameter). This factor was changed in experiments in proportion of 5:95–99:1. The term c_{mk} denotes the average CH₄ concentration along the capillary. The turning point of the $c_{mP}(k_S)$ curve is close to $k_S = 1$ that corresponds with flow rates ratio 50:50. Crossing that point one can observe detrimental increase of methane in permeate, while concentration in retentate gets stable.

Polyimide membranes allow separation of CO₂ and CH₄ gas mixture producing methane-enriched fuel gas. Permeability of CO₂ in polyimide membrane is 13-fold higher than of CH₄ gas. As a result of that, biogas of methane concentration c_{mF} , which enters the membrane module with flow rate of Q_F is split into two streams: permeate Q_P of c_{mP} concentration and retentate Q_R of c_{mR} concentration. The methane concentration in retentate is higher than inlet feed concentration and the relation $c_{mP} < c_{mF} < c_{mR}$ comes true. Running the process with splitting the streams as $Q_P:Q_R = 50:50$, one can obtain methane

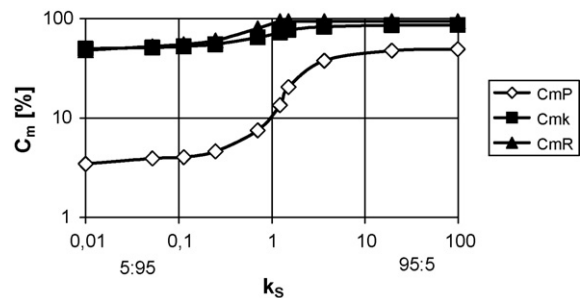


Fig. 3. The methane concentration in permeate c_{mP} , retentate c_{mR} and the average concentration in capillary c_{mk} in relation to the splitting factor k_S .

Table 4

Separation of CO₂/CH₄ from gaseous mixture (CH₄:CO₂ = 50:50) with A-2 module at different pressures p_F/p_R and temperatures of the feed

T (°C), p_F , p_R (MPa)	Feed		Permeate		Retentate	
	Flow rate, Q_F (N dm ³ /h)	CH ₄ conc., c_{mF} (%)	Flow rate, Q_P (N dm ³ /h)	CH ₄ conc., c_{mP} (%)	Flow rate, Q_R (N dm ³ /h)	CH ₄ conc., c_{mR} (%)
$T = \text{const. (40 °C)}, p_F, p_R$ —variable (0.30/0.28–1.0/0.99 MPa)						
0.30/0.28	46.60	50.0	23.66	10.46	22.94	89.96
0.40/0.38	65.36		32.25	10.61	33.11	88.93
0.50/0.48	82.20		40.84	10.57	41.36	88.93
0.60/0.58	102.65		51.22	10.49	50.03	89.77
0.70/0.68	119.89		59.37	10.53	60.52	90.24
0.80/0.78	140.05		70.21	10.63	69.84	88.96
0.90/0.88	160.09		79.87	10.36	80.22	89.58
1.0/0.98	183.64		91.60	10.71	92.04	90.14
$p_F, p_R = \text{const. (0.60/0.58 MPa)}, T$ —variable in the range of (20–50 °C)						
20	96.37	50.0	48.03	10.23	48.34	89.52
30	99.54		49.70	10.37	49.84	89.48
40	102.18		50.85	10.52	51.33	89.41
50	106.44		53.53	10.70	52.91	89.76

concentration in permeate and retentate $c_{mP} = 10.5\%$ and $c_{mR} = 89.5\%$, respectively. Higher concentrations of methane in the range of 91–94.4% are also possible.

In Table 4 the results of the experiments with variation of feed and retentate pressures and temperatures are presented. The CH₄ (50%) + CO₂ (50%) mixture was treated keeping the $Q_P:Q_R$ proportion as 50:50. The p_F and p_R pressures were adjusted in the range of 0.30/0.28–1.0/0.98 MPa at the stable feed temperature of 40 °C. Then, at constant feed and retentate pressures of 0.60/0.58 MPa, the temperature was changed in the range of 20–50 °C. The results showed four-fold increase of permeate flow rate with feed pressure increase from 0.3 to 1.0 MPa. There was no change of methane concentration in permeate observed in that feed pressure range. When temperature was changed from 20 to 50 °C, slight increase of permeate flow rate was noticed: $Q_{P(50\text{ °C})}/Q_{P(20\text{ °C})} = 1.12$ and growth of methane concentration in permeate: $c_{mP(50\text{ °C})}/c_{mP(20\text{ °C})} = 1.05$. The separation factors $\alpha_{\text{CH}_4/\text{CO}_2}$ calculated from Eq. (1) were in 0.114–0.120 range, that means permeate fraction was enriched in CO₂, however concentration of methane in that stream was 10.23–10.71%. To avoid the CH₄ lost the additional treatment of permeate is necessary. It can be achieved by the next stage of processing, e.g. two-step membrane installation.

5. Conclusions

The data collected in laboratory experiments demonstrated the potential of membrane separation for biogas upgrading. The tests showed the influence of such a process parameters as inlet gas concentration, temperature and pressure on the level of methane enrichment. The design parameters like splitting factor k_S influenced separation, as well.

The polyimide membranes tested in the work can be applied for methane enrichment in biogas produced by biomass fermentation, as well as for other applications aimed in CH₄/CO₂ separation (landfill gas, natural gas). At common concentration of CH₄ a single stage unit is sufficient to achieve 94% enrich-

ment, and multistage systems are not required. For lower CH₄ concentrations (<60%) the standard gas GZ-50 can be produced only with additional enrichment stages. The high permeability of the polyimide membranes to H₂O and H₂S, common impurities of gas produced in biomass fermentation process, makes them useful for biogas processing without special pre-treatment. For further evaluation of the technology the site experiments with real biogas from anaerobic fermentation will be of great importance.

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