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Membrane enrichment of biogas from two-stage pilot plant using agricultural waste as a substrate

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ABSTRACT

The separation of methane from raw biogas was the main purpose of this study. A polymer membrane was used in order to obtain the high energy product, which can be utilized in cogeneration systems (CHP) or as a natural gas substitute. The study showed that using a polyimide hollow fiber module for biogas purification was an efficient method (low energy consumption, small-sized device and a simple separation module). The satisfying results of laboratory tests caused scale up the installation. Different synthetic gas mixtures were used at the lab-scale, while in the field tests, raw biogas from a Polish two-stage agricultural biogas plant was processed. The plant used the following substrates: maize silage, grass silage and blends of these substrates with different supplements. The concentration of methane in the raw gas was up to 70% volume and contained up to 250 ppm of H₂S. In both cases (laboratory and field tests), the retentate after membrane treatment was characterized by high methane concentration (up to 90% volume) and was free of H₂S. The applied membrane demonstrated high selectivity for separating CH₄ from CO₂, H₂S and H₂O. The permeate stream contained less than 5% volume of CH₄, which ensured low losses of the desired biogas component. The influence of pressure (below 10 bars) and stage cut on the quality of the product were analyzed to develop optimal process conditions for mobile plant construction.

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1. Introduction

The objective of the study was membrane upgrading of the raw biogas obtained from two-stage pilot plants. Biogas is an alternative carrier energy, which can be used as a substitute of natural gas. Biomethane can be produced in controlled fermentation such as in agricultural biogas plants. Biogas is a mixture of gases generated from the anaerobic microbial digestion of organic wastes such as manure, maize silage,

grass silage and whey. Typically, agriculture biogas contains 45–70% CH₄, 25–45% CO₂, small amounts of hydrogen sulphide (from 0 to 30,000 ppm), water vapor and traces of other gases [1]. The composition of biogas and yield fermentation depends on the source of the substrates and process conditions. The substrates used in biogas production can be divided, depending on their origin, into: municipal, industrial or agricultural waste or energy plant farming. Methane fermentation is a good method of using waste such as manure, whey and sewage. The most productive feedstock

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(high value of biogas production from dry organic matter) used in agricultural biogas plants is maize silage and grass silage, and blends of these substrates with different supplements. Separation of hydrolyzes from methanogenesis is the most effective way of generating biogas (this method is applied in the biogas installation that was used in this study, constructed in Szewnia Dolna – Lublin Voivodeship, Poland).

Raw biogas exhibits a significantly lower Wobbe index (heating value) compared to natural gas. The removal of carbon dioxide from biogas to attain a level of methane concentration of 90% volume can not only effectively increase the Wobbe index, but also reduce corrosion caused by acidic gas components. The purified biogas (with a high concentration of methane) can feed cogeneration systems in order to simultaneously produce heat and electricity (CHP – combined heat and power). Upgraded biogas may also be compressed and liquefied for vehicle fuel or injected into a public natural gas grid. Water washing, chemical absorption, pressure swing adsorption (PSA) and membrane separation are the most well-known and some of them are commercially available techniques that can be used for biogas upgrading [2]. A new method of gas separation is represented by ionic-liquid membranes (main advantages: high fluxes through membranes and a very good selectivity) [3]. It seems that membrane technology has the most potential. In comparison to the conventional methods, membrane separation exhibits many advantages, including low operation cost, an easy-to-maintain system with process flexibility and no additional chemical substances [4]. The important advantages of membrane separation also comprise continuity of the process. In accordance with the SWEA (Severn Wye Energy Agency) data, the investment cost of membrane installation for biogas plant of 250 m³ biomethane/h capacity is in the range from 4700 to 4900 €/m³/h. For the same capacity of the installation with water scrubbing device the price is 5500 €/m³ biomethane/h and 5400 €/m³ biomethane/h for biogas plant with PSA. Membrane technique provides widely adapt the plant layout to the local conditions by the application of different module configurations and multiple membrane stages. Many reviews and research reports about membrane methods have been published; however, most of them concern theoretical and laboratory tests performed using a model gas mixture containing CO₂ and CH₄ [5–10]. Our team published one of the earliest reports on laboratory investigations on this subject [6]. The good results enabled the continuation of the study of upgrading raw biogas using membrane techniques. Therefore, in this work, we tested a polyimide hollow fiber module for enriching raw biogas produced by two-stage pilot plants using agricultural wastes and cultivated plants as substrates.

2. Dense membrane separation theory

Membranes for the separation of gas mixtures can be divided into porous and dense ones. When the pore size is small compared to the mean-free-path of the gas molecules, gas with lower molecular weights permeates much faster. The selectivity of porous materials is proportional to the square root of the molecular weights ratio; therefore, the enrichments that can be achieved with this method are small. The low efficiency

of using a single module requires many separation stages. The membrane technique became more popular when the method of dense membrane manufacturing was developed.

Gas transport through dense polymeric membranes is based on a solution-diffusion mechanism, which occurs in three steps. First, on the high pressure side (in the upstream), the gas molecules dissolve on the membrane face. Next, the penetrate molecules diffuse across the membrane until it is desorbed at the downstream face of the membrane. The relationship between diffusivity and solubility can be described by the equation:

$$P = D \cdot S \quad (1)$$

where P is the permeability coefficient in the Barrer ($10^{-10} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$), D is the diffusivity coefficient ($\text{cm}^2 \text{ s}^{-1}$), the mobility of molecules across the membrane, and S is the solubility coefficient ($\text{cm}^3 \text{ (STP) cmHg}^{-1}$), which measures the solubility of gas molecules within the membrane [11,12].

The permeability of a polymer for gases is dependent on the membrane state, the nature of the gas and the interactions between them. The state of the polymer is characterized by the glass transition temperature, T_G . Below T_G , the polymer is in its glassy state and above, it is rubbery. Glassy polymers are most often used in CO₂/CH₄ separation because of their high permeability and outstanding thermal/chemical stability. In Table 1, the permeability of different polymers is presented.

As shown in the table above, polyimides have high permselectivity compared to the other polymers used in separating CO₂. For many years, the most widely used glassy polymer in CO₂ separation has been cellulose acetate (CA). The first industrial plants using CA were installed in the 1980s and it currently dominates the natural gas processing market. However, the huge concern regarding CA membranes is their susceptibility to plasticization by CO₂, which reduces its mechanical stability while decreasing its separation performance and increasing the aging of the material. It is increasingly becoming clear that CA is used only as the porous support structure in asymmetric polymeric membranes. This is due to the low cost of CA production and the well-known method of its manufacturing. At present, there is much effort being put to develop plasticization-resistant materials with increased CO₂ permeability and CH₄ selectivity.

Good mechanical properties and thermal/chemical stability are presented by polyimides. They are commonly prepared by reacting a diamine and an anhydride. A large number of different types of these two compounds contribute to a wide range of polyimides with great selective properties. This explains the fact that polyimides comprise one of the most studied types of polymers for membrane separation of CO₂/CH₄. There are a lot of publications describing properties of polyimides [16–18]. In particular, polyimides have robust mechanical properties to withstand high-pressure processes. They are characterized by long durability and high chemical stability. The polyimides are less susceptible to plasticization by carbon dioxide than CA; therefore, they are supposed to be more suitable for CO₂ separation. At present, polyimide membranes are commercially available from a few manufacturers: Medal (Air Liq-uide), IMS (Praxair) and UBE Industries Ltd.

Table 1 – Permeability and selectivity of CO₂ and CH₄ in various polymers.

Polymer	P _{CO₂}	P _{CH₄}	$\alpha_{\frac{CO_2}{CH_4}}$	Source
PDMS (polydimethylsiloxane)	2700–4550	800	3.37	[15]
PC (polycarbonate)	4.23	0.13	32.5	[15]
PSU (polysulfone)	5.6	0.25	22.4	[8]
CA (cellulose acetate)	6.3	0.21	30	[8]
PPO (polyphenylene oxide)	75.8	11	6.89	[8]
EC (ethyl cellulose)	26.5	19	1.39	[8]
PI (polyimides)				
BTDA–ODA/pPDA (3,3'-4,4'-biphenyltetracarboxylic dianhydride – 4,4'-oxydianiline/1,4-phenylenediamine)	0.213	0.01	22.17	[13]
6FDA/BTDA–ODA (4,4'-hexafluoroisopropylidene-diphthalic anhydride/3,3'-4,4'-biphenyltetracarboxylic dianhydride–4,4'-oxydianiline)	2.559	0.083	30.95	[13]
BTDA–ODA/DAM (3,3'-4,4'-biphenyltetracarboxylic dianhydride – 4,4'-oxydianiline/2,4,6-trimethyl-1,3-phenylenediamine)	1.70	0.066	25.56	[13]
PMDA–ODA (pyromellitic dianhydride/4,4'-oxydianiline)	3.55	0.0937	37.88	[3]
PMDA–MDA (pyromellitic dianhydride/mellitic dianhydride)	4	0.093	43	[8]
6FDA–MDA (4,4'-hexafluoroisopropylidene-diphthalic anhydride/mellitic dianhydride)	19	0.42	45.24	[8]
6FDA–IPDA (4,4'-hexafluoroisopropylidene-diphthalic anhydride/isopropylidene dianiline)	30	0.7	42.85	[8]
6FDA–ODA(4,4'-hexafluoroisopropylidene-diphthalic anhydride/4,4'-oxydianiline)	16.70	0.341	48.97	[8]
6FDA–DAF(4,4'-hexafluoroisopropylidene-diphthalic anhydride/diaminofluorene)	32.2	0.630	51.11	[8]
6FDA–BAHF (2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride/2,2-bis(4-aminophenyl)hexafluoropropane)	51.2	1.34	38.2	[8]
BPDA–mTrMPD (3,3'-4,4'-biphenyltetracarboxylic dianhydride/2,4,6-trimethyl 1,3-phenylenediamine)	137	8.08	16.95	[8]
6FDA–mPD (4,4'-hexafluoroisopropylidene-diphthalic anhydride/m-phenylene diamine)	11.03	0.19	58	[14]

The polyimides are glassy polymers of high glass transition temperature and are characterized by lower density and extremely large free volume (up to 20%). This feature is caused by a non-thermodynamic equilibrium state during fast chilling. Therefore, the polymer chains are packed imperfectly, leading to excessive free volume in the form of microscopic gaps in the polymeric matrix. In this case, sorption can be described by complex sorption isotherms (Fig. 1). The total concentration of dissolved gas in the bulk membrane can be expressed as Henry–Langmuir's sorption model [19]:

$$c = k_D \cdot p + \frac{c_L \cdot b \cdot p}{1 + b \cdot p} \quad (2)$$

where k_D (cm^3 (STP) cm^{-3} Pa^{-1}) is Henry's constant, p (Pa) is partial pressure, c_L (cm^3 (STP) cm^{-3}) is the maximum sorption capacity, and b (Pa^{-1}) the hole affinity constant.

The sorption coefficient of gas in the polymer depends on the condensation ability of this gas. For example, CO₂ and H₂S are more condensable than CH₄, so they can be more easily separated from each other. This feature is more significant for rubbery than glassy polymers.

While permeating through the membrane, the gases are separated due to the differences in their diffusivity and solubility in the membrane matrix. The diffusion process in glassy polymers is more complex compared to that in rubbery ones and depends on the diameter of the gas molecule. Gas

diffusion in polymer matrix proceeds only in free volume, which generally occurs in glassy polymers.

The balance between solubility and diffusivity determines whether a membrane material is selective for the different gaseous contents of the mixture. Membrane selectivity determines the ability of a membrane to separate two molecules and can be described as the ratio of their permeabilities:

$$\alpha_{AB} = \left(\frac{D_A}{D_B} \right) \left(\frac{S_A}{S_B} \right) \quad (3)$$

where index A always concerns a more permeable gas.

Permeability is defined as the gas flux passing through a unit area of membrane and under a pressure gradient and is expressed as:

$$P = \frac{Q \cdot \delta}{A \cdot \Delta P} = \frac{Q}{n \cdot \pi \cdot d \cdot l \cdot \Delta P} \quad (4)$$

where P is permeability, Q the normalized gas flux, δ the thickness active layer, ΔP the pressure difference between the feed side and the permeation side of the membrane, A the membrane effective surface area, n the number of fibers in the module, d the outer diameter of hollow fibers, and l the length of the hollow fibers.

Membrane permeability is inversely proportional to the membrane area required for separation. Of all the types of membrane modules, the hollow fiber has the most extensive

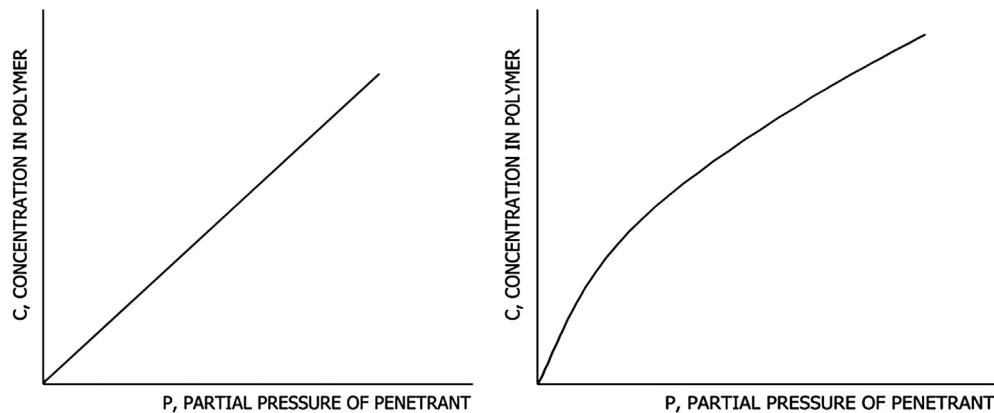


Fig. 1 – Isotherms of sorption Henry's and dual model.

contact surface. To maximize the area, very small tubes are packed closely together. The scheme of the used module is presented in Fig. 2.

The high pressure stream feeds into the inner side of the tubes and the low pressure permeate on the outside of the fiber bundle (bore-side feed) is collected. The most used polyimide membrane is prepared as an asymmetric hollow fiber module, which can achieve a three-times larger area per unit volume than the spiral wound modules. The manufacturing costs of hollow fibers are considerably lower at \$2–5 m² compared to spiral wound modules at \$10–100 per m² [5].

The hollow fiber membranes are enclosed in a module. The efficiency of the gas separation process can be described by two parameters: the purity of the product gas and the fraction of the gas in the feed recovered as the product (the recovery). These parameters are determined by the membrane's intrinsic properties, its permeability and selectivity, as well as by operating factors such as total and partial pressure on the feed and permeate sides, feed flow rate and pressure drop on either side of the membrane. These factors determine the membrane area and compression work that is needed for an economic evaluation of the separation process.

3. Biogas production pilot plant

Methane fermentation is an anaerobic process consisting of four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. A large number of microbial species are capable of using organic substrates such as carbohydrates, proteins and lipids to produce volatile fatty acids (VFAs), which can then be converted into methane and carbon dioxide by methanogenic microorganisms. Acidogens and methanogens have different physical, biochemical and environmental requirements. Therefore, biogas production can be conducted in a two-stage process – separation of hydrolyzes from methanogenesis [20]. This is used in the two-stage biogas system in Szewnia Dolna. This plant works according to the following scheme: raw material is fed into the shredder and then directed through the biomass inlet to a hydrolyzer. To the hydrolyzer can be added post-fermentation effluent or water to achieve proper dry matter content in suspension. Then, the hydrolyzed biomass is transported by a pump to the fermentor. The slurry in the digester is mixed with the circulation induced by a pump-hydro mixing (the pumped slurry feeds the fermentor by a free-falling stream of liquid that breaks the scum formed during methane fermentation). The biogas is removed from

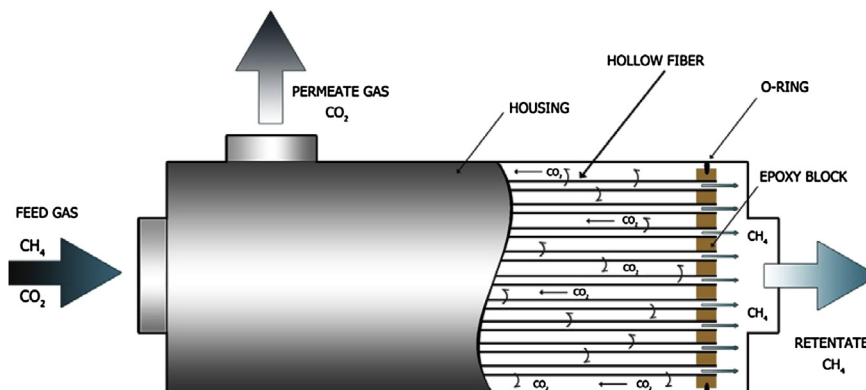


Fig. 2 – Scheme of the hollow fiber module.

the free volume over the surface of the fermentation mixture to the biogas reservoir and subsequently led to a membrane separation unit. The digested biomass (organic fertilizer) is directed into the digestate tank. In comparison to the single stage process, the two-stage method is characterized by the greater the stability of the process, the shorter the residence time, the higher the load of dry matter in the digester and contributes to the higher the efficiency. The pilot plant scheme is presented in Fig. 3.

The hydrolyzer and fermentor are horizontal tanks made of polyethylene (PE-HD), and are thermally insulated with a layer of glass wool, having a volume of $V_h = 1.5 \text{ m}^3$ and $V_f = 8 \text{ m}^3$, respectively. The aqueous suspension of biomass in the digester takes about 70% of the volume of the tank. Above the surface of the suspension is the gas cushion of biogas with a volume of about 2 m^3 . The efficiency of biogas production is $0.2 \text{ m}^3/\text{h}$ and the resulting concentration of CH_4 in the raw biogas is 55–70%.

4. Laboratory tests

In this work, the tests were performed using the hollow fiber module supplied by UBE Europe GmbH, with a productivity of less than $0.2 \text{ Nm}^3/\text{h}$. The effective area of the membrane used in the test was 0.18 m^2 .

Gas mixtures from a cylinder were transported to the membrane module using the reduction valve (pressure

adjustment device). The pressure of the gas in the feed stream was changed from 0.2 to 0.8 MPa in the upstream side. Flow, pressure and temperature of the gases were measured before entering the membrane. The feed gas was divided in the module into two streams: permeate and retentate. The permeate stream was released at low (atmospheric) pressure; a throttle valve was installed at the retentate line to induce a pressure difference that was the driving force of the process. The pressure in the system and the stage cut depended on the degree of the valve opening. Gas flow of all the streams was measured by panel flow meters. The membrane module was thermostated to provide stable process conditions. The installation containing the thermostated hollow fiber membranes is schematically shown in Fig. 4.

For the lab-scale tests, pure CO_2 or CH_4 gas, as well as their mixture, was purchased from Multax Ltd. The compositions of all the gas streams were determined by a gas chromatograph and three kinds of handheld biogas analyzers (Gas Data GFM416, GA 45 PLUS Geotechnical Instruments and DP 27 Bio Nanosens). Different synthetic mixture compositions of CH_4/CO_2 were used in the assays to test module performance. The methane content in these mixtures ranged from 50% volume to 80% volume, which corresponded to the content of CH_4 in raw biogas.

The effect of pressure, feed flow and stage cut of the streams were measured. The membrane stage cut was defined as the fraction of the feed gas stream permeating the membrane, and was expressed as:

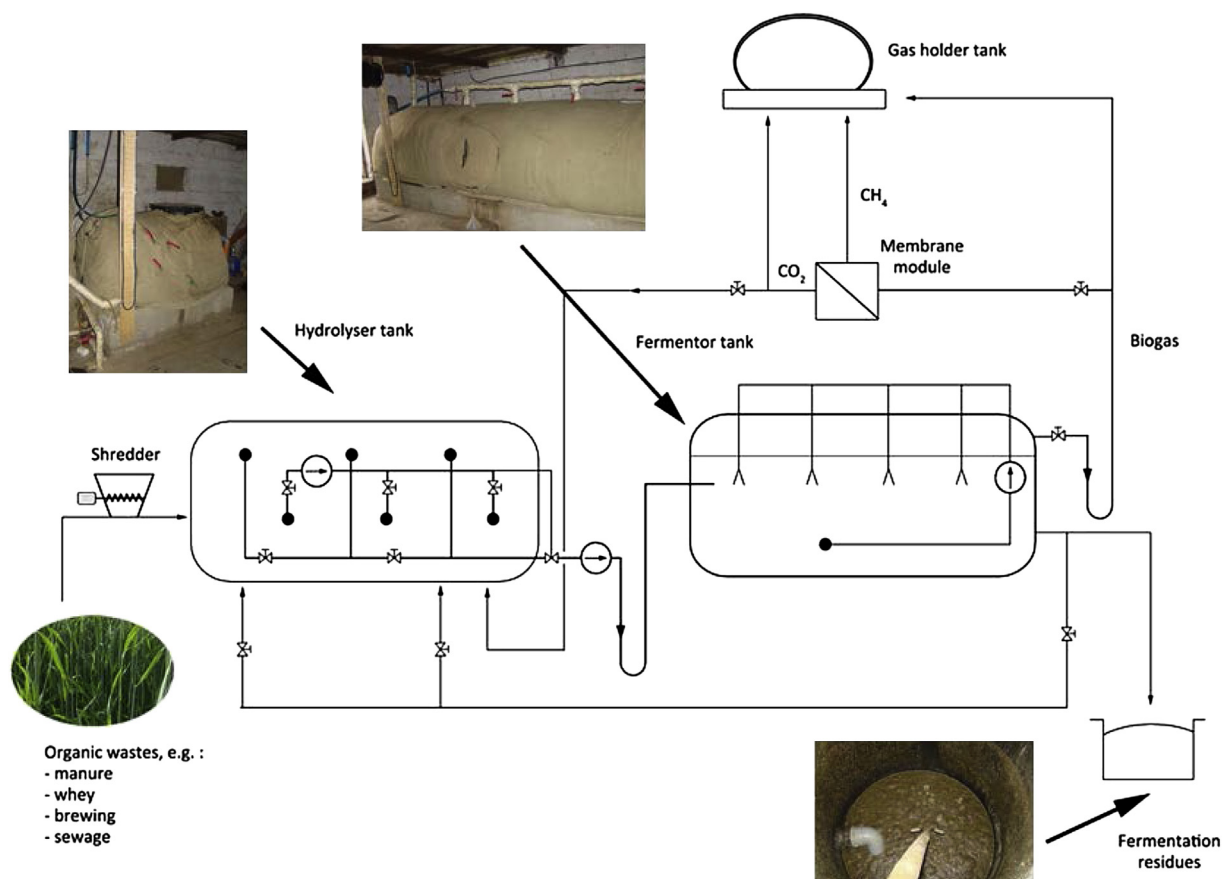


Fig. 3 – The scheme of the two-stage plant (Szewnia, Poland).

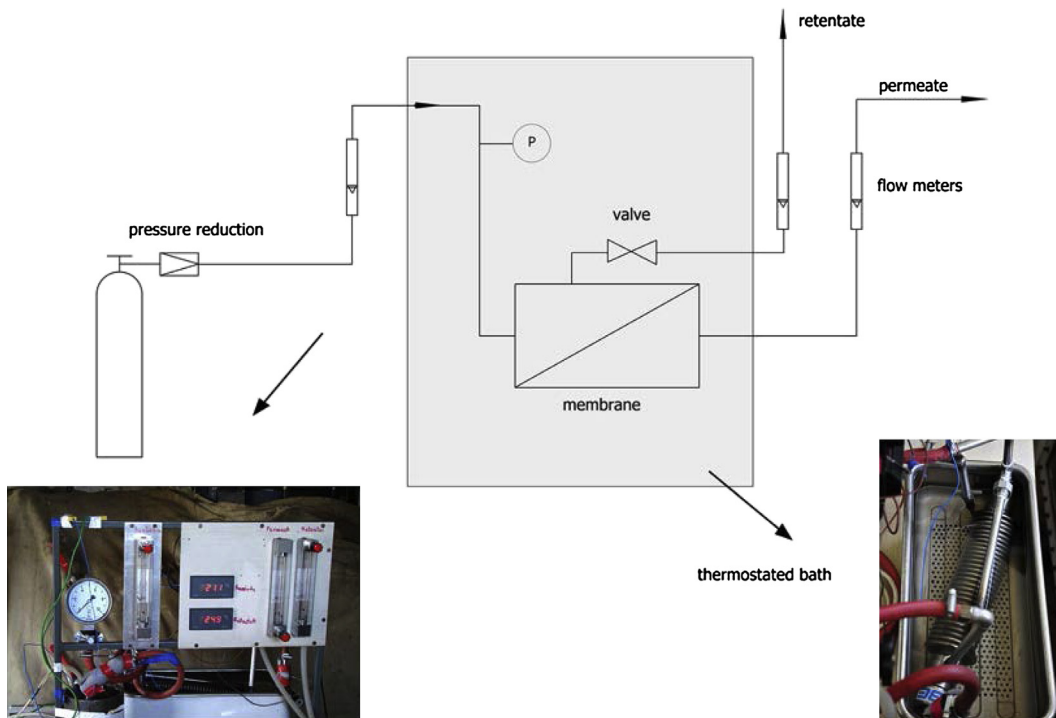


Fig. 4 – The scheme of the laboratory installation.

$$\theta = \frac{Q_P}{Q_F} \tag{5}$$

The upper stream pressure influences the process presented below in Fig. 5. As an example, the mixture with 70% volume of CH₄ is shown. With an increase in the pressure feed, the methane content in the retentate increases too. Raw biogas also displays this trend and will be discussed later in the text.

The feed flow was changed to the range of 10 NI/h–1200 NI/h in the laboratory study. The best methane enrichment was obtained for low flow and a stage cut of less than 0.5. However,

such small flows were not acceptable from a practical point of view. Fig. 6 illustrates methane enrichment depending on the quantity of feed flow.

According to the membrane’s manufacturer, the stage cut should be 0.5. This was confirmed in the laboratory-scale tests. The best methane enrichment was obtained for low product flow (Fig. 7). Small amounts of methane from the feed permeated through the membrane and was lost to the permeate stream. Fig. 7 shows that methane concentration in the permeate stream also increased with a rising stage cut.

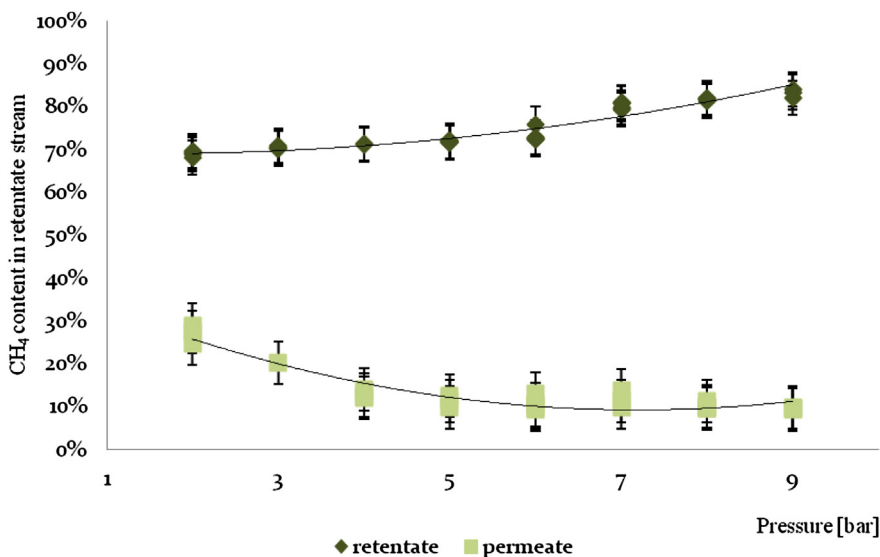


Fig. 5 – Effect of pressure on methane content in the retentate and permeate streams [feed mixture: 70% volume of CH₄ and 30% volume of CO₂; feed flow: 100 NI/h].

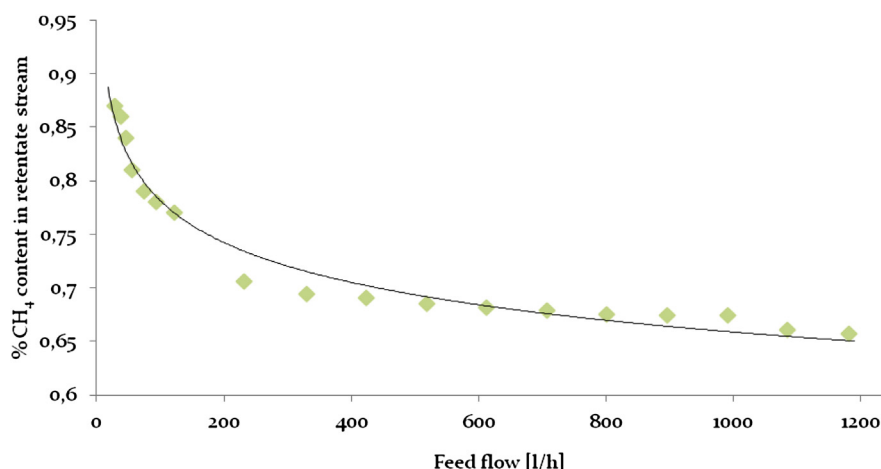


Fig. 6 – The effect of feed flow on methane enrichment in the retentate [feed mixture: 60% volume of CH₄ and 40% volume of CO₂; feed pressure: 0.6 MPa].

This is a technical and economic problem that requires optimization of the industrial installations when biogas is used as a fuel.

The effective area of the polyimide membrane used was calculated as 0.18 m². The hollow fibers were immersed in liquid nitrogen and fractured to prepare samples for SEM examination. Membrane structure was determined by the Phenom Scanning Electron Microscope (SEM). An SEM image of a used polyimide membrane is shown in Fig. 8, where it can be observed that the surface morphology did not have pores.

Asymmetric membranes are characterized by a two-layer structure. Inside the membrane, there is a thick support layer (more or less porous), while the surface of the support is coated by a dense layer. The investigated polyimide membrane had a very thin active layer, which contributed to good separation properties. To achieve large permeance, it is important to make a very thin dense layer. The effective layer was observed using

a magnification of 9600 times and the thickness of it was determined as approximately 1 μm.

5. Field tests

The field tests were conducted in the biogas installation in Szewnia Dolna (East-South Poland, near the town of Zamosc) in the summer. Maize and grass silage, beet pulp and whey were used as substrates for biogas production. The module under investigation was installed at the bypass of the main biogas stream after the water vapor condensation unit. Water vapor removal is necessary to protect pipelines, aggregates and other equipment. The relative moisture of the biogas in the fermentor was 100%; thus, the biogas was saturated with water vapor. As a result of biogas cooling (below the dew point), water vapor was separated into the condensate form.

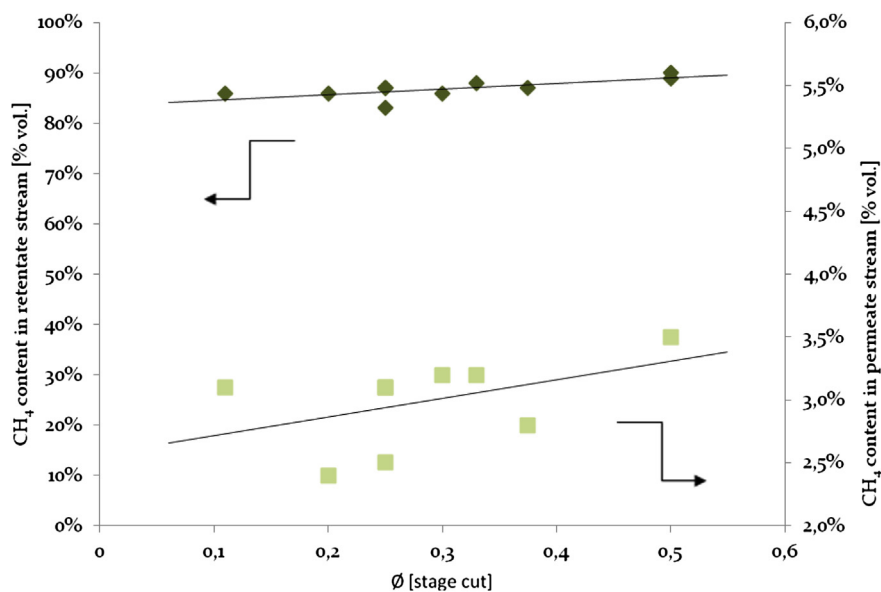


Fig. 7 – The effects of stage cut on methane content in the retentate and permeate [feed mixture: 54% volume of CH₄ and 46% volume of CO₂; feed pressure: 0.6 MPa].

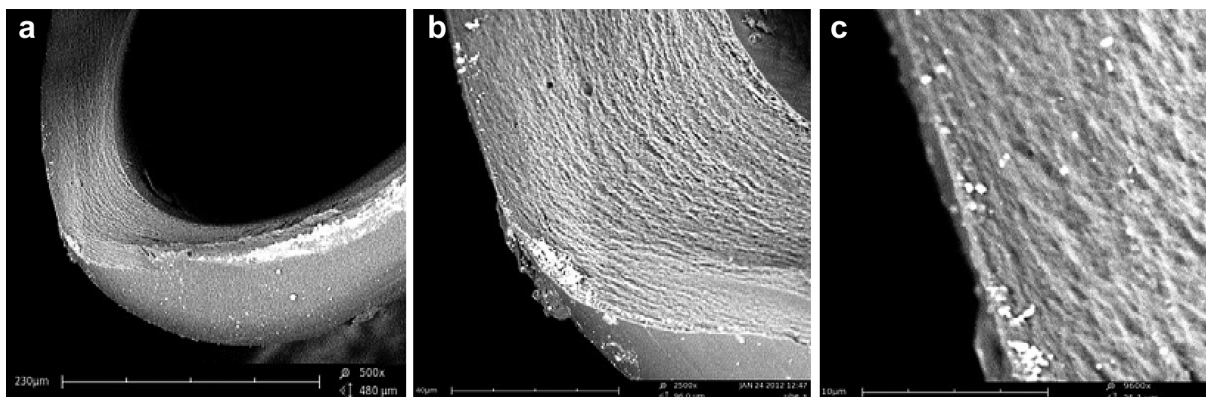


Fig. 8 – SEM image of the polyimide's hollow fiber structure (magnitude: (a) 500 \times , (b) 2500 \times and (c) 9600 \times).

This can be removed from biogas by the adsorption methods. To prevent the module from corrosion, water from the gas flow was collected in a condensate trap placed on a gas pipeline during the cooling of warm gas leaving the digester. In addition, zeolite 3-A was used as an adsorbent to remove the water after a compression process.

In addition to methane, carbon dioxide and water vapor, biogas contains hydrogen sulphide. Even trace amounts of H_2S are toxic and cause corrosion of the installation. For this reason, desulphurization and dehydration of biogas should be carried out by: biological desulphurization, iron chloride dosing to digester biomass, as well as adsorption onto iron oxide (pellets or impregnated wood chips), activated carbon, and caustic soda, or absorption in water or Selexol. The membranes used in this study, in conjunction with the hydro piston compressor, allowed the almost complete removal of hydrogen sulphide, which permeated the membrane with the carbon dioxide that was eventually recycled to the hydrolyzer.

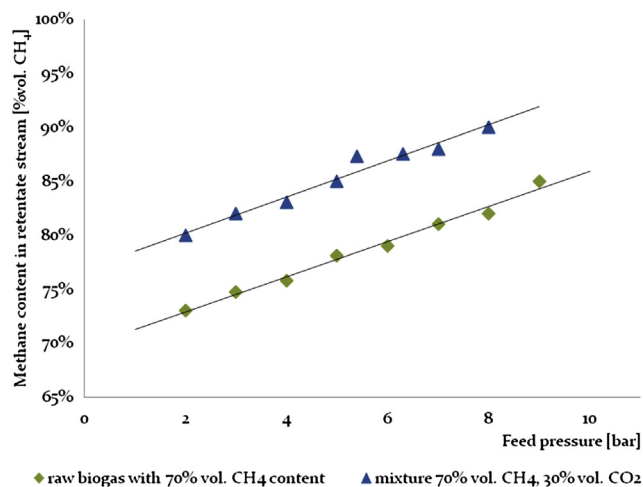


Fig. 9 – A comparison of the effect of pressure on methane content in the retentate between the synthetic mixture (laboratory test) and raw biogas (field test) [mixture: 70% volume of CH_4 and 30% volume of CO_2 , biogas: 69% volume of CH_4 and 30% volume of CO_2 , 20 ppm H_2S ; feed flow: 100 Nl/h].

As mentioned earlier, maize silage, grass silage, beet pulp and whey were used as a substrate during the tests. The biomass was periodically loaded into the hydrolyzer and the operation of the plant was semi-continuous. Biogas yield was 0.2 m^3 (0.35–0.46 m^3/kg dry matter) depending on the substrate applied, retention time – 21 days, the process was mesophilic. Methane concentration in the raw biogas obtained from the biogas plant was higher than that reported in the literature (Table 2), thus demonstrating the advancement of this new technology.

The applied pressure of the biogas feed ranged from 0.2 to 9 MPa. The results are presented below on the graphs. As mentioned above, the same pressure recovery of methane in the retentate stream was less effective than that obtained in the laboratory-scale tests. This could be explained by the presence of a plasticizing agent in the biogas. The most important plasticizing ingredient is carbon dioxide, but it should be mentioned that other gases such as water vapor and trace components (e.g. siloxanes, hydrocarbons) could also exert similar effects. The absorbed components swell the polymer and change the packing of the polymer chains. In accordance with the dual model, gas transport occurs by diffusion and sorption inside the polymer. Mixtures with CO_2 contribute to membrane swelling, which increases the segmental mobility of the polymer chains and decreases the sorption of CH_4 . This unwanted process affects mass transport and changes the separation efficiency.

Compared to the results obtained at the laboratory-scale, methane enrichment from raw biogas was acceptable from a practical point of view (Figs. 9 and 10).

The measured content of H_2S in the gas stream during the experiments ranged from a dozen to several hundred ppm. The highest concentration measured in the yield tests was 243 ppm. After membrane separation, the product contained only 40 ppm of this acidic gas.

6. Conclusions

The results demonstrated the possibility of biogas enrichment in a single step from 60% CH_4 to 80% CH_4 , with a stage cut of less than 0.5. The losses of CH_4 in permeate did not exceed 5%. H_2S

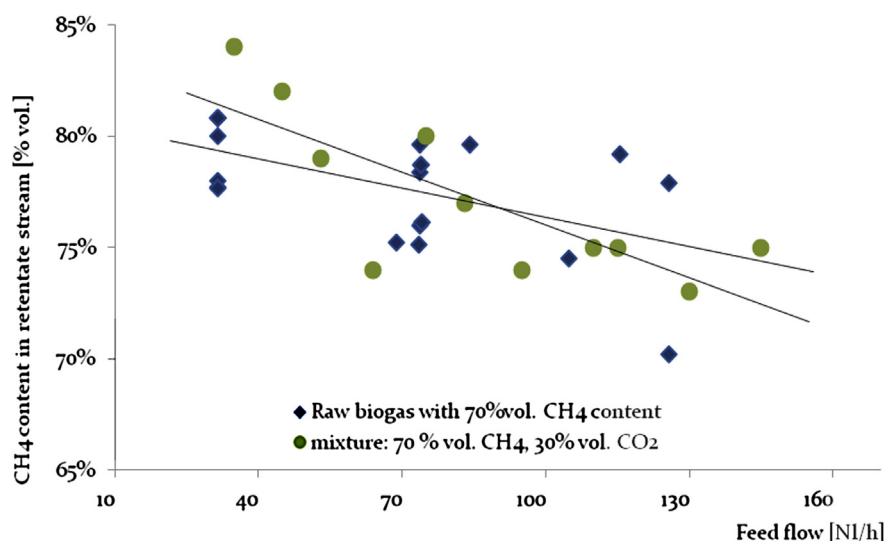


Fig. 10 – A comparison of membrane enrichment between synthetic mixtures (laboratory test) and raw biogas (field test) with similar methane content (mixture: 70% volume of CH₄ and 30% volume of CO₂, biogas: 69% volume of CH₄ and 30% volume of CO₂, 20 ppm H₂S; feed pressure: 0.6 MPa).

Table 2 – Methane content in biogas produced from various wastes.

	CH ₄ [% vol.]	
Maize silage	73	This work
Maize silage	68	[21]
Grass silage	72	This work
Grass silage	55	[22]
Beet pulp	62–69	This work
Beet pulp	54	[23]
Whey	64–70	This work
Whey	62	[24]

was almost completely concentrated in permeate, which was recirculated to the hydrolyzer to achieve an oxygen-free atmosphere. To obtain better enrichment, a membrane cascade or recirculation of the exhaust gas stream is suggested. The upgraded biogas could be employed for household uses and after an additional enrichment using a second step; it can be used for all applications designed for natural gas. To achieve a methane enrichment of 92%, a three-stage cascade has to be applied. On the basis of these experiments, a mobile membrane installation with a yield of 10 m³/h of enriched gas flow has been constructed and long-term operational tests will be performed.

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