New composite polymer membranes for biogas separation

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Biogas can be used as an alternative energy source. Unfortunately presence of carbon dioxide in a composition of biogas makes compression and transportation difficult. In addition CO_2 makes biogas lower calorific. That is why new methods for carbon dioxide separation from biogas are to be explored. Obtained results for polypropylene membranes modifications by polydimethylosiloxanes are presented in this paper.

Keywords and phrases: biogas, gas separation, membranes for gas separation.

Introduction

In recent years a continuous climate changes, such as global warming, are noted. This tendency is related to the carbon dioxide emission. Therefore scientists are looking for new sources of energy, which can reduce CO_2 emission. According to the European Union by the year 2020, 20% of energy in Europe has to come from renewable sources [1].

Biogas is one of the many renewable energy sources. It is attractive as a source of energy, because its production method is one of the oldest in industrial wastes disposal [2]. Biogas can be produced during anaerobic fermentation of biological wastes such as: municipal solid waste, industrial waste water or vegetable wastes [3]. Composition of biogas depends on fermentation method, but it contains 50–70% of methane, 30–45% of carbon dioxide, 1–5% of hydrogen, 0,1–0,5% of hydrogen sulphide and trace amounts of other gases and organic vapors [4].

Presence of non-flammable gases in biogas, such as carbon dioxide may reduce its calorific value, simultaneously compression and transport of biogas is uneconomical [3]. These gases limit application of biogas and eliminate biogas as a fuel for car engine [5]. To increase calorific value of biogas carbon dioxide should be removed [6]. Removal of carbon dioxide can be achieved by: chemical or physical absorption, adsorption on solid medium, cryogenic separation or membrane separation.

Membrane separation is a method consisting in going through a thin membrane part of biogas components. Transport in membrane is driven by pressure difference which depends on ingredients permeability [3]. To separate carbon dioxide from biogas are widely used “glassy” polymers such as: cellulose acetate, polyimides or polysulphones [7], but some rubbery polymers, as PDMS are also used. Membrane technology is energy efficient and most effective. Membrane techniques are simple and easy to scale up to meet industrial needs.

Experimental

In our study composite membranes were manufactured by applying polysiloxane on a surface of support. Applied polymer creates thin selective layer on a support. As a support we used polypropylene capillary membranes produced by Polymem Ltd. Average pore diameter in these membranes is 0.3 μm, while its outer and inner diameter is 2.7 mm and 1.7 mm, respectively.

For membrane modification three polydimethylosiloxanes such as: Polastosil M33, Polastosil M60 (Silikony Polskie Sp. z o.o.) and Sylgard 184 (Dow Corning Corporation) were used.

Modified membranes were inspected using scanning electron microscope. The most promising modifications were selected for further investigations. Modules were constructed from previously selected modified membranes and analyzed in three separate experiments. In the first experiment bore side feed were applied, while in the second and the third experiments shell side feed were applied. Feed in the first experiment contained three gasses: CO_2, CH_4 and H_2, while in the second experiment it was a mixture of CH_4 and H_2, and in the third experiment — a mixture of CO_2 and H_2. During the second and the third experiments permeate flow measurement was available. In all experiments composition of permeate was analyzed by gas chromatography [8].

Results

Selective layer made on the support by Polastosil M33 was not uniform. Also this polymer was not migrating into a support. In fact of empty spaces in the selective layer these modifications were eliminated from further researches, because small molecules such as: carbon dioxide, methane and hydrogen might go freely through selective layer.

Solution of Polastosil M60 formed a suspension which was sedimenting after awhile. Also selective layer made by this polymer was chipping from the surface of the support. This fact eliminated membranes modified by Polastosil M60 from further researches.

Selective layer made by Sylgard 184 was uniform. Also this polymer in contrast to Polastosil M33 and M60 was migrating into a support. According to SEM pictures membranes modified by this polymer were selected for further researches.

An example of membrane used in the first module is presented in Fig. 1. These membranes were modified once on the outside of the support surface by Sylgard 184.

Membrane used in construction of the second module is presented in Fig. 2. These membranes were modified on the outside and inside surface of a polypropylene membrane by Sylgard 184.

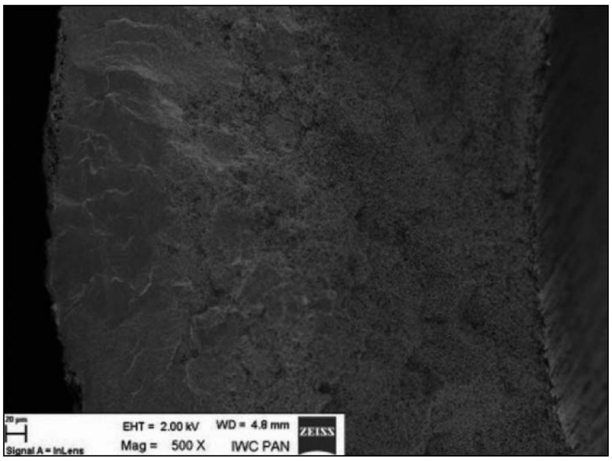

Fig. 1. Cross-section of membrane used in the first module. Modified on the outside of the support surface by Sylgard 184.

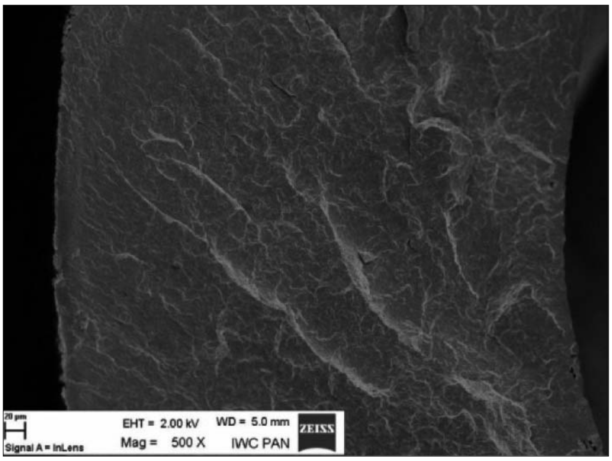

Fig. 2. Cross-section of membrane used in the second module. Modified on the outside of the support surface by Sylgard 184.

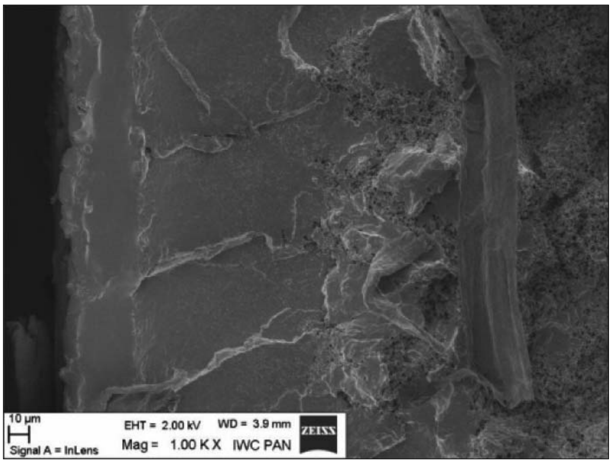

Fig. 3. Cross-section of membrane used in the third module. Modified three times on the outside of the support surface by Sylgard 184.

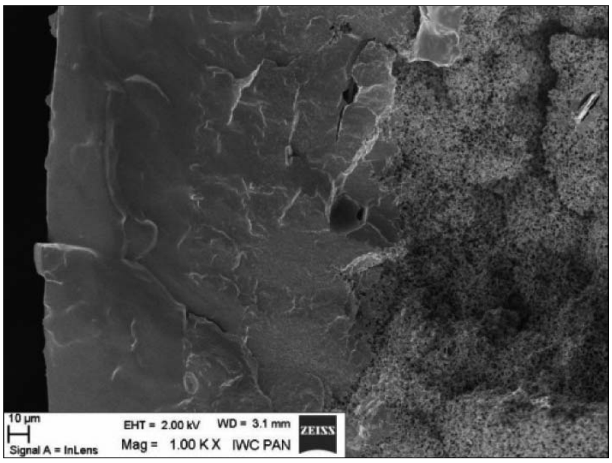

Fig. 4. Cross-section of membrane used in the fourth module. Modified two times on the outside of the support surface by Sylgard 184.

Membranes used in construction of the third and the fourth module are presented in Fig. 3 and 4, respectively. Membranes used in construction of the third module were modified two times on the outside of a support surface by Sylgard 184. Also by this polymer membranes used in construction of the fourth module were modified. These membranes were modified three times on the outside of the support surface.

Results obtained in the first experiment are presented as a relationship between the ideal separation factor and linear mass (Fig. 5). The ideal separation factor is defined as a ratio of the mole fraction of some component in permeate to the mole fraction of this component in feed [9], while linear mass represents thickness of the selective layer. In this experiment feed was a mixture of three gases applied into the inner surface of the capillary (bore side feed).

The difference between values of the ideal separation factors for CO_2 and for CH_4 and H_2 may indicate that these membranes are selective. The highest value of the ideal separation factor was achieved for CO_2.

Results achieved in the second and the third experiments, where feed was a mixture of two gases, applied on the outer surface of membranes, are presented in Fig. 6 and 7 as a relationship between the ideal separation factor and the linear mass. In case of both mixtures value of the ideal separation factor increases with growing linear mass, no matter what pressure was used. Higher value of the ideal separation factor was achieved for CO_2 and H_2 mixture.

Other results for both mixtures used in the second and in the third experiment are presented in Fig. 8 and 9 as a relationship between permeate flux and linear mass. In both cases decreasing of permeate flux with growing linear mass was observed, no matter what pressure was used.

Conclusions

According to obtained results, it can be assumed, that these membranes can separate carbon dioxide from methane and

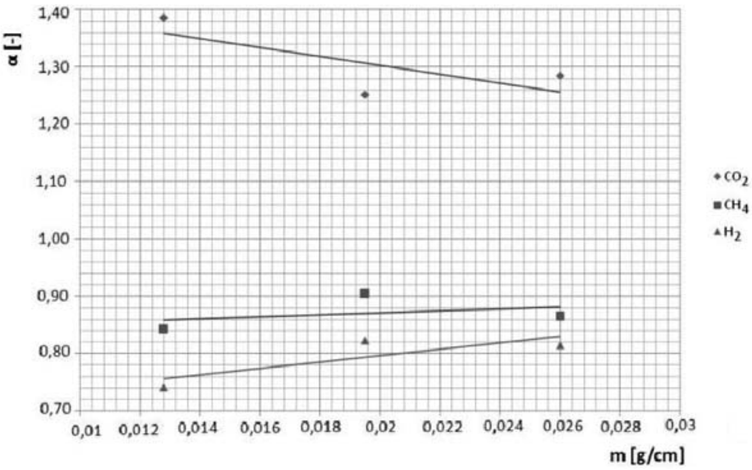

Fig. 5. Relationship between the ideal separation factor and linear mass; bore side feed; mixture of CH_4, CO_2 and H_2 in feed.

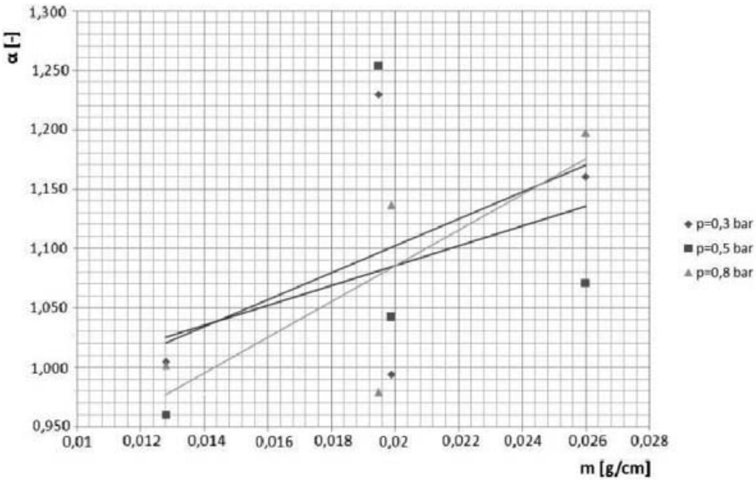

Fig. 6. Relationship between the ideal separation factor (counted against CH_4) and linear mass; shell side feed; mixture of CH_4 and H_2. in feed.

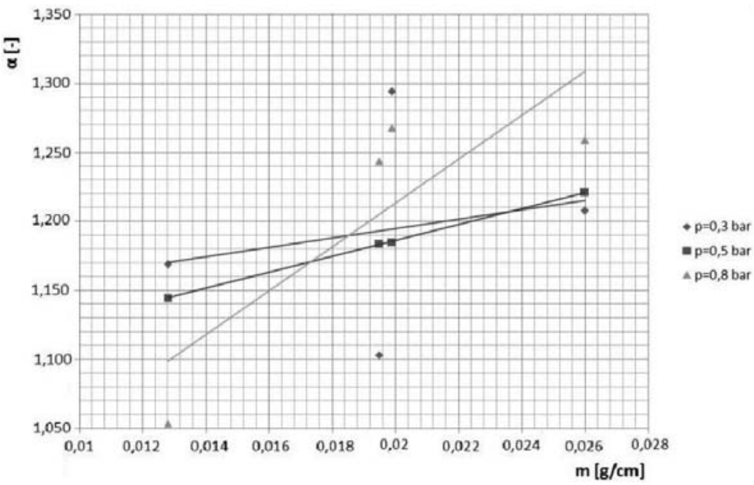

Fig. 7. Relationship between the ideal separation factor (counted against CO_2) and linear mass; shell side feed; mixture of CO_2 and H_2 in feed.

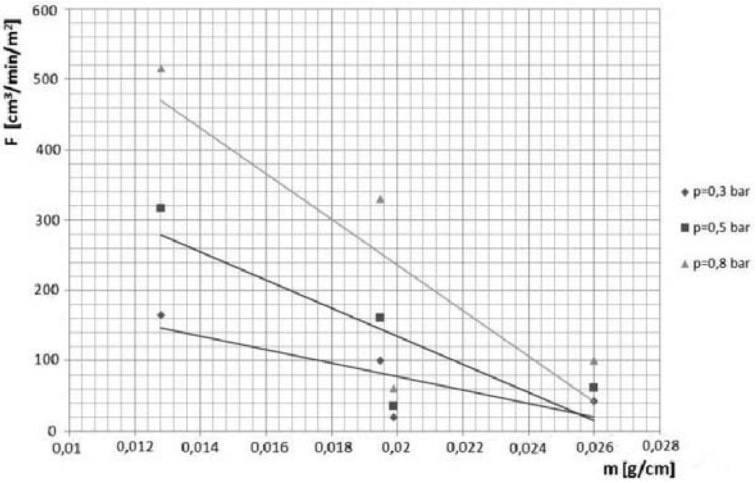

Fig. 8. Relationship between permeate flux and linear mass; shell side feed; mixture of CH_4 and H_2 in feed.

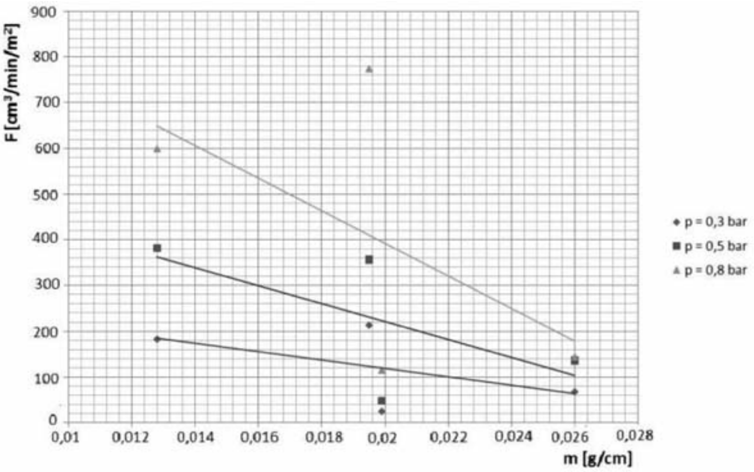

Fig. 9. Relationship between permeate flux and linear mass; shell side feed; mixture of CO_2 and H_2 in feed.

hydrogen. Increasing thickness of selective layer, makes value of the ideal separation factor higher. Capacity, which is represented by permeate flux, of these membranes was decreasing with growing linear mass. The best results were achieved for membranes modified on the outside and inside of a support surface (second module). These membranes represent relatively high value of the ideal separation factor with satisfyingly high permeate flux.

Thanks to this research, the need for further examination was demonstrated. There should be more research in the range of selecting: an adequate support, polymer creating selective layer and modification method.

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