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INVESTIGATION ON MEMBRANE-ASSISTED CO₂ REMOVAL PROCESS FOR OXIDATIVE COUPLING OF METHANE IN MINI-PLANT SCALE

BADANIE MEMBRANOWEGO PROCESU USUWANIA CO₂ DLA OKSYDACYJNEGO SPRZĘŻENIA METANU W SKALI MINI-APARATURY

Abstract

In this paper the application and the performance of a membrane unit for preliminarily removing CO₂ from the product gas mixture in the Oxidative Coupling of Methane (OCM) process based on a mini-plant scale experimental facility are presented and discussed. The model for the membrane unit is validated via experiments based on the comparison of concentrations and recoveries, respectively, with a brilliant agreement <5% under operating pressure up to 5 and 10 bar. It is found that the C₂H₄ loss rate could not be reduced less than 5% with the CO₂ removal rate of 50% in a given membrane module. Since ethylene (C₂H₄) is the target product in OCM process, a two-stage membrane system is therefore proposed to enhance the C₂H₄ recovery. This configuration could further reduce the product loss rate while keeping the same CO₂ removal rate as that of the single stage process.

Keywords: membrane-assisted separation, CO₂ removal, oxidative coupling of methane, aspen customer modele

Streszczenie

W artykule niniejszym zaprezentowano i omówiono zastosowanie oraz wydajność pojedynczej membrany dla wstępnego usuwania CO₂ z mieszaniny gazowej w procesie oksydacyjnego sprzężenia metanu (OCM) w oparciu o skalę mini-aparatury doświadczalnej. Model pojedynczej membrany weryfikowany jest drogą eksperymentów opartych odpowiednio na porównaniu stężeń i odzysków przy bardzo dobrej zgodności <5% i ciśnieniu operacyjnym do 5 i 10 barów. Ustalono, że tempa strat C₂H₄ nie można ograniczyć o mniej niż 5% przy tempie usuwania CO₂ wynoszącym 50% w danym module membrany. Ponieważ docelowym produktem procesu OCM jest etylen (C₂H₄), zaproponowano dwuetapowy system membranowy, który ma zwiększyć jego odzysk. Konfiguracja taka mogłaby w dalszej perspektywie zmniejszyć tempo strat produktu przy niezmiennym tempie usuwania CO₂, właściwym dla procesu jednoetapowego.

Słowa kluczowe: rozdzielanie membranowe, usuwanie CO₂, oksydacyjne sprzężenie metanu, wibrujący model odbiorczy

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1. Introduction

Ethylene is widely used in chemical industries as the classified unsaturated hydrocarbon and is also the most produced organic compound in the world. To satisfy the increasing demand for ethylene, some efficient, environment friendly, low pollution and low energy consumption methods of ethylene production have to be developed. Methane, as the main component of the natural gas with the percentage of 70-90%, has been used as relatively cheap, clean-burning fuel and feedstock in some chemical fields and the reserves of the natural gas is estimated to be higher than that of the crude oil in the future [1, 2]. Thus, in contrast to the existing thermal and steam cracking, the oxidative coupling of methane process converting methane to C_2 (ethylene and ethane) becomes an alternative. The fact that the high selectivity and high conversion of catalyst for OCM reaction could not be satisfied simultaneously [3] implies the coexistence of the unreacted methane and by-products such as CO , CO_2 , H_2 and H_2O [2-4] in the OCM product gas mixture. Therefore, CO_2 removal and product separation are necessary in the downstream processing of OCM process.

The conventional and most widely used separation method for CO_2 removal is absorption [5, 6]. The amine process has some disadvantages although it could achieve a high potential of CO_2 removal. First, amount of energy is needed to regenerate the absorber in the desorption process; second, the cost and the maintenance of the equipment are expensive, moreover, the operation is complicated. However, the hybrid system with membrane unit and amine process could reduce the energy consumption and the scale of columns for the given flow compared with the amine process alone. In this system, membrane unit is used to remove bulk CO_2 from feeding gas while the amine process to polish the gas stream. The general process of OCM reactor and hybrid system for CO_2 removal is presented in Fig. 1, tak-

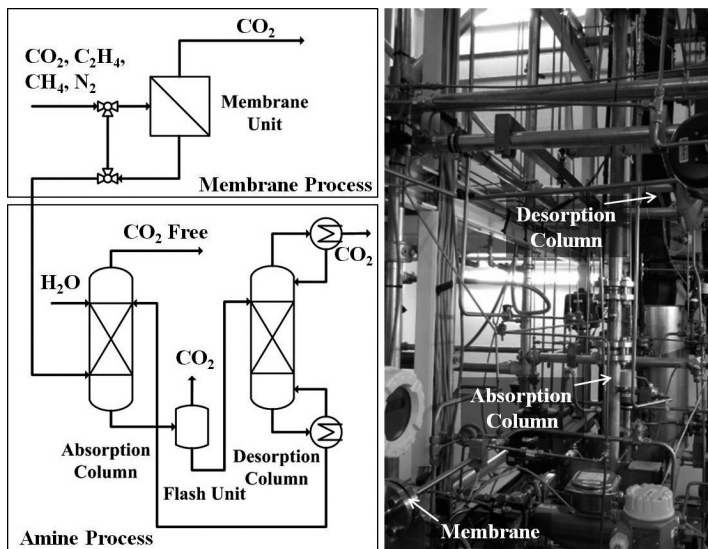


Fig. 1. Flowchart of the OCM process with reactor, hybrid CO_2 removal system

Rys. 1. Blokowy schemat procesu OCM z reaktorem, hybrydowy system usuwania CO_2

ing amine process as an example in this paper. Since the gas permeation is pressure driven process and the feeding to amine system is in the high pressure condition, no extra compressor is necessary for membrane unit. Moreover, membrane unit has the following advantages: (1) low capital and operating cost, (2) high efficiency of space utilization and (3) flexibility of installation and removal.

The main task of this paper is to simulate and analyze the gas permeation process in membrane unit in a mini-plant scale, and validate the model with experimental data. The polyimide (PI) flat-sheet envelope membrane module is used in the experiments and the simulation work is done by Aspen Plus® and Aspen Custom Modeler® (ACM). In addition, separation behavior of a two-step membrane system is studied via simulation.

2. Experimental set-up

An experimental set-up for OCM process in a mini-plant scale has been built in the Chair of Process Dynamics and Operation of Berlin Institute of Technology. It consists of a reactor, a membrane unit and absorption columns. Siemens SIMATIC PCS7 control system was used to obtain experimental data and control the operating variables. The membrane module used in this work is a kind of flat-sheet envelope structure [7], shown in Fig. 2, with 0.5 m² effective permeation area. In this configuration, several membrane envelopes are parallel fixed on a steel tube and packed in a metallic shell. In this module, the high pressure gas mixture flows between membrane envelopes and flows out of the membrane unit at retentate outlet with high fraction of the low-permeable components. Meanwhile, the fast-permeable gas is collected in the steel tube and flows out at permeate end under atmosphere pressure.

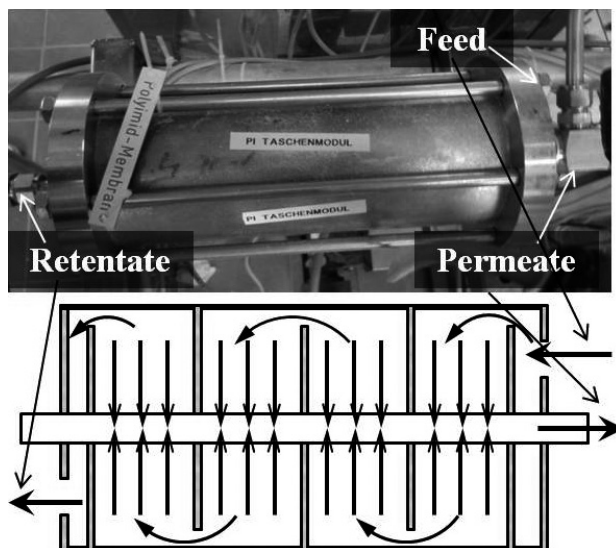


Fig. 2. Structure of flat-sheet envelope membrane module

Rys. 2. Struktura płaskiego modułu membrany osłonowej

The gas mixture used in the experiments consisted of CO₂, CH₄, C₂H₄ and N₂ only. Here, carbon dioxide and ethylene were the main studied components of products, methane was the non-reacted feeding, and nitrogen was the component for composition balance.

Before running the experiment, the membrane system was purged with the inert gas for 5 minutes. After that the high pressure feeding gas mixture was fed into membrane unit at the inlet, with the pre-defined composition. The feeding gases were from gas cylinders with almost 200 bar, but the pressure was reduced through a pressure regulator before flowing into the membrane system. The composition of the gas stream was detected by the online infrared (IR) device with the accuracy of ±1%. When no large fluctuation of flow rate was observed, the studied variables consisting of pressure, temperature, flow rate and mole fraction at both retentate and permeate sides were recorded. During the experiments, the samples were also taken out from the gas pipe and analyzed in the gas chromatography to obtain the composition of the gas mixture.

Two groups of experiments were done with total feed pressure of 5 and 10 bar, respectively. For each group, there were three cases with different CO₂ mole fraction, 15~25%. Meanwhile, two flow rates were considered in every group to investigate the influence on the performance. The feeding conditions of the investigated cases in this paper are presented in Table 1.

Table 1

Details of feeding stream in different investigated cases

	p [bar]	F [kmol/h]	Composition [%]			
			CO ₂	C ₂ H ₄	CH ₄	N ₂
case 1	5	0.37	15	13	17	55
case 2	5	0.36	25	15	14	46
case 3	5	0.70	24	15	14	47
case 4	10	1.06	14	10	15	61
case 5	10	0.70	15	10	15	60
case 6	10	0.71	23	12	15	50

3. Modelling of membrane unit

3.1. Gas permeation

In the permeation process, the partial pressure difference of each component provides the driving force of the permeation, and fugacity coefficient has to be taken into account for the high pressure gases [8, 9]. Thus, the gas flux permeating through the dense membrane can be defined as Equation 1.

$$J_i = \frac{P_i}{\delta} (f_i \cdot p_{HP,i} - p_{LP,i}) = L_i (f_i \cdot p_{HP,i} - p_{LP,i}) \quad (1)$$

Permeability coefficient P , i.e., affecting the gas flow rate through the membrane, is a complicated membrane parameter. P is dependent on the membrane materials and the operating conditions such as temperature, pressure and etc. Permeance, the ratio of permeability coefficient and the thickness of the dense membrane is often used in the simulation. Permeability is the crucially important parameter for simulation and usually obtained through experiments.

3.2. Modelling of membrane unit

In this work, the following characteristics and assumptions are made in this work: one-dimensional plug flow, isothermal flow, flawless membrane, fixed permeability in the whole zone, permeate-free flow pattern and steady-state simulation. Here, the permeate-free flow pattern means the concentration of gases at permeate side is determined by local fluxes, with no influence of upstream and downstream flows. In each control element, the total mass balance is written as Equations 2 and 3,

$$F_{\text{Re tentate}} = F_{\text{Feed}} - F_{\text{Permeate}} \quad (2)$$

$$F_{\text{Permeate}} = \sum_{i=1}^n J_i A_E \quad (3)$$

$$F_{\text{Re tentate}} = F_{\text{Feed}} - \sum_{i=1}^n (f_i p_{HP} x_i - p_{LP} y_i) A_E \quad (4)$$

According to Dalton's law of partial pressure and Equations 1-3, the mass balance used in the model can be written as Equation 4. And the physical properties, such as the fugacity coefficient, are calculated by Aspen Plus based on Peng-Robbins equation of state. Based on the beforehand assumption of permeate free flow pattern, the mole fraction of each component at permeate side can be defined as Equation 5.

$$y_i = J_i / \sum_{j=1}^n J_j \quad (5)$$

The pressure drop occurring along the flow direction inside the module is taken into account with the assumption that the shape of membrane module shell causes no pressure drop for flowing gases. The total pressure drop is shown as following [9].

$$p_{\text{Re tentate}} = p_{\text{Feed}} - 32 \frac{l \eta v}{d_h^2} \quad (6)$$

4. Flowsheeting

Aspen Plus® as one of the widely used commercial software for simulating and designing the given chemical processes does not provide the simulation model of membrane process. However, Aspen Custom Modeler® provides a choice to develop user's models to complete the simulation of the whole process in some situation. The flowchart of simulation task is

exhibited in Fig. 3, containing not only the membrane unit but also the compressor and the cooler for pre-treating the OCM product gas. The water-removed stream of OCM-GAS is at atmospheric pressure and room temperature. After the cooler, the gas stream of OCM-GAS, with the same composition as experiments, will reach the operating status. The permeabilities of all the components used in the experiments of the membrane material are taken from literature [7], and assumed to be constant in the simulation.

Component mole fractions and the recovery are studied and used in the validation. The recovery is defined as Equation 7.

$$r = F_{\text{Retentate}} / F_{\text{Feed}} \quad (7)$$

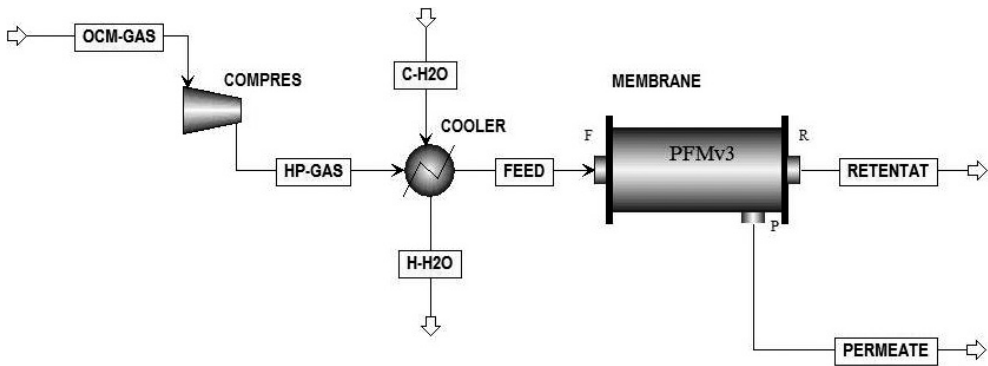


Fig. 3. Configuration of the single membrane module

Rys. 3. Konfiguracja pojedynczego modułu membrany

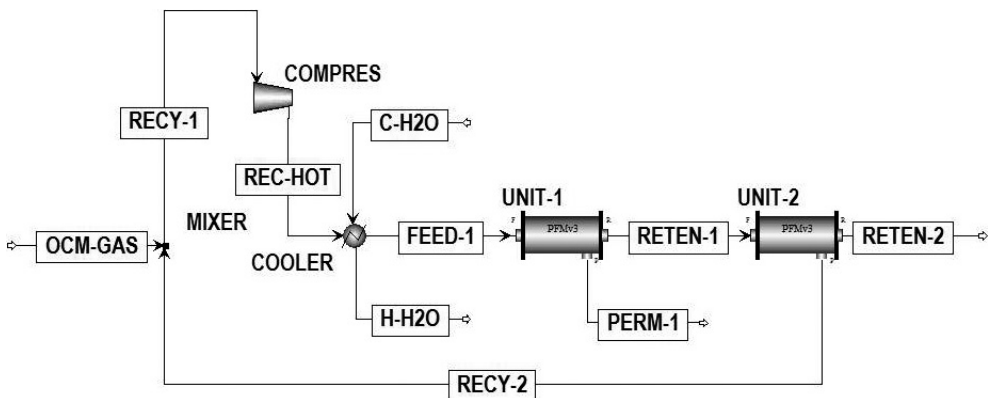


Fig. 4. Schematic of two sequential connected membrane modules

Rys. 4. Schemat dwóch połączonych modułów membrany

Additionally, the investigation of a two-step membrane system has also been done in this paper to improve the performance of gas separation, due to the limitation of the optimization for one stage membrane unit. It is obvious that two sequential connected membrane modules could increase not only CO_2 removal rate but also C_2H_4 loss rate, because of the increased effective permeation area. On the other hand, in the 2nd stage of membrane module the residue gas mixture contains lower concentration of CO_2 and higher concentration of C_2H_4 compared with the 1st stage. Therefore, it is an alternative to recycle the permeate stream of the 2nd module and re-feed to the 1st module. The schematic diagram is presented in Fig. 4.

5. Result and discussions

The experimental and simulated results of component mole fractions at residue side and the system recoveries in different cases are exhibited in Fig. 5. Obviously, the simulated results show a perfect agreement with the experimental values, with the relative error < 5%. And the deviations should be caused by the following reasons. Firstly, the membrane is assumed to be flawless with uniform permeability in the simulation, but it is difficult to fabricate so perfect thin membrane. Second, the permeance is assumed to be fixed in the simulation, while it is influenced by pressure, temperature and etc. Additionally, due to the accuracy of the measuring instruments, about $\pm 1\%$, the fluctuation was always observed in experiments, and the experimental data were the average values of several repeated experiments. Thus, this model could reasonably assist to estimate and investigate the separation performance of the given membrane system in OCM process in a mini-plant level for other operating conditions.

The influence of operating pressures and flow rates on the carbon dioxide removal rate and the ethylene loss rate is presented in Fig. 6. It can be seen that CO_2 removal rate has the same changing trend with C_2H_4 loss rate at different operation conditions, and this performance is because of the inherent characteristic of membrane material. Besides that, the geometry of the membrane module and the composition of gas mixture are usually fixed in the real situation, and the feeding pressure and the flow rate are the only adjustable and controllable variables. And Fig. 6 shows that, to remove 50% CO_2 out of the system, it is impossible to keep ethylene

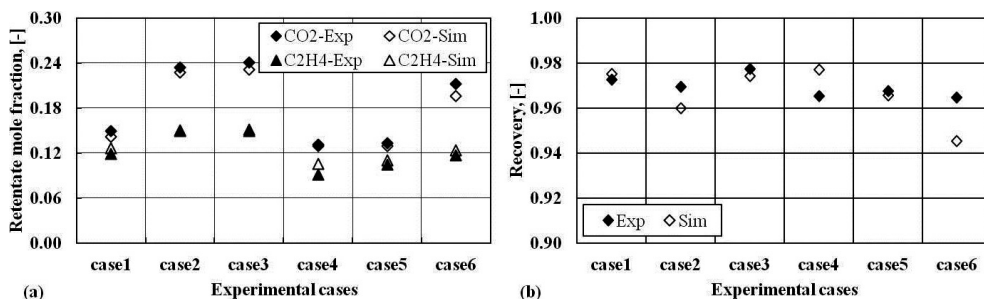


Fig. 5. Results comparison between simulations and experiments (Exp-experiment, Sim-simulation)

Rys. 5. Porównanie wyników symulacji i eksperymentów (Exp-eksperyment, Sim-symulacja)

loss rate below 5%. Thus, finding a better operating point for a high CO_2 removal rate with a low C_2H_4 loss rate is limited in the single stage membrane system. However, a sequential connection of two membrane modules could provide an alternative to improve the system. Fig. 7 illustrates that this configuration could either increase the CO_2 removal rate while keeping the same ethylene loss rate in the single stage, or reduce the ethylene loss rate with the same CO_2 removal rate in the former structure. This is more clearly illustrated in Table 2.

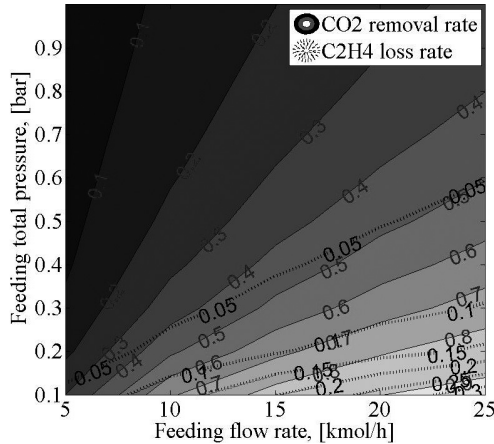


Fig. 6. Simulation of the influence of feeding pressure and flow rate on CO_2 removal rate and C_2H_4 loss rate for the given composition in the single membrane unit

Rys. 6. Symulacja wpływu ciśnienia zasilania i tempa przepływu na tempo usuwania CO_2 oraz tempa strat C_2H_4 dla danej kompozycji w pojedynczej membranie

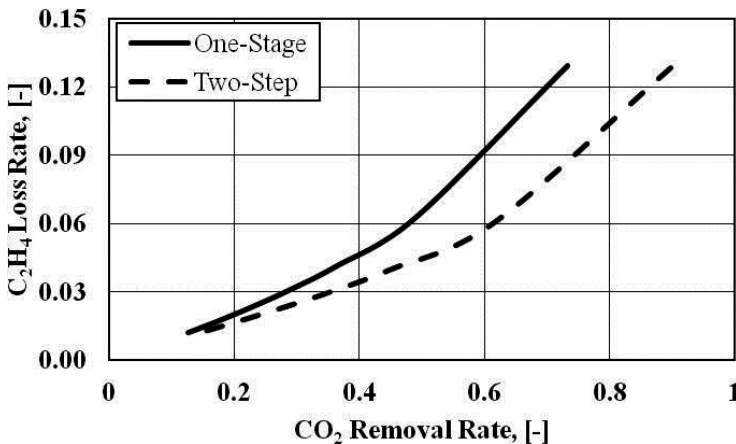


Fig. 7. Simulation of the C_2H_4 loss rate plotted with CO_2 removal in both single and two-step membrane systems

Rys. 7. Wykres symulacji tempa strat C_2H_4 i usuwania CO_2 w jedno- i dwustopniowych systemach membranowych

Comparison of single and two-step membrane system

	CO ₂ removal rate	C ₂ H ₄ loss rate
Single Module	43%	5%
Two-step System	53%	5%
Single Module	50%	7%
Two-step System	50%	4%

6. Conclusions

In this work a model for the simulation of the membrane-based gas separation in the flat-sheet envelope membrane module by ACM and Aspen Plus® is presented. The model has been validated through experiments and could be used for investigating the separation performance of the membrane system. In the downstream processing of OCM, both CO₂ removal rate and C₂H₄ loss rate are important variables to be monitored since they will affect the costs. Although these variables could be adjusted by manipulating both feeding pressure and feeding flow rate in the single membrane system, the improvement is limited due to the material inherent characteristic, for instance, the permeating flux of every component increases with the increasing feeding pressure. However, the sequential connection of membrane modules provides an alternative to enhance the separation performance. It could either reduce ethylene loss rate while keeping the same CO₂ removal rate in the single stage, or improve CO₂ removal efficiency with the same C₂H₄ loss of the single membrane process. More information about the whole OCM process will be described by Godini et al. in this year and the adsorption, as an alternative for removing CO₂ in this process, has been proposed by Nghiem et al. in [10].

Symbols

A	–	area [m ²]
d_h	–	hydraulic diameter [m]
E	–	control element
F	–	mole flow rate [mol/s]
f	–	fugacity coefficient
HP	–	high pressure side
i, j	–	component i, j
J	–	permeate flux [mol/m ² s]
L	–	permeance [mol/m ² sbar]
LP	–	low pressure side
l	–	length of flow path [m]
n	–	number of components

P	– permeability coefficient [mol m/m ² sbar]
p	– total pressure [bar]
p_i	– partial pressure of component i [bar]
r	– recovery
v	– average velocity [m/s]
x	– mole fraction at high pressure side
y	– mole fraction at low pressure side
δ	– thickness of membrane selective layer [m]
η	– viscosity [bar·s]

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References

- [1] Baker R., Lokhandwala K., *Natural Gas Processing with Membranes: An Overview*, Ind. Eng. Chem., **47**, 2008, 2109-2121.
- [2] Kondratenko E., Baerns M., *Oxidative Coupling of Methane*, Handbook of Heterogeneous Catalysis, 2008, 3010-3023.
- [3] Jaso S., Godini H., Arellano-Garcia H., Wozny G., *Oxidative Coupling of methane: Reactor Performance and Operating Conditions*, Computer Aided Chemical Engineering, **28**, 2010, 781-786.
- [4] Lunsford J., *The catalytic Oxidative Coupling of Methane*, Angew. Chem. Int. Ed. Engl., **34**, 1995, 970-980.
- [5] Baker R., *Future Directions of Membrane Gas Separation Technology*, Ind. Eng. Chem., **41**, 2002, 1393-1411.
- [6] Brunetti A., Scura F., Barbietri G., Drioli E., *Membrane technologies for CO₂ separation*, Journal of Membrane Science, **359**, 2010, 115-125.
- [7] Abertz V., Brinkmann T. et al., *Developments in Membrane Research: from Material via Process Design to Industrial Application*, Advanced Engineering Materials, **8**, 2006, 328-357.
- [8] Wijmans J., Baker R., *The solution-diffusion model: a review*, Journal of Membrane Science, **107**, 1995, 1-21.
- [9] Ohlrogge K., Ebert K., *Membranen: Grundlagen, Verfahren und industrielle Anwendungen*, WILEY-VCH, 2006.
- [10] Nghiem X., Arellano-Garcia H., Wozny G., *Adsorptive Separation In the Downstream of the Oxidative Methane Coupling Process*, AIChE Annual Meeting, 2011.