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Scientific paper

A METHOD FOR DETERMINATION OF SEPARATION PROPERTIES OF MEMBRANES

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Abstract

In this study, design of lab scale device for determination of separation properties of membranes is presented and analyzed. Device operates with different gas pressure between chambers, whereby gas streams perpendicular to the membrane. Using appropriate acquisition system and applying mathematical formulas, mechanism for gas transfer through the membrane is determinate.
Polymer membranes based on zeolite are synthesized and tested by lab scale device. The membranes with various content of zeolite are tested with CO_2 *gas until optimal composition of membrane components is established. Beside good mechanical and structural properties of applied membrane, suitable values of permeability with good agreement with the literature data are obtained.*

Keywords: *separation, permeability, membrane, zeolite.*

1. INTRODUCTION

Separation of chemical species is an essential part of many processes for final and semi-finished goods production. Distillation, crystallization, partial condensation and vaporization are the processes that use thermal energy for the separation of chemical species. Separation in these processes is based on differences in boiling temperature or crystallization rate of species in the mixture. A large amount of heat and a considerable amount of electricity in the case of cryogenic distillation and crystallizationare required.

Extraction and absorption are the separation processes based on the difference in solubility of the chemical species in the mixture. After absorption of desired chemical species from a mixture, it is necessary to separate from absorption or extraction mediumapplying one of the processes that use thermal energy. The heat energy required for the separation is generated by burning fossil fuels. Emissions of CO_2, designated as one of the major components that cause the greenhouse effect, are directly linked to the consumption of fossil fuels. It should be noted that the above mentioned processes require significant capital investment.Increasing trend of the investment is present in cases where the temperature range of chemical species in a mixture is low and when the boiling point of the chemical species in the mixture has similar values.Membrane separation process is one of the promising technologies for replacing the above mentioned separation processes. The motivation lies in fact that separation in these systems is basedon the physical-chemical principles and differences in the driving force.

Modern research activities and practical applications aredirected towardto the processes of thesustainable development. Sustainable development requires simultaneous consideration of economic and environmental aspects of the production process [1-5]. This is one of the reasons for applications of new separation technologies that reduce production costsand environmental impact. It should be noted that the development and innovation in the field of materials and process technologies will contribute to higher increase in the share of membrane systems on the separation technology market [6].

The removal or concentration of dissolved ions could be conducted by electrodialysis process. Industrial application of ion-exchanger membrane was first started in electrodialysis (ED). Further development has led to improvements in ED technology [7]. Pervaporation process allows concentrate liquid mixtures, especially aqueous-organic azeotropes [8]. Ultrafiltration systems occupy the largest part of the market with a share of about 35%. Other membrane processes such as membrane contractors, electrodialysis and pervaporation have only a small share of the market.Membrane technologies have found application in the food industry. The most abundant membrane technology in the food industry processes are microfiltration, ultrafiltration, nanofiltration and reverse osmosis. In the food industry, membrane processes are mostly applied in the dairy industry, as well as in the production of alcoholic and non-alcoholic beverages (beer, fruit juices, wine, etc.) [9]. In the petrochemical industry, reaction and separation have a key a role in the achievement of the required quality of the product. Using membrane reactors these two parameters can be simultaneously controlled. In case of application of nanotechnology in the production of gas separation membranes, nanocomposite membranes can simultaneously improve permeability and selectivity [10]. MF/RO systems are used for re-cultivation and reuse of waste water [10].

The membrane system application is increasing in the process of obtaining biofuels where membrane facilitates conduct the reuse of water, especially in areas with lack water. Membrane technology for storage and purification of organic acid is commonly used as a basis for obtaining new biodegradable plastics [11].

Under the impact of the driving forces, individual chemical species pass easily, while others harder, through specific membrane. Separation of chemical species through the membrane depends on the pass rateof different chemical species. Permeability is defined as the amount of chemical species that passes through the membrane area per time in the unit of driving force.Thee selectivity of the membrane is the ability of membrane to perform the separation of the different components. The selectivity of the membrane is numerically defined as the molar ratio of the fluxes of chemical species through specific membranes. The molar flux can be represented by equation (1):

$$J_i = P_i(\Delta\Pi)\cdot\Delta\Pi \tag{1}$$

where: P_i - permeability of chemical species$i$, Π - the driving force.

The permeability of the components depends on the mechanism by which the chemical species are transmitted through the membrane. It can be considered a constant value; for example in the case of molecular diffusion, while in the case where the mechanism is a combination of two or more mechanisms, permeability is defined by a complex function. Consequently, for adequate determination ofseparation characteristics of membrane, the mechanisms fortransferring the individual chemical species through the membrane should be determined.

2. EXPERIMENTAL

Experiments are performed using special designed lab scale device for determination of separation properties of membranes.The device characteristics are significantly different from the conventional laboratory equipment for membrane testing. If the gas is introduced perpendicular to the membrane, than the membrane properties can be measured by pressure difference at the opposite sides of membrane [12,13]. Schematic illustration of device with three separate chambers is presented in Fig. 1.

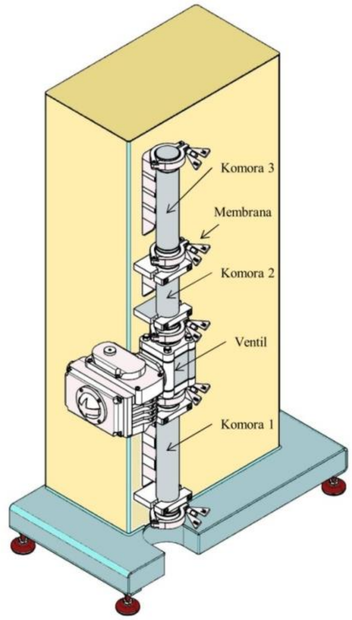

Figure 1. Schematic illustration of lab scale device for membrane separation

Chambers 1 and 2 are separated by valve, while the chambers 2 and 3 are separated by membrane. The gas is fed into the chamber 1 with the closed valve which means that the pressure in this chamber is higher than the pressure in chambers 2 and 3. The chambers are equipped with transmitters and connected with the appropriate system for acquisition data with possibility to measure pressure drop in real time. After opening the valve, gas passes into chamber 2 due to concentration (pressure) difference.Practically, at the same time mass transfer from chamber 2 to chamber 3 is starting if the diffusion through the membrane occurs. Vacuum pump is used to set up the sub pressure environment in chamber 3 (and 2). Gas CO_2 is supplied for membrane testing. The tests are performed at ambient temperature.

3. RESULTS AND DISCUSSION

Using the equations forreal gas (2), pressure drop in chambers are proportional to the number of moles in chambers:

$$P_i \cdot V_i = Z\left(P_i, V_i, n_i\right) n_i RT \quad (2)$$

where: P_i – pressure in chamber$i$, V_i – volume of chamber$i$, n_i – number of moles in chamber$i$, R – universal gas constant, T – temperature in the system, Z – factor of compressibility

Differentiating equation (2) by the time (where the chamber volume is *Vi* and system temperature is constant value), the equation that directly link the pressure drop with time and change the number of moles in the chamber is obtained.

$$V_i \frac{dP_i}{dt} = Z\left(P_i, V_i, \mathrm{T}, n_i\right) \frac{dn_i}{dt} RT \qquad (3)$$

In equation (3), pressure drop with time is experimental value.Factor of compressibility can be determinate by applying the appropriate equation of state.Due to fact that volume and temperature in all chambers are known, from equation (3) changes of moles in chamber*i*per time (dn_i/dt) can be estimated.

Mass flux between chambers can be determinate and defined as:

- Mass flux between chambers 1 and 2

$$\Phi_1 = \frac{1}{A_1}\left(-\frac{dn_1}{dt}\right) \qquad (4)$$

- Mass flux between chambers 2 and 3

$$\Phi_2 = \frac{1}{A_2}\left(\frac{dn_3}{dt}\right) \qquad (5)$$

where: A_1andA_2– pipe cross-sectional area between chambers 1 and 2, and chambers 2 and 3, respectively.

By comparing the values of the mass flux between the chambers, it is possible to determine the resistance to mass transfer through the membrane, depending on the driving forces.
After determining the mass flux between the chambers 2 and 3, it is required to determine the relationship between the driving force that occurs between chambers 2 and 3, and mass flux (Fig. 2). Generaly, the dependance is not linear, which indicate that different mechanisms of transfer are presented, such as viscous flow with surface diffusion. Using Fig. 2, dominant mechanism of transfer can be designated.

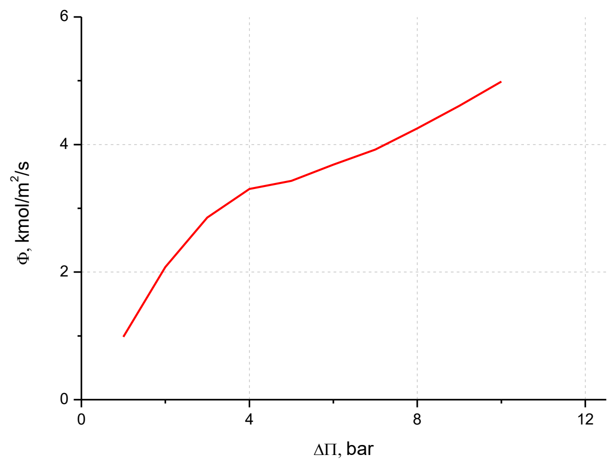

Figure 2. Diagram of dependence: mass flux vs. driving force

3.1 Permeability and mechanism of CO_2 transfer through the synthesized membrane

The membrane with composition of 30 mass% of n-tetradeciltrimetilamonium-bromide (TDTMAB) and 70 mass% zeoliteclass FAU was prepared for determination of CO_2 permeability (Fig. 3). Cubic cells of zeolite with circle pores allow optimal CO_2 diffusion. The optimal concentration of zeolite is distinguished at 20 mass% in regard to polymer. Higher concentrations of zeolite have direct impact on membranes elasticity and mechanical properties while lower concentrations of zeolite would not be sufficient for diffusivity of CO_2.

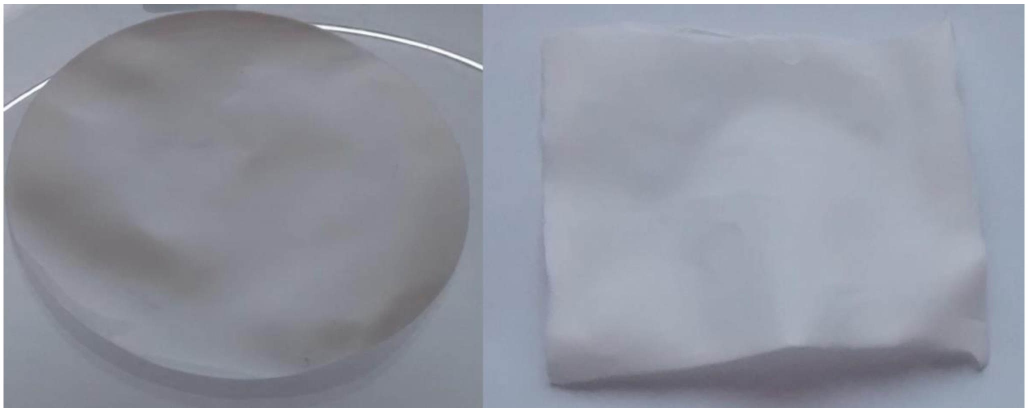

Figure 3. Membranes for determining the permeability and mechanism of CO_2 transfer

Changes in pressure through the device chambers are presented in Fig. 4. In chamber 1, CO_2 is introduced up to a pressure of 5 bar. In chambers 2 and 3,sub-pressure of 0.2 bar is achieved. By opening the valve mass transfer from chamber 1 to chamber 2 starts, while the driving force is established between the chambers 2 and 3, respectively on both sides of the membrane.

Changes in pressure are detected by pressure transmitter connected with a system for data acquisitionand presented in Fig. 4.

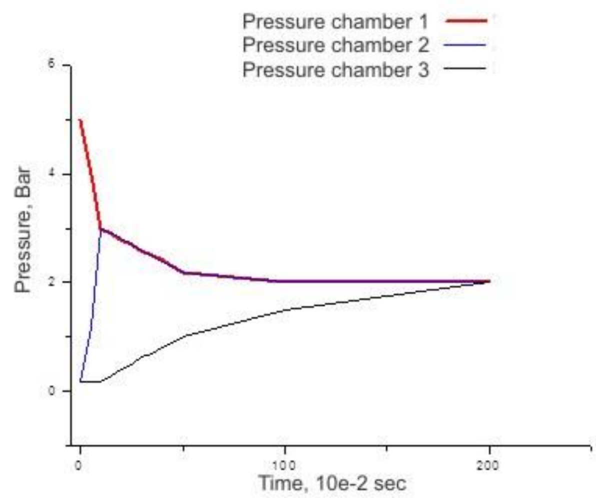

Figure 4. Pressure changes in chambers 1, 2 and 3

Dependence of mass transfer flux vs. driving force is obtained by applying the equations (1-5) and Soave-Redlich-Kwongequation of state and presented in Fig. 5.

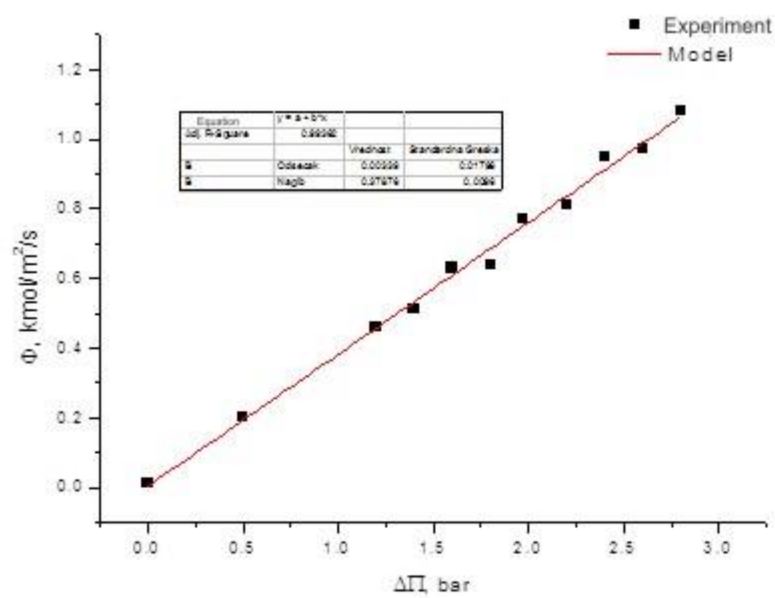

Figure 5. Mass transfer flux vs. driving force for CO_2

The analysis of the experimental results show linear dependence of the mass flux vs. driving force, indicating that diffusion through the pores of the membrane is dominant mechanism of transmission.

According to equation (1), slope indicates the permeability of CO_2 for the observed membrane (0.37876). This result is in accordance to the results of other authors [14]. It confirms that applying the depicted apparatus, separation characteristics of the membrane for various chemical species and different type membrane can be determined.

CONCLUSION

The lab scale device for determination of separation properties of membranes is designed for ease use and high accuracy of the measurements. The device can be used to determine the permeability, the transmission mechanism and selectivity for both gases and liquids in the broadest spectrum of membranes that can be produced. Setting of the membrane in the system is relatively simple, as well as the delivery of fluids into the system. It is possible to supplement the heating system for fluids, as well as systems for the direct analysis of fluid output.

The membranes based on zeolite are synthesized by casting method and used for gas CO_2 separation. For applied membranes diffusion is dominant mechanism of transfer. By varying the zeolite composition, different properties of membranes can be obtained, and consequently different test outputs could be estimated.

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Naučni rad

METODA ZA ODREĐIVANJE SEPARACIONIH SVOJSTAVA MEMBRANA

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Izvod

U ovom radu je prikazano i analizirano konstrukcijsko rešenje laboratorijskog uređaja za određivanje separacionih svojstava membrana. Rad uređaja je baziran na razlici pritisaka između komora, pri čemu gas struji normalno na poprečni presek membrana. Odgovarajućim sistemom za akviziciju podataka i primenom odgovarajućih matematičkih formula određen je mehanizam prenosa kroz membranu.

Polimerne membrane na bazi zeolita su sintetizovane i testirane na uređaju. Membrane sa različitim udelim zeolita su testirane na CO_2 gas, dok nije ustanovljen optimalan sastav komponenti za sintezu membrana.Pored dobrih mehaničkih i strukturnih svojstava testirane membrane, dobijene su zadovoljavajuće vrednosti permeabilnosti koje su u saglasnosti sa drugim autorima.

Ključne reči: *separacija, propustljivost, membrana, zeolit.*