



# Gas permeation applied to biogas upgrading using cellulose acetate and polydimethylsiloxane membranes

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## ABSTRACT

Membrane gas permeation has great potential for the biogas upgrading. The present work evaluates the performance of membranes made of two different polymers aiming at the carbon dioxide (CO<sub>2</sub>) removal: cellulose acetate and polydimethylsiloxane (PDMS). The results indicated that CO<sub>2</sub> caused membrane plasticization, which led to lower separation factors in tests with gas mixtures, in comparison to the pure gas experiments. Based on experimental results, a simplified model was developed which considered the permeability variation with the CO<sub>2</sub> partial pressure in the gas feed. The modeling approach for a single stage process pursued a compromise between methane (CH<sub>4</sub>) purity and recovery. For a given purity, the highest recoveries were obtained for the cellulose acetate membrane, due to its higher selectivity. For this membrane, a CH<sub>4</sub> purity of 97% led to a recovery of 86.8%, while the PDMS membrane presented a CH<sub>4</sub> recovery of only 19.8%, considering the same CH<sub>4</sub> content. A multiple stage design improved methane recovery considerably in comparison to the single stage process for both membranes, making it possible to attain 99.6% CH<sub>4</sub> purity associated with 99.8% CH<sub>4</sub> recovery for the cellulose acetate membrane.

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## 1. Introduction

Biogas is generated in anaerobic conditions by microorganisms from organic substrates. It consists of a gas mixture, composed mainly of methane and carbon dioxide. Biogas is produced in large scale in sewage treatment plants, landfills and anaerobic digestion plants (Niemczewska, 2012). Its chemical composition varies as a function of the substrate type and operational conditions (Ryckebosch et al., 2011).

Amongst the possible uses of the produced biogas, purification for injection into the natural gas grid is known as the most interesting option from an economic point of view. The use of biogas as a fuel is also advantageous for the environment, because methane is a greenhouse gas approximately 20 times more aggressive than carbon dioxide (Dirkse, 2007). After purification, biogas is called biomethane and has typically 95–97% of CH<sub>4</sub> and 1–3% of CO<sub>2</sub> (Ryckebosch et al., 2011).

The importance of biogas purification before natural gas grid injection comes from the inconvenience caused by its contaminants, such as CO<sub>2</sub>, that could reduce the calorific value and

increase the gas volume to be transported, water, which reacts with several components forming acids that cause corrosion, and H<sub>2</sub>S, toxic and corrosive.

The first biogas upgrading plants, separating carbon dioxide from methane, were installed using technologies found in the natural gas industrial processing. These technologies are well established but have disadvantages, such as (Scholz et al., 2013):

- High energy demand;
- Low pressure biomethane flow;
- Complex systems, involving many steps to remove CO<sub>2</sub>, H<sub>2</sub>S and H<sub>2</sub>O, which makes them difficult to operate;
- Large footprint;
- Other materials are needed, like water, amines or activated carbon.

A membrane separation process is an alternative to address these drawbacks. Among the membrane technologies available for biogas upgrading, gas permeation is the most widely used as it has already been developed for industrial scale applications. It was first established in the 1980's for CO<sub>2</sub> removal from natural gas. The separation is based on the sorption-diffusion mechanism using dense membranes, for which there is a compromise between selectivity and permeability.

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Equation (1) describes gas transport through a polymeric matrix, showing that the flux ( $J_i$ ) of a component across the membrane is proportional to the pressure difference between feed and permeate sides ( $p_i^F - p_i^P$ ), and it is inversely proportional to the membrane thickness ( $\ell$ ) (Klopffer and Flaconnèche, 2001). The proportionality constant is the permeability ( $P_i$ ).

$$J_i = P_i \frac{p_i^F - p_i^P}{\ell} \quad (1)$$

The ability of a membrane to discriminate gases  $i$  and  $j$  is given by the ratio of their permeabilities and is called ideal selectivity ( $\alpha_{ij}$ ). Thus, this selectivity is calculated by the expression (Baker, 2004):

$$\alpha_{ij} = \frac{P_i}{P_j} \quad (2)$$

Many polymeric or inorganic materials can be used in membrane manufacturing for CO<sub>2</sub>/CH<sub>4</sub> separation. However, in industrial scale, only polymeric materials have been used, mainly due to their low cost (Basu et al., 2010). Table 1 presents some of the polymeric materials commercially used and their main characteristics: permeability and ideal selectivity. Nowadays, cellulose acetate is the most used polymer for full scale CO<sub>2</sub> separation.

One of the main challenges in high pressure membrane separation is plasticization. By definition, this is a pressure dependent phenomenon, caused by the dissolution of certain substances in the polymeric matrix. Plasticization causes swelling and increases segmental mobility of polymeric chains. In gas separation membranes, swelling induced by CO<sub>2</sub> affects process performance and increases the probability of material failure. For example, the selectivity reduction when processing a gas mixture in comparison to the pure gases data is attributed to plasticization. Plasticization occurs typically in glassy polymers, leading to a decrease in the glass transition temperature by reducing the interaction between adjacent segments of polymeric chains (Ismail and Lorna, 2002). The magnitude of plasticization depends on the quantity of sorbed gas.

Due to plasticization, cellulose acetate (CA) membranes have a carbon dioxide/methane selectivity of about 12–15 under normal operating conditions, which is very low in comparison to the value reported in Table 1 considering pure gas permeation (Baker, 2002). Numerous membrane materials with better separation performance have been reported in the literature, but most of them do not maintain their properties when tested under real-world conditions. Polydimethylsiloxane (PDMS) is stable at process condition and exhibits higher permeability than CA, but lower selectivity. Taking into consideration the low pressure biogas stream,

**Table 1**  
Materials commercially used in gas permeation and their characteristics (Basu et al., 2010).

Material <sup>a</sup>	CO <sub>2</sub> permeability (Barrer) <sup>b</sup>	Ideal selectivity (CO <sub>2</sub> /CH <sub>4</sub> )
PDMS	2700	3.4
PMP	84.6	5.8
PPO	75.8	6.9
EC	26.5	1.4
PI	10.7	42.8
PSf	5.6	22.4
CA	6.3	30.0
PC	4.2	32.5

<sup>a</sup> PDMS – polydimethylsiloxane; PMP – polymethylpentene; PPO – polyphenyleneoxide; EC – ethyl cellulose; PI – polyimide; PSf – polysulfone; CA – Cellulose acetate; PC – polycarbonate.

<sup>b</sup> 1 Barrer = 10<sup>-10</sup> cm<sup>3</sup> cm/cm<sup>2</sup>·s·cmHg.

permeability seems to be a major factor to reduce the energy demand of the separation process. Therefore, the objective of this work was to compare both membrane materials through an experimental evaluation and their performance in biogas upgrading using a simplified process simulation. Experimental data considering plasticization of the membrane material were used in the process modeling for a better understanding of its performance.

## 2. Experimental

Gas mixtures used in the experiments were prepared online using CH<sub>4</sub> (99,995%, Linde AG) and CO<sub>2</sub> (99,99%, Linde AG). Gas permeation tests were performed using pure gases and gas mixtures containing 20, 40, 50, 60 and 80% of CO<sub>2</sub>. Differential pressure between feed and permeate varied from 6 to 16 bar.

Two membranes were tested: a composite commercial cellulose acetate membrane and a dense film of polydimethylsiloxane (PDMS). The dense film was prepared using a polymeric solution (RTV615A – Momentive) and a cross-linking agent (RTV615B – Momentive) in the proportion of 10:1.

The tests with pure gases and mixtures were carried out in an automatized system whose schematic diagram is presented in Fig. 1. Gas composition and flow rate were adjusted by the mass flow controllers MFC-1 and MFC-2. Feed pressure was controlled by the valve VSP-1. The three permeation cells (C1, C2 and C3) could be operated independently, allowing up to three tests running simultaneously sharing the same feed gas. An isothermal bath whose liquid flowed through the exterior of the cells controlled the temperature during the experiments. The permeation cells operated with membrane areas in the order of 10 cm<sup>2</sup>. The permeate collection system was equipped with valves VS-3 to VS-13, pressure sensors PI-2, PI-3 and PI-4, a vacuum pump and the carrier gas, Helium. In the experiments using gas mixtures, gas composition was determined using an online gas chromatograph (MicroCG CP 4900, Varian). The permeate pressure increase with time was measured continuously during the experiments, starting from vacuum.

The determination of the permeability coefficient for pure gases was possible using Equation (3), valid for ideal gases, where  $\left(\frac{P}{V}\right)_i$  is

the permeance in GPU,  $\frac{dp_i^P}{dt}$  is the slope of pressure as a function of time, determined in the permeation experiment,  $V$  is the permeation cell volume,  $A$  is the membrane area,  $\Delta p_i$  is the differential pressure applied through the membrane,  $T$  is the temperature in which the experiment was performed, and  $T_{STP}$  and  $p_{STP}$  are the temperature and pressure at standard conditions (Dorosti et al., 2015).

$$\left(\frac{P}{V}\right)_i = \frac{dp_i^P}{dt} \frac{V}{A \Delta p_i} \frac{T_{STP}}{T p_{STP}} \quad (3)$$

The permeability for mixtures was obtained by isolating  $\frac{dp_i^P}{dt}$  from the previous equation, and solving the differential equation for each component. As the mixture is composed of CH<sub>4</sub> and CO<sub>2</sub>, the total pressure is given by the sum of the partial pressures for CH<sub>4</sub> and CO<sub>2</sub>.

$$p^P(t) = p_{CO_2}^F \left\{ 1 - \exp \left[ - \left(\frac{P}{V}\right)_{CO_2} \frac{A}{V} \frac{T_{STP}}{T} t \right] \right\} + p_{CH_4}^F \left\{ 1 - \exp \left[ - \left(\frac{P}{V}\right)_{CH_4} \frac{A}{V} \frac{T_{STP}}{T} t \right] \right\} \quad (4)$$

Equation (4) has two unknown parameters:  $\left(\frac{P}{V}\right)_{CO_2}$  and  $\left(\frac{P}{V}\right)_{CH_4}$ .

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