



# Mixed gas separation study for the hydrogen recovery from H<sub>2</sub>/CO/N<sub>2</sub>/CO<sub>2</sub> post combustion mixtures using a Matrimid membrane

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## ABSTRACT

In this work, the membrane separation of hydrogen from binary, ternary and quaternary mixtures of H<sub>2</sub>, N<sub>2</sub>, CO and CO<sub>2</sub> is presented. Hydrogen permeability through a polyimide Matrimid 5218 membrane was experimentally obtained using the constant pressure technique. The influence of the feed gas composition, temperature (30–100 °C), pressure range (up to 6 bar), and flow rates was experimentally analyzed. As expected, the pure gas permeability of H<sub>2</sub> was only slightly dependant on pressure and had an average value of  $17.7 \times 10^{-14} \text{ m}^3(\text{STP}) \text{ m m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1}$  at 30 °C. Hydrogen permeability was not affected by the presence of nitrogen and carbon monoxide, and as a result the mixed gas selectivities for the H<sub>2</sub>/N<sub>2</sub>/CO mixtures are very close to the selectivities calculated from pure gas permeation data. On the contrary, a strong dependency of the hydrogen permeability on CO<sub>2</sub> concentration was observed even at low concentrations of CO<sub>2</sub>. A reduction of 42% of the hydrogen permeability coefficient was obtained when a mixture of 10/90 vol.% H<sub>2</sub>/CO<sub>2</sub> was used as feed gas. Accordingly H<sub>2</sub>/CO<sub>2</sub> selectivity decayed from a value of 4.2 calculated from pure gas permeabilities to 2.7 when permeation data were obtained in mixed gas experiments. The preferential sorption of CO<sub>2</sub> on the Langmuir sites of the excess free volume portion of the polymer allowed explaining and quantifying this phenomenon. The “dual-mode sorption, partial immobilization” model was used to describe H<sub>2</sub> and CO<sub>2</sub> permeation behavior of pure, binary, ternary and quaternary mixtures. The model sorption parameters for N<sub>2</sub> and CO<sub>2</sub> in the polymer Matrimid 5218 were obtained from the literature meanwhile those for H<sub>2</sub> and for CO were unknown and resulted from the fitting of the experimental data to the proposed model. Satisfactory agreement between predicted permeability results and experimental data with a correlation coefficient (*R*) higher than 0.95 and mean squared relative error (MSRE) lower than 0.01 was attained. Thus, this work reports useful knowledge related to the intrinsic material properties, considering gas mixtures of industrial interest and essential when other membrane configurations like hollow fibers, mixed matrix membranes or polymer blends are proposed.

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## 1. Introduction

One particular area which is becoming of more and more interest to researchers is hydrogen. This includes the possibility of hydrogen production from hydrogen containing gases and continuous hydrogen removal from those thermodynamically unfavorable reactions [1]. Membrane science and technology are recognized today as powerful tools in solving some important global prob-

lems, developing new industrial processes needed for a sustainable industrial growth [2]. The major benefits that membrane technology presents over other gas separation alternatives like pressure swing adsorption and cryogenic distillation are: its lower power usage and costs, simplicity in operation and its compactness and portability; assuming hydrogen purity requirements of <99.5% and relatively modest operating temperatures, polymeric membranes are preferred among the various alternatives [3].

The major traditional applications of hydrogen-permeable membranes for gas separation are: hydrogen recovery from ammonia purge gas streams, hydrogen/methane separation in refinery off-gas and hydrogen/carbon monoxide adjustment in oxo-chemical synthesis plants [4,5]. Another important emerging application is the separation of hydrogen from carbon dioxide in the product leaving the water gas shift reaction when producing hydrogen and the recovery of H<sub>2</sub> from the tail-gas stream from carbon black manufacturing. All these processes produce hydrogen mixed

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with other gases; therefore in the present work we have studied the membrane permeation for pure gases, binary, ternary and quaternary mixtures of H<sub>2</sub>, CO, N<sub>2</sub> and CO<sub>2</sub>. These four components are found in the dry post combustion gas stream obtained in the production of carbon black, a commodity powdered product with widespread applications, that is obtained by combustion of a fuel under reducing conditions. The tail gas is formed, in a dry basis, by the following gas mixture, in vol.%: 60.5% N<sub>2</sub>, 17.9% CO, 16.4% H<sub>2</sub>, 5.3% CO<sub>2</sub>.

Today the application of polymeric membranes for the H<sub>2</sub> recovery is limited due to the well known trade off relationship between the permeability and the selectivity and therefore alternatives such as inorganic and mixed matrix membranes (MMMs) are proposed in many studies. The MMMs are composed by molecular sieving materials inserted in the polymer matrix and the properties of the polymer used are an important factor in determining the performance of these membranes [6,7]. Therefore the permeation behavior of pure and mixed gases must be thoroughly known. In this work a commercial polyimide, Matrimid 5218, was chosen for the manufacturing of the membranes. We decided to choose this glassy polymer because it presents a good trade off between H<sub>2</sub> permeability and both H<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub>/CO<sub>2</sub> selectivities. Also, this polyimide is frequently used in the manufacture of MMMs and has attracted a lot of attention for gas separation membranes due to the combination of relatively high gas permeability coefficients and separation factors coupled with excellent mechanical properties, solubility in non-hazard organic solvents and commercial availability [8].

Generally, the permeation behavior of a pure gas through a membrane depends mainly on the properties of the gas and membrane as well as the operation conditions. As for gas mixtures, the transport behavior of one component through the membrane is affected by the presence of other penetrants so that it deviates from that of the pure gas. Therefore, using the permeation data of pure gases to estimate the separation properties of gas mixtures may lead to wrong results [9,10]. The deviations are in general attributed to different factors. The solubility coupling by competitive sorption effects, plasticization and the concentration polarization phenomena are more prevalent in this study. The solubility coupling occurs between the penetrants and the polymer matrix, in the case of glassy polymers is negative which means that induces a decrease in the gas permeability. In the polymer matrix a fixed amount of sorption sites are present, which get saturated at a certain pressure, thereby leading to a decrease in solubility at higher penetrant pressures [11]. This may be explained in terms of the simple dual-mode sorption, partial immobilization model: penetrants compete for sorption sites which are associated with the non-equilibrium free volume in glassy polymers [12]. On the other hand, some penetrants sorb into polymers to such a degree that they plasticize the polymer. Plasticization effectively increases the chain spacing in the polymer and increases the chain mobility so that the diffusion and permeation coefficients increase with increasing penetrant pressure. Finally, the concentration polarization phenomenon is a consequence of the depletion of fast permeating molecules at the membrane surface due to the accumulation of slow permeating molecules in the gas phase adjacent to the membrane.

The present study reports new gas permeability data for the commercially available and industrially applicable Matrimid 5218 membrane, related to pure and gas mixtures of H<sub>2</sub>, CO, N<sub>2</sub> and CO<sub>2</sub> and reveals phenomena related to gas mixtures like concentration polarization and competitive sorption effects. Also, the “dual-mode sorption, partial immobilization” model was used to describe H<sub>2</sub> and CO<sub>2</sub> permeation behavior for pure, binary, ternary and quaternary gas mixtures. To this date, the majority of the work is still carried out in single gas experiments rather than with gas mixtures even though is well accepted that single and mixed gas experiments

will differ significantly [13,14]. In this way new knowledge on membrane behavior related to real process conditions are revealed. The satisfactory agreement between predicted results and experimental data allows the use of the proposed model and parameters to predict transport behavior of H<sub>2</sub> and CO<sub>2</sub> in real mixtures.

## 2. Theoretical background

The transport, i.e. permeability  $P_i = D_i \cdot S_i$  of a gas through a dense polymeric film can be described as a solution–diffusion mechanism where the solubility  $S_i$  is a thermodynamic parameter and the diffusivity  $D_i$  is a kinetic parameter. The separation factor characterizes membranes in terms of separation and is defined, in the case of negligible downstream pressure, as the ratio of permeabilities [15].

Gas sorption and diffusion in glassy polymeric membranes has been described by several established models but the use of the “dual-mode sorption, partial immobilization” theory has been more prevalent [16]. This model originally proposed by Barrer et al. [17] has been extended by Michaels et al. [18], Paul et al. [19], Koros et al. [20] and many others. According to the dual-mode sorption model, gas sorption ( $C_m$ ) in a polymer occurs in two types of sites, Henry and Langmuir sites respectively. The first type is filled by gas molecules dissolved in the equilibrium free volume portion of the material (concentration  $C_D$ ) and the second one corresponds to the population dissolved in the excess free volume of the glassy polymer ( $C_H$ ) [15].

$$C_m = C_D + C_H = k_D \cdot p + \frac{c'_H \cdot b \cdot p}{1 + b \cdot p} \quad (1)$$

$$S \equiv \frac{C_m}{p} = k_D + \frac{c'_H \cdot b}{1 + b \cdot p} \quad (2)$$

Here,  $p$  (bar) is the pressure and  $k_D$  ( $\text{m}^3(\text{STP})\text{m}^{-3}\text{bar}^{-1}$ ) represents the Henry law constant.  $c'_H$  ( $\text{m}^3(\text{STP})\text{m}^{-3}\text{bar}^{-1}$ ) is the Langmuir capacity constant and characterizes the total sorption capacity of the lower density regions (unrelaxed gaps) in a glassy polymer for a particular penetrant. The parameter  $b$  (1/bar) is the Langmuir affinity constant which characterizes the tendency of a given penetrant to sorb in the Langmuir mode. The affinity constants for “non-condensable” penetrants such as helium and hydrogen are small, while more easily condensable polar and polarizable penetrants such as carbon dioxide tend to have significantly larger affinity constants [20].

The dual-mode theory has been extended to multicomponent gas mixtures and is presented in Eq. (3) [21]:

$$S_i = k_{Di} + \frac{c'_{Hi} \cdot b_i}{1 + \sum_{i=1}^n b_i \cdot p_i} \quad (3)$$

The primary effect for a mixture is the simple competition by the various penetrants for the excess free volume fraction of the polymer which causes a significant depression in the sorption of all components of the mixture [20]. All the parameters in Eq. (3) are for pure components and their use for predicting mixture sorption assumes that plasticizing effects on  $k_D$ , penetrant–penetrant interactions influences on both  $b_i$  and  $c'_H$  of the components and bulk flow are negligible.

As a consequence of the existence of two types of adsorption sites in glassy polymeric membranes two diffusion coefficients can be defined.  $D_D$  is used for the mobility of the gas population dissolved in the equilibrium free volume of the polymer and  $D_H$  for the mobility of the gas population contained in the excess free volume. Then, the Fick's law expression for flux ( $J$ ) through the membrane has the form:

$$J = -D_D \cdot \frac{dC_D}{dx} - D_H \cdot \frac{dC_H}{dx} \quad (4)$$

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