

Membrane Technology for Hydrogen Separation in Ethylene Plants

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ABSTRACT

The use of membranes for hydrogen separation has been applied commercially in recent years. Several new membrane materials, which are now commercially available, are seriously being considered for the separation of hydrogen both effectively and efficiently within the ethylene process. This study investigates the feasibility of hydrogen separation from the cracked gas in an optimal manner before entering the low-temperature section of the ethylene plant. This separation would consequently reduce the refrigeration load as well as the equipment size of the cold-box section. Polyimide membrane materials are very selective for hydrogen transport as compared to other hydrocarbons, such as methane and ethylene. Polysulfone has also proven to be selective for the separation of hydrogen from hydrocarbons. This study evaluates two new commercial polyimide membranes as well as a new polysulfone membrane and determines the feasibility of hydrogen separation before entering the low-temperature section of the ethylene plant. The performance of the membranes and their effects on the overall ethylene process are also presented.

INTRODUCTION

A quick review of the chemical literature indicates that ethylene is one of the most important as well as one of the largest volume petrochemicals in the world today and serves as a key building block in the petrochemical industry. Conventional ethylene production involves the cracking of a hydrocarbon feed to form a mixture of hydrogen, methane, ethylene, ethane and heavier components that are separated by expensive cooling and distillation processes. The realization that the separation and purification process steps in the ethylene production consume more than 70% of the total energy required, provides a strong motivation for evaluating the impact of new technology on this part of the production process.

Membrane technology has many advantages over other conventional technologies. These include lower capital and operating costs, low maintenance cost and the ease of installation and operation [1]. Membrane technology for hydrogen separation from other gases was successfully applied in the last few years to recover hydrogen from tail gases in oil refineries. The first-large commercial application for membrane-based hydrogen systems was the separation of hydrogen from nitrogen in ammonia plants. Membrane technology is also used commercially for hydrogen/carbon monoxide (synthesis gas) ratio adjustment [2].

The membrane-based hydrogen separation in the past was based on low selective materials such as cellulose acetate polymers. However, new polymer membranes with improved selectivity and flux rate are now available in the market. For example, polyimides (Ube, Praxair), brominated polysulfone (Permea) are new selective membranes [3]. The selective membranes provide a major opportunity to improve the economics for different gas separation applications.

This study investigates the use of membrane-based technology for hydrogen separation in a commercial ethylene process. The goal has been to study the feasibility of separating the hydrogen from the cracked gas in an optimal manner before it enters the cryogenic section, to further decrease the refrigeration load in the latter unit. Different membrane materials available from recent studies are evaluated for this separation to obtain the maximum

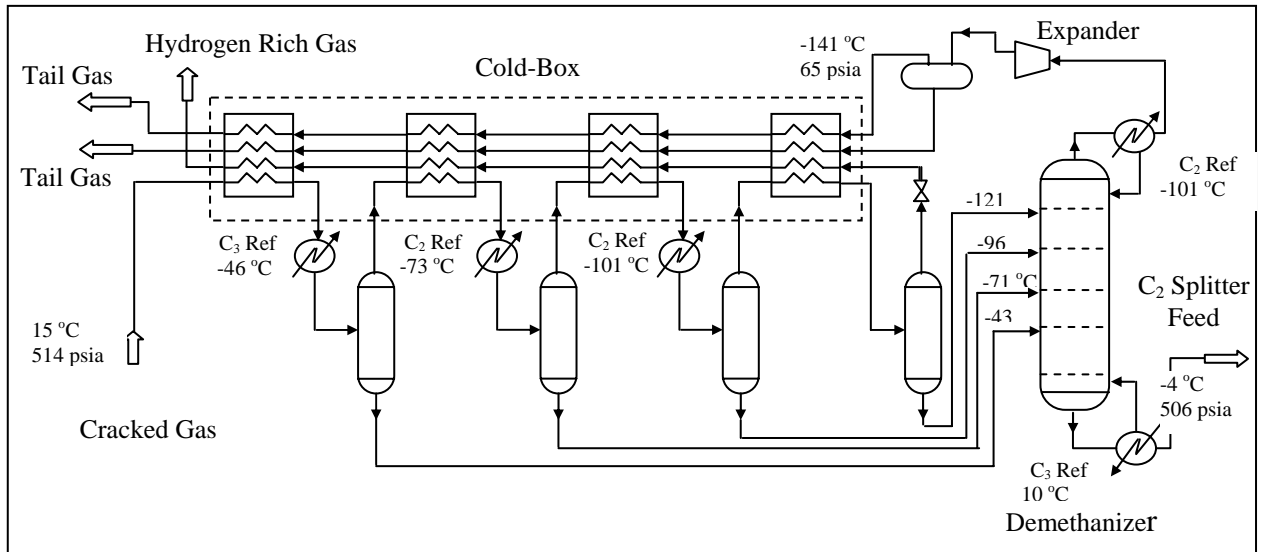


Figure 1: Chilling and demethanization section of the front-end deethanizer ethylene process.

selectivity and flux performance. Figure 1 shows the chilling and demethanization section of the front-end deethanizer ethylene process.

MEMBRANE MATERIALS

Hydrogen has a relatively small molecular size compared to other gases and exhibits high selectivity ratios in glassy polymers [4]. The ideal membrane possesses a high flux as well as a high selectivity. However, there is a trade-off between selectivity and flux rate. The degree of separation is highly dependent on both membrane selectivity and permeability. For our application, the separation goals require selection of membranes that provide high selectivity for hydrogen transport over ethylene to decrease the ethylene loss in the permeate stream. On the other hand, the membrane should also have a relatively high flux rate for hydrogen transport to lower both the capital and operating costs of the process. Additionally, the membrane must be stable at the operating conditions of the process. The fluxes and selectivities of hydrogen are provided for three new commercial membranes in Table 1 [2,5].

Table 1: Hydrogen separation membranes.

Membrane Type	Selectivity				Hydrogen Permeance (GPU)*
	H ₂ /CO	H ₂ /CH ₄	H ₂ /C ₂ H ₄	H ₂ /C ₂ H ₆	
Polyimide A	100	250	200	1000	100
Polyimide B-H	56	125	250	590	500
Polysulfone	1.7	33	35	50	100

$$* 1 \text{ GPU} = 10^{-6} \frac{\text{cm}^3(\text{STP})}{(\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg})} = 7.501 \times 10^{-12} \frac{\text{m}^3(\text{STP})}{(\text{m}^2 \cdot \text{s} \cdot \text{Pa})}$$

The first polyimide membrane (polyimide A) has higher selectivities for hydrogen over CO, CH₄ and C₂H₆ compared to the second polyimide membrane (polyimide B-H). The latter, however, has better selectivity for hydrogen over ethylene ($\alpha_{\text{H}_2/\text{C}_2\text{H}_4} = 250$). On the other hand, the hydrogen permeance of the polyimide B-H membrane is five times higher than that for the polyimide A membrane. This has the advantage of a high flux

membrane but at the same time the ethylene flux is higher compared to the first polyimide membrane. The polysulfone provides no advantages over the two polyimide membranes.

The three membranes can operate over wide pressure and temperature ranges. The polyimide membrane of Ube can operate for a feed gas pressure of up to 40 barg with a maximum temperature of 150 °C and from 40 to 150 barg feed pressure with a maximum temperature of 100 °C [5]. The lifetime of the polyimide membrane is in the range of seven to ten years.

PROCESS DESIGN CONSIDERATIONS

The feed to the membrane unit must be maintained at a temperature similar to that of the experimental data. In general, a low feed temperature increases the selectivity, but the flux rate is also decreased. The cracked gas which leaves the front-end acetylene reactor is cooled from 94 °C to 60 °C using cooling water before being sent to the membrane unit. On the other hand, the retentate stream (cracked gas with low hydrogen content) that leaves the membrane unit is cooled against the overhead of the deethanizer before sending this stream to the cold-box. In this way, the modified design does not require a steam heat exchanger and the cracked gas can be sent to the cold-box at a temperature of 15 °C.

The recovery and purity of the ethylene product are the most important specifications by which we can make an equivalent comparison between the membrane-based hydrogen technology and the conventional cooling and distillation system. Usually in the ethylene industry, the overall ethylene recovery loss is minimized to less than 1% in order to achieve an economical process.

The goal of this study is to design a membrane system such that the hydrogen recovery using the membrane-based technology is equivalent to the hydrogen recovery obtained from the conventional process. At the same time, the ethylene loss in the hydrogen rich gas (permeate stream) must be minimized to that level of ethylene loss obtained in the conventional process. To obtain the complete recovery of hydrogen with a minimum loss of ethylene, a cascade membrane system is required.

The operating temperature is maintained at the same temperature as that used in obtaining the experimental data. Furthermore, the hydrogen permeate stream is maintained at a pressure of 3.45 to 6.89 barg (50-100 psig) for export and further processing. Credit for the hydrogen rich gas product is based on the concentration.

MEMBRANE MODEL

The three membranes used in this study are nonporous polymer membranes. The transport of gases through nonporous polymer membranes can be described by the solution-diffusion mechanism. This transport is a concentration gradient driven process, which is generally well described by Fick's first law

$$J_i = - D_i \frac{dc_i}{dx} \quad (1)$$

where J_i is the flux of species i through the membrane, D_i is the diffusion coefficient of species i in the membrane and dc_i/dx is the local concentration gradient of species i at a given position in the membrane.

Equation 1 can be expressed in terms of the partial pressure of species i by using Henry's law as given by

$$c_i = S_i P_i \quad (2)$$

where S_i is the Henry's law solubility coefficient of species i and P_i is the partial pressure of species i outside the membrane. A more common way of measuring the flux of different species through the membrane is by applying the permeability coefficient

$$P_i = D_i S_i \quad (3)$$

The permeability coefficient, P_i , expresses the overall degree of permeation regardless of the actual transport mechanism. Integrating Equation 1 with the assumption of constant permeability coefficient yields

$$J_i = P_i \frac{(P_h x_i - P_l y_i)}{\delta} \quad (4)$$

where δ is the membrane thickness, P_h and P_l are the pressures on the feed side and the permeate side, respectively, x_i and y_i are the mole fractions of species i on the feed and permeate side, respectively.

The ability of a membrane to separate two gases i and j is obtained from the ratio of their permeabilities. This ratio is defined as the membrane selectivity α_{ij}

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{D_i S_i}{D_j S_j} \quad (5)$$

The performance of the membrane module can be described by a number of flow patterns: complete mixing, counter-current flow, co-current flow, and cross flow. For gas separation, counter-current and cross flow are normally used [6]. In addition, different module types are available. However, tubular hollow-fiber and spiral-wound modules are commercially used for gas separation applications. The counter-current flow pattern shown in Figure 2 best describes the flow in a hollow-fiber module. The latter is normally used in applications involving hydrogen separations [2].

The multicomponent transport through a membrane involves material balances along with a pressure drop calculation. The resulting model in differential forms can be solved by various computational algorithms such as approximate solution [7], finite elements [8] and collocation method [9]. The latter technique used in this study converts the boundary-value differential equations into a set of algebraic equations that can be solved by Newton's procedure.

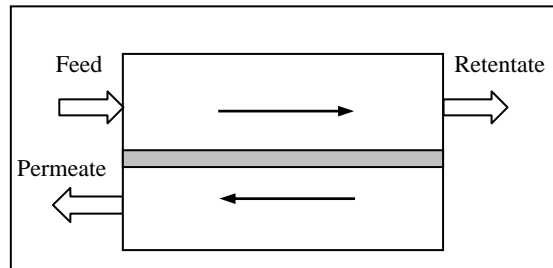


Figure 2: Schematic diagram of counter-current membrane module.

MEMBRANE PERFORMANCE

The performance of polyimide and polysulfone membranes has been investigated for the separation of hydrogen from the cracked gas in an ethylene plant. The hydrogen product leaves the membrane process as the lower-pressure permeate stream. The feed pressure and compositions are fixed in all calculations. The simulations were accomplished to evaluate the design variables such as permeate pressure on the performance of the membrane systems.

There is a trade-off between the purity and the recovery of hydrogen. At the same time, there is a trade-off between the purity and recovery of hydrogen and the permeate pressure. Figure 3 shows the effect of the permeate

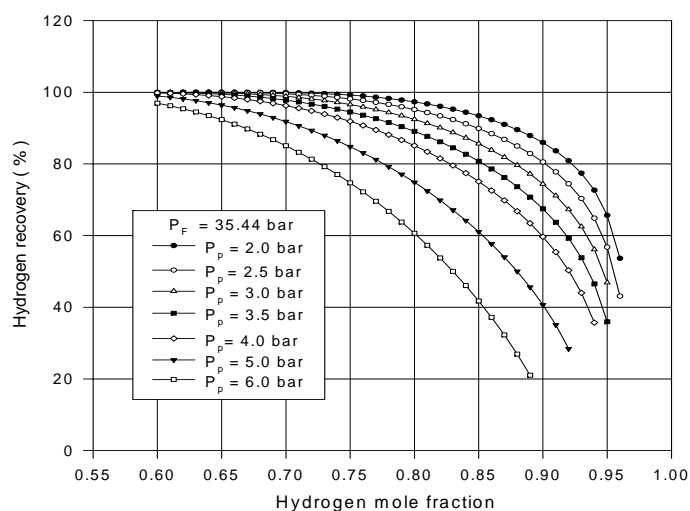


Figure 3: Impact of the permeate pressure on the recovery and purity of hydrogen using polyimide A membrane.

pressure on the recovery and purity of hydrogen on the membrane permeate side for the polyimide A membrane. A decrease in permeate pressure increases both the recovery and purity of hydrogen. However, the compression cost increases when the permeate pressure is decreased. Figure 3 also shows that the mole fraction of hydrogen increases on the permeate side is associated with a decrease in hydrogen recovery.

Concentration profiles of gases on the permeate side are presented in Figure 4 as a function of the hydrogen recovery. This figure shows that the ethylene mole fraction increases with an increase in the hydrogen recovery. In fact, the ethylene mole fraction could increase to 0.2 in the permeate stream when complete hydrogen recovery is under consideration.

Figure 5 shows the hydrogen recovery as a function of the relative membrane area and ethylene loss for a permeate pressure of 3.5 bar. Ethylene loss is defined as the ratio of ethylene in the permeate side to the ethylene in the feed side. Figure 5 reemphasizes the point that the ethylene loss increases as the hydrogen recovery is increased.

The performance of the polyimide B-H membrane is illustrated in Figure 6. Equivalent permeate pressures were used for this figure to provide a comparison with the performance of the polyimide A membrane shown in Figure 3. Polyimide B-H membrane provides a high hydrogen recovery but with a low hydrogen concentration in the permeate when compared to polyimide A. Note that the feed operating conditions are identical for both membranes.

Figure 7 shows a comparison between polyimide A and polyimide B-H with respect to relative membrane area and hydrogen purity on the permeate side as a function of the hydrogen recovery for a permeate pressure of 3.5 bar. Polyimide B-H membrane can provide a high hydrogen recovery using a relatively small membrane area compared to the polyimide A membrane. The relatively small area of polyimide B-H is a result of the high flux rate of the polyimide B-H membrane (see Table 2). On the other hand, polyimide A can provide a higher purity hydrogen compared to polyimide B-H but requires a larger membrane area. This suggests that the polyimide B-H membrane is the better choice for high hydrogen recovery since it requires a smaller membrane area. However, polyimide A is the choice for separations requiring high hydrogen purity. The membrane area is a function of several design variables including the permeate pressure and the hydrogen feed concentration. The required membrane area decreases with an increase in the hydrogen feed concentration as well as a decrease in the permeate

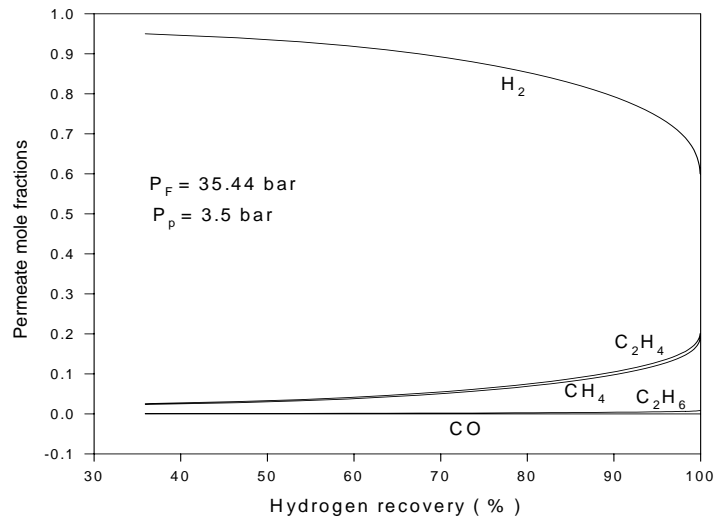


Figure 4 Concentration profiles of gases as a function of the hydrogen recovery in the permeate side of the membrane using polyimide A membrane.

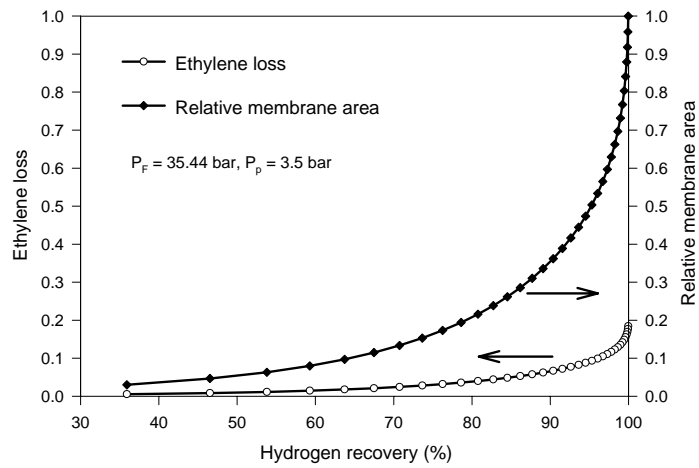


Figure 5: Ethylene loss and relative membrane area as a function of the hydrogen recovery using polyimide A membrane.

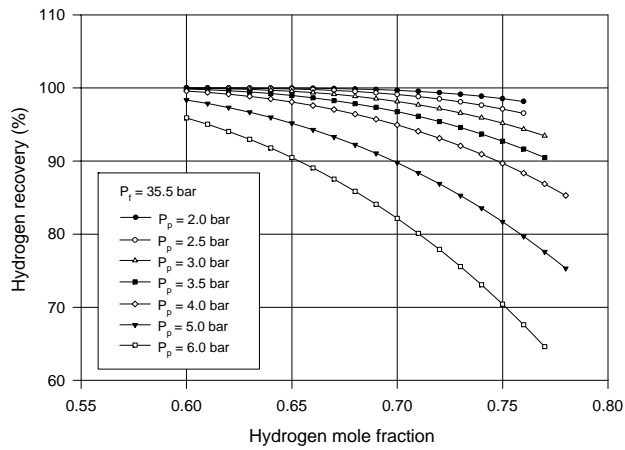


Figure 6: Impact of the permeate pressure on the recovery and purity of hydrogen using polyimide B-H membrane.

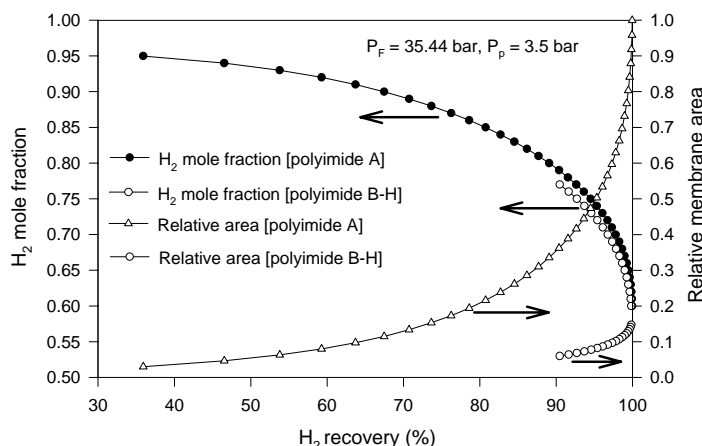


Figure 7: Comparison between polyimide A and polyimide B-H in relative membrane area and hydrogen purity in the permeate side as a function of hydrogen recovery for a permeate pressure of 3.5 bar.

pressure. Note that the comparison shown in Figure 7 was performed for a hydrogen feed concentration of 19.25 mol% and a permeate pressure of 3.5 bar. The performance of the polysulfone membrane does not compare to the performance of the polyimide membranes. The low flux as well as the low selectivities indicate that the polysulfone membrane is a poor choice for this particular hydrogen separation.

CONCLUSIONS

Economic evaluation of the cascade membrane systems shows that the two-stage cascade with recycling is a more profitable scheme when compared to the conventional designs. Implementation of this membrane technology in ethylene plants for improving the hydrogen separations shows considerable potential in either conventional grass-root ethylene plants or retrofits of existing ethylene plants. The savings in operating and capital costs for ethylene plants utilizing the proposed membrane systems are annually more than 9 million US dollars when the higher cost membranes are included in the economic analysis.

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