

SEPARATION OF CO₂ AND H₂ MIXTURES USING REACTIVE ION EXCHANGE MEMBRANES

by

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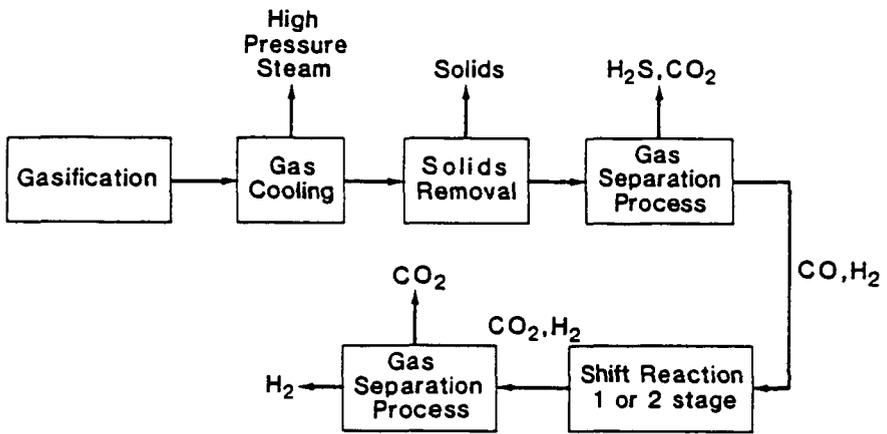
Introduction

Currently, the most widely used method for producing hydrogen is steam reforming of methane. The volatility in the price of natural gas has created increased interest in finding alternative feedstocks for the manufacture of hydrogen. Thus, it is appropriate at this time to conduct research which has the best opportunities for reducing H₂ production costs from coal gasification.

Bartis and Marks (1984) have identified low energy separation processes such as membranes as a key research opportunity in reducing capital and operating costs and hence the H₂ production costs. They state that technical improvements in gas separation could lead to production cost reductions of 15 to 20 percent. Figure 1 is a block flowsheet of a process to produce hydrogen from synthesis gas. There are two points in the process where gas separation processes take place. Acid gases must be removed from the gas stream after gasification and prior to the shift reaction. This separation step prevents sulfur poisoning of the shift catalysts and maximizes hydrogen production from the shift reaction. The second gas separation occurs after the shift reaction. CO₂ must be removed from the product stream to produce high purity H₂.

Membrane Separations

The use of membrane separations for the gas separation processes described above is an area deserving special attention because of its great potential for low capital cost and energy efficiency (Matson et al., 1983). A membrane process could theoretically separate a binary mixture reversibly, and therefore consume only the minimum work to accomplish the separation. The implicit simplicity and energy



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FIGURE 1 BLOCK FLOW DIAGRAM OF HYDROGEN PRODUCTION FROM SYNTHESIS GAS

efficiency of membrane processes have stimulated basic and applied research for many years.

The selective removal of CO₂ from mixtures of H₂, CO, and other gasification products using membranes depends on the appropriate choice of the membrane material. Many glassy polymers commonly used in commercial gas separation membranes are more permeable to H₂ than CO₂. The ideal separation factor, $\alpha(H_2/CO_2)$ for commercial asymmetric cellulose ester membranes is 2.2 (W. R. Grace, 1986) while the value for the polydimethylsiloxane/polysulfone composite membranes is 2.3 (Henis and Tripodi, 1980). Due to the large diffusivity of H₂ in typical glassy polymer materials the permeability coefficient (product of the diffusivity and solubility) of H₂ is greater than that of CO₂. While diffusivity controls the selectivity in glassy polymers, in rubbery polymers such as polydimethylsiloxanes (PDMS) or PDMS copolymers the solubility of penetrant gases controls the selectivity. In this case, the selectivity of the rubbery polymer membranes is reversed, and the membranes are more permeable to CO₂ than to H₂. The ideal separation factors (CO₂/H₂) are 4.9 and 4.6 for PDMS and PDMS/polycarbonate copolymers, respectively (Robb, 1968; General Electric, 1982). A separation factor of 6.4 was measured using a commercial GE PDMS membrane with a 50/50 mole % CO₂/H₂ feed gas mixture at ambient conditions. The measured CO₂ permeability was 2310 Barrer (1 Barrer=10⁻¹⁰ cm³(STP)cm/cm²·s·cm Hg) which is within 7% of the pure component value (General Electric, 1982). However, the H₂ permeability was 359 Barrer, only 70% of the pure component value. This observation could be explained if the H₂ solubility, and therefore the permeability, during the mixture experiment is lower than the pure component value due to the presence of CO₂ in the membrane.

Facilitated Transport Membranes

Liquids and solvent swollen ionomer membranes can also be used as membrane materials (Ward and Robb, 1968; LeBlanc et al., 1980; Way et al., 1987).

Incorporation of a complexation agent in these membranes can enhance the flux of a reactive species through a process known as facilitated transport. Way et al. (1987) have demonstrated facilitated transport of CO₂ through water-saturated perfluorosulfonic acid ion exchange membranes (IEMs) containing monopositive ethylene diamine as a counterion.

Ion exchange membranes containing EDA were prepared using the method of Way et al. (1987) using nominal 30 μm NE-111 perfluorosulfonic acid membranes. The experimental NE-111 membranes have an equivalent molecular weight of 1100 g/eq and are not available commercially. Preliminary transport measurements were performed at 25 °C and 1 atm to determine the CO₂ and H₂ permeabilities of the NE-111 IEMs. The pure component CO₂ permeability was 145 Barrer, in good agreement with the value of 146 Barrer previously reported by Noble et al. (1988). The H₂ permeability was 21.2 Barrer, corresponding to an ideal separation factor of 6.84 for the NE-111 IEM. The ideal separation factor for water, calculated by determining the ratio of permeability coefficients, is 17.2 at 25 °C and 1 atm (Kohl and Riesenfeld, 1985; Cussler, 1984). A possible explanation of the lower separation factor for the water-swollen IEM is that H₂ may diffuse through both the water containing cluster-channel network phase of the IEM (Gierke, 1977) and the fluorocarbon polymer phase. Further experiments will be performed to determine the permeability and separation factor for mixtures of CO₂ and H₂ using water as a solvent.

Selectivity improvements may be obtained by preparing facilitated transport IEMs using polar organic solvents such as propylene carbonate which are used commercially in physical absorption processes for removing CO₂ from gas mixtures. Propylene carbonate has the property that CO₂ is 121 times more soluble than H₂ at ambient conditions (Kohl and Riesenfeld, 1985). Assuming that the ratio of the diffusion coefficients (CO₂/H₂) in propylene carbonate is the same as water, an ideal separation factor (CO₂/H₂) of approximately 50 can be calculated.

Summary

Liquids and rubbery polymers are good candidate membrane materials for the separation of CO₂ from mixtures with H₂ because the solubility selectivity controls the separation that can be obtained. Facilitated transport IEMs containing monopositive ethylene diamine counterions have been shown to be selectively permeable to CO₂ over H₂. Transport measurements will be conducted to determine the influence of feed gas mixture composition, pressure, temperature, and solvent on the CO₂ and H₂ permeabilities and separation factor.

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