

SEPARATION OF COAL HYDROGASIFICATION GASES BY PERMSELECTIVE MEMBRANES

W. J. Schell

Chemico Process Plants Co.
El Monte, California 91734

INTRODUCTION

It has been recognized for many years that non-porous polymer films exhibit a higher permeability toward some gases than towards others. As early as 1831 (1), investigations were reported on the phenomenon of enrichment of air with rubber membranes; however, not until 1950 (2) had the practical possibility of this and other gas separations with permselective membranes been seriously studied. Weller and Steiner (2, 3) in their classic papers, demonstrated the feasibility of separating oxygen from air and described practical processes for separation of hydrogen and helium from methane. Although their results were highly valuable in the development of the science of membrane separation, the calculated membrane area requirements for industrial processes were enormous.

The technical breakthrough in the application of membranes to gas separation came with the development of a process for preparing cellulose acetate membranes in a state which retains the permselective characteristics of ordinary cellulose acetate but which yields vastly increased gas permeability. These cellulose acetate membranes are prepared from a solution of the polymer which is cast on a smooth surface, partially dried then set or gelled in an ice-water bath. At this stage the membranes are heated in water to improve their selectivity characteristics and are then dried by a solvent exchange technique. The reason for the highly permeability values, together with the permselective characteristics of ordinary cellulose acetate, is the formation of an "active" layer on the air-dried surface of the membrane. This active layer has characteristics similar to those of ordinary cellulose acetate and has a thickness of the order of 0.1 micrometer (μm) or less, whereas the total membrane thickness may range from approximately 75 to 125 μm . Thus, the membranes are said to be asymmetric. The major portion of the membrane is an open-pore sponge-like support structure through which gases may flow freely. The permeability and selectivity characteristics of these membranes are functions of casting solution composition, film casting conditions, and post-treatment and are relatively independent of total membrane thickness.

GAS SEPARATION THEORY

The steady state mass flux (J_i) of component i through a homogeneous film of uniform thickness separating two gaseous phases is given by Fick's "First Law" of diffusion:

$$J_i = -D_i \frac{dC_i}{dx} = \text{constant} \quad 1)$$

where

$$D_i = \text{local diffusivity (cm}^2/\text{sec)}$$

$$C_i = \text{local concentration of component } i$$

$$x = \text{the distance through the film}$$

This relationship can be simplified when the gases do not chemically associate with each other and when the gases are sparingly soluble in the membrane material. In such cases, the diffusivity of the permeating gas is constant through the film and the solubility of the gas at the membrane surface is essentially directly proportional to its partial pressure in the gas phase adjacent to that surface, i. e., Henry's Law applies:

$$C_i = k_i P_i \quad 2)$$

where k_i is the solubility parameter and P_i is the partial pressure.

If we let superscript I refer to the high pressure or upstream side of the membrane and superscript II refer to the low pressure or downstream side of the membrane, Equation 1, after integration between C_i^I at $x = 0$ and C_i^{II} at $x = l$, becomes:

$$J_i = \frac{k_i D_i (P_i^I - P_i^{II})}{l} \quad 3)$$

The product $k_i D_i$ is termed the permeability coefficient (\bar{P}_i) of the membrane for component i. This coefficient is independent of membrane thickness and pressure differential and the frequently used units are, cc(STP)-cm/cm²-sec-cm Hg. Another parameter of interest is the permeability rate, defined as \bar{P}_i/l , which is a measured characteristic of a given membrane with units, cc(STP)/cm²-sec-cm Hg. The total pressures, P^I and P^{II} , are given by the sums, $P_i^I + P_j^I$ and $P_i^{II} + P_j^{II}$, respectively.

The ratio of fluxes of two gases through a membrane is given by:

$$J_i = \frac{\bar{P}_i (P_i^I - P_i^{II})}{\bar{P}_j (P_j^I - P_j^{II})} \quad 4)$$

The ratio \bar{P}_i/\bar{P}_j is defined as the ideal separation factor for component i with respect to component j in the membrane and is written $\alpha_{i/j}$.

From the previous discussion it can be seen that, if component i is the more permeable, increasing P_i^I , either by increasing the total pressure or the concentration of component i, will result in a higher membrane permeability rate. In addition, higher values for $\alpha_{i/j}$ result in greater efficiency in gas separation.

If we define a permselectivity of the membrane to component i with respect to component j by σ_{ij} ,

$$\sigma_{ij} \equiv \frac{P_j^I P_i^{II}}{P_i^I P_j^{II}} \quad 5)$$

it can be shown from Equations 4 and 5 that:

$$\sigma_{ij} = \alpha_{i/j} \frac{P_j^I}{P_i^I} \frac{(P_i^I - P_i^{II})}{(P_i^I - P_j^{II})} \quad 6)$$

It can be seen from Equation 6 that as $P^{\text{II}} \rightarrow 0$ or $P^{\text{I}}/P^{\text{II}} \rightarrow \infty$, the permselectivity of the membrane approaches the ideal separation factor, i. e.:

$$\lim_{P^{\text{II}} \rightarrow 0} \sigma_{ij} = \alpha_{i/j} \quad 7)$$

It is evident then that by increasing the feed pressure to product pressure ratio, $P^{\text{I}}/P^{\text{II}}$, an increase in the efficiency of the separation of the gas mixture is obtained.

Other system variables that will have an effect on the separation process are temperature and relative humidity of the gas. Usually an increase in temperature increases the permeability and decreases the separation factor. The effect of relative humidity is variable and has not been reported in the literature to any great extent.

MEMBRANES AND MEMBRANE SYSTEMS

The casting solutions for preparation of the membranes discussed herein contain cellulose diacetate, cellulose triacetate, acetone, dioxane, methanol and acetic acid or maleic acid. The solution is cast at a thickness of 0.010 in. and is gelled in ice water. The resulting membranes are heat-treated in water at 85 to 98°C for several minutes and are then dried by solvent exchanging the water with organic solvents followed by evaporation of the remaining solvent. Drying is necessary for application to gas separation and this procedure serves to prevent the membrane from shrinking and losing its asymmetric character upon removal of water.

The gas permeability measurements for the flat membranes were made in circular (2.93 cm² membrane area or 0.0316 ft²) test cells. Single gases at 23 to 25°C were brought into contact with the dense active layer side of the membrane at a regulated pressure of 15 to 750 psig, causing a portion of the gas to permeate through the membrane. The permeate gas was removed from the opposite side of the membrane at atmospheric pressure. The permeation rates were measured either by the displacement of a soap bubble in a 5 ml gas buret or with a wet-test meter. The measured permeation rates and separation factors for the single gases with flat-sheet membranes are shown in Table 1, measured at 100 psi pressure differential, along with literature values for 0.001-in. cellulose acetate films. It can be seen that the permeation rates of the asymmetric membranes range from 600 to over 1000 times those of the films while essentially retaining the selectivity for gases. The membranes exhibit an exceptionally high permeation rate for hydrogen and helium and are particularly permselective for hydrogen relative to carbon monoxide and methane. This evidence confirms the continuity of the thin active layer and demonstrates the improvement in membrane separation technology.

Cellulose acetate membrane modules have been manufactured in our facilities for several years now for use in water desalination. These modules have a spiral-wound configuration (6) that has the advantage of compactness and low cost. For example, the dimensions of such a module are 4-in. in diameter by 3-ft in length containing approximately 70 ft² of membrane. Development of similar modules with dry membrane for gas separation will provide gas permeability rates of the order of 3200 - 9500 SCFH at 750 psig for hydrogen.

TABLE I

PERMEABILITY PROPERTIES OF FLAT CELLULOSE ACETATE MEMBRANES AND FILMS

	Permeability*, $\frac{\text{cc(STP)} \times 10^8}{\text{cm}^2 \text{-sec-cm Hg}}$				Separation Factor, α							
	H ₂	CO ₂	O ₂	CO	CH ₄	N ₂	He/CH ₄	H ₂ /N ₂	H ₂ /CH ₄	CO ₂ /CO	CO ₂ /CH ₄	O ₂ /N ₂
Film, 0.001-in. thick (4)	53.5	-	-	-	0.55	0.55	97	-	-	-	-	-
Film, 0.001-in. thick (5)	19.7	20-24	2.8-3.5	-	-	0.7-0.95	-	~25	-	-	-	~4.0
Membrane, Sample 1	32,400	28,000	15,800	2110	606	583	486	55	58	48	46	27
Membrane, Sample 2	32,800	29,310	16,100	2110	612	601	467	55	63	49	48	27
Membrane, Sample 3	33,900	28,600	16,400	2230	639	627	506	54	57	46	45	26

*A permeability of 30,000 cc(STP) $\times 10^{-8}$ /cm²-sec-cm Hg corresponds to 0.184 SCFH/ft² membrane/psi pressure differential.

APPLICATION OF MEMBRANE SYSTEM TO COAL UTILIZATION PROCESSES

The feasibility of adapting permselective membranes to coal utilization processes is described in the following paragraphs. Two processes were chosen from contract reports to the U. S. Department of Interior (7, 8).

In the two processes, the membrane separation units described are assumed to have the permeability and separation properties of the asymmetric cellulose acetates described previously in Table 1. It is also assumed throughout that all gas streams will have been pretreated for removal of acid gases. The resulting feed gases may then be considered to be a two-component system of hydrogen and methane-carbon monoxide (carbon monoxide and methane have similar permeabilities) and a computer program can be used to predict the permeate stream compositions.

Hydrogasification of Lignite

Figure 1 is a schematic diagram showing how membrane gas separators could be used to advantage in processing the gas from the hydrogasification of lignite. In this case the desired product is high Btu pipeline gas and the membrane separations are incorporated into the Institute of Gas Technology overall Process Block Flow Diagram (7) in order to reduce the size of several pieces of equipment and to produce 4% more methane with a higher Btu value.

The Prepurification Unit I effluent gas is cooled to 100°F to remove water and is then fed (Figure 1) into a spiral wound membrane separation unit which separates almost all of the hydrogen from the carbon monoxide and methane. The carbon monoxide and methane stream then has about 65% of the volume of the original stream and can be fed to a carbon monoxide shift reactor where the low concentration of hydrogen enables the reaction to be shifted further to the right ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$), therefore consuming considerably less steam than otherwise required. The overall result is that the carbon monoxide shift reactor size is reduced and the heat load of the waste heat recovery unit is reduced. The hydrogen-bearing permeate stream comes from the membrane unit at low pressure and must be compressed and cooled before it is sent to the Prepurification Unit II. After removal of carbon dioxide and the trace of hydrogen sulfide, the hydrogen stream is fed to the methanation unit where carbon monoxide is converted into methane.

The second membrane separation unit processes the effluent gas after waste heat recovery by removing most of the 4.4% hydrogen and recycling it back to the methanation unit. The recovered hydrogen allows about a 4% increase in the volume of methane produced and an increase in the Btu value of the pipeline gas.

The cost of the membrane units is believed to be small in comparison with the savings to be gained by reducing the size of the carbon monoxide shift reactor and waste heat recovery unit and reducing the amount of steam consumed so that the overall plant should be less costly. In addition, the incorporation of the membrane separators should allow greater variation in operating conditions and compositions of intermediate gas streams.

Coal Oil Hydrogenation

Membrane gas separation may also be applied to coal oil hydrogenation such as the Coal Oil Energy Development (C. O. E. D.) process (8). The hydrogenation unit is fed C. O. E. D. oil from the pyrolysis unit along with a mixture of fresh and recycle hydrogen. The membrane separator removes most of the methane

and heavier hydrocarbons from the recycle hydrogen stream at high pressure. The one-pass membrane unit operating at 1050 psig increases the recycle hydrogen concentration from 43% to over 90%, with the accompanying improvement in the hydrogenation efficiency and reduction in size of the hydrogenation unit. The methane and hydrocarbon gas stream contains less than 2% hydrogen and after extraction of the higher hydrocarbons would be ideal for pipeline gas.

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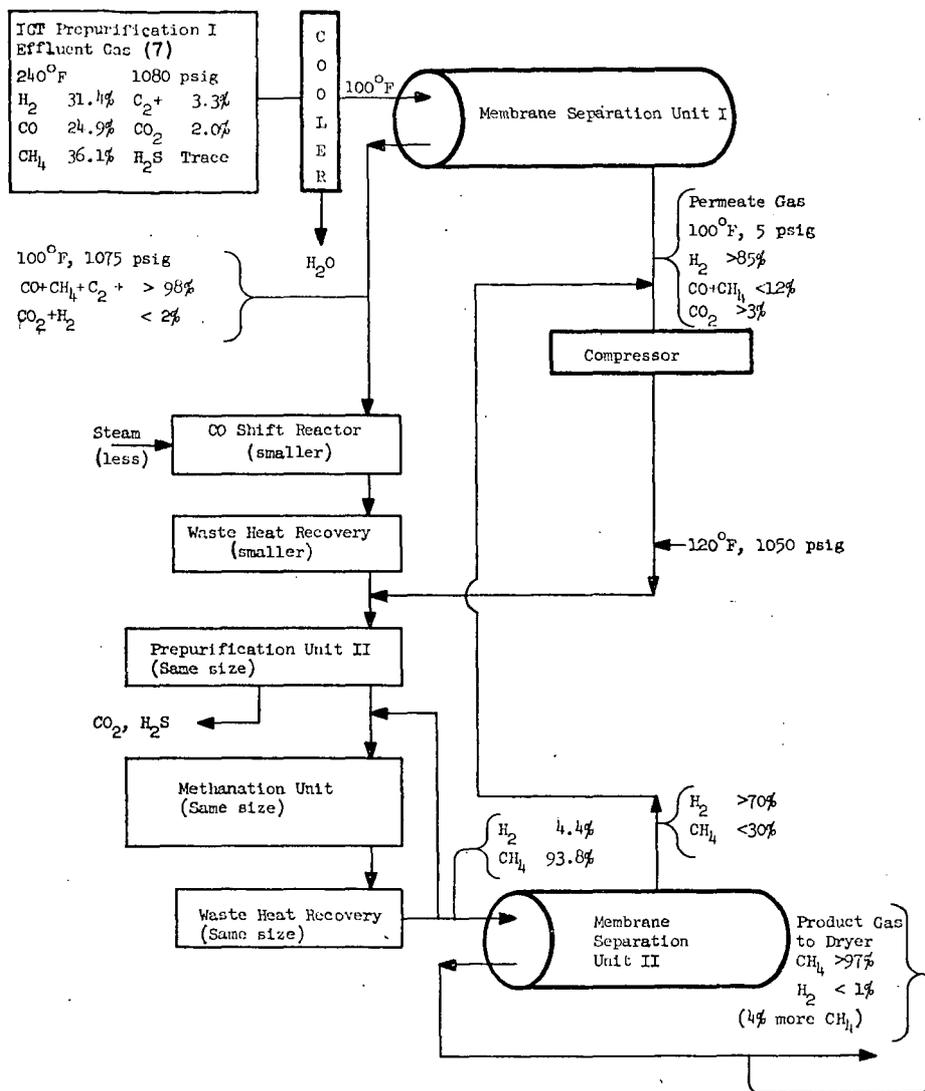


Figure 1. SCHEMATIC - APPLICATION OF MEMBRANE GAS SEPARATIONS IN A LIGHT GAS HYDROGASIFICATION PROCESS