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LOW COST HYDROGEN/NOVEL MEMBRANE TECHNOLOGY FOR HYDROGEN SEPARATION FROM SYNTHESIS GAS

Topical Report: Task 1, Literature Survey

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I. INTRODUCTION AND SUMMARY

Recent increases in the price of natural gas have prompted interest in alternative feedstocks for the manufacture of hydrogen. Coal appears to be one of the more attractive alternatives due to its abundance and stable price in the U.S. However, the production of hydrogen from synthesis gas made by gasification of coal is expensive because of the larger capital investments that are required compared to traditional steam-methane reforming plants. To make the coal-to-hydrogen route economically attractive, improvements are being sought in each step of the process: coal gasification, water-carbon monoxide shift reaction, and hydrogen separation.

This report addresses the use of membranes in the hydrogen separation step. The separation of hydrogen from synthesis gas is a major cost element in the manufacture of hydrogen from coal. Separation by membranes is an attractive, new, and still largely unexplored approach to the problem. Membrane processes are inherently simple and efficient and often have lower capital and operating costs than conventional processes. In this report we begin by summarizing current and future trends in hydrogen production and use. Methods of producing hydrogen from coal are then discussed, with particular emphasis on the Texaco entrained flow gasifier and on current methods of separating hydrogen from this gas stream. The potential for membrane separations in the process is then examined. In particular, the use of membranes for H_2/CO_2 , H_2/CO , and H_2/N_2 separations is discussed.

II. HYDROGEN PRODUCTION AND USE

Hydrogen has been termed the energy carrier of the future. Though not itself a primary energy source, it serves as a medium through which such a source can be stored, transmitted, and utilized. Hydrogen production is currently at 3% of total U.S. energy consumption and is predicted to grow by a factor of five by the year 2000(1). There are several distinct advantages to using hydrogen as an energy medium. First, hydrogen is readily made from fossil fuels and from water, two abundant resources. Second, on combustion, water is the main product; thus hydrogen is a clean, nonpolluting fuel. Finally, the technology to store hydrogen in the gas and liquid forms is well developed, as are systems to transport it.

Hydrogen is produced by several methods, the choice of which is determined by such factors as the quantity and purity of hydrogen required, and the availability and cost of raw materials. Currently, most hydrogen is produced by steam reforming of methane, a process in which methane and steam are reacted to form CO_2 and H_2 . Electrolysis of water is another proven reliable method, but the high cost of electricity is a limitation in this case. Other methods under development include thermochemical decomposition of water and coal gasification.

In 1981 3.9×10^{12} scf of hydrogen was produced and consumed in the U.S.(1) The largest single use is the synthesis of ammonia which alone employs some 37% of the total. The bulk of the remaining hydrogen is used in the petroleum refining industry, encompassing hydroprocessing (36.4%, principally hydrocracking and hydrodesulphurization), or as a refinery fuel (14.3%). A further 9.6% share goes to methanol synthesis, while the remaining 2.7% is used in specialty merchant applications, e.g. hydrogenation of oils and fats, and the aerospace industry. Figure 1 summarizes these figures for 1982(1).

It is anticipated that the demand for hydrogen will increase in the future, partly because of growth in present markets, particularly petroleum refining, but primarily because of the emergence of new needs. Industrial applications that could become large consumers of hydrogen include manufacture of synthetic fuels such as CH_4 , CH_3OH , OH and liquified coal, hydrogen-oxygen turbines and fuel cells. The use of hydrogen as a fuel for transportation is another possibility; hydrogen is already in use in the space program, serving as the rocket propellant for the shuttle, and it may well be employed as an alternative automobile fuel by the year 2000. As demand rises and gas and oil resources are depleted, it is likely that coal will become the primary source of hydrogen.

III. COAL GASIFICATION

A. An Overview

Hydrogen is produced from coal by the water gas reaction, i.e. reacting the coal with water. Because this reaction is endothermic, heat must be supplied. This is achieved by reacting a portion of the coal in the gasifier with oxygen to produce CO and CO_2 , both highly exothermic reactions. The process is usually performed in a large gasifying vessel where the coal is in contact with steam and either air or oxygen. The more important chemical reactions that take place in the process are shown in Table I(2).

Table I. Major Coal Gasification Reactions(2)
(All ΔH° at 2980K and 1 atm)

Combustion	$\text{C} + \text{O}_2 \rightarrow \text{CO}_2$	$\Delta H^\circ = -394 \text{ KJ/mol}$
Gasification	$\text{C} + 1/2\text{O}_2 \rightarrow \text{CO}$	$\Delta H^\circ = -111 \text{ KJ/mol}$
	$\text{C} + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO} + \text{H}_2$	$\Delta H^\circ = +131 \text{ KJ/mol}$
	$\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$	$\Delta H^\circ = +173 \text{ KJ/mol}$

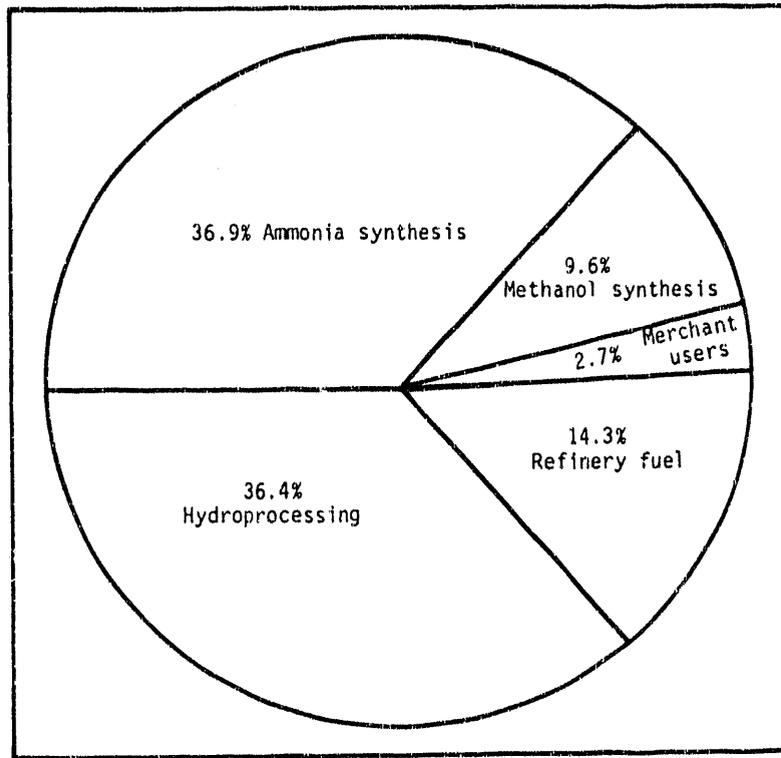


Figure 1. Distribution of the 3.9×10^{12} scf of hydrogen produced and consumed in the U.S. in 1981(1).

At the temperature of the gasifier coal breaks down and reacts with steam and oxygen to produce a mixture of gases commonly called synthesis gas. Synthesis gas comprises carbon monoxide, hydrogen, carbon dioxide, and water vapor, along with varying amounts of methane and impurities. The precise composition of the mixture depends upon the makeup and origins of the coal, the proportion of air (oxygen), steam, or other reactants used, gasifier temperature, operating pressure, residence time of the coal, and other parameters. Generally, the gasifier type and operating conditions are chosen to produce a synthesis gas best suited for the intended application.

There are many commercial or near commercial gasification processes(3-5). These can be grouped into four principal types of gasifier: fixed-bed, fluid-bed, molten bath, and entrained flow. Over the years a large number of coal gasification schemes have been suggested but many of these efforts are now inactive or have been abandoned. Of the processes being actively pursued entrained flow best suited for hydrogen production because of the high hydrogen and carbon monoxide content of the synthesis gas. The composition of the gas streams produced by some of these entrained flow gasifiers is listed in Table II. Of these processes the Texaco gasifier appears to be a good choice for our study based on its proven reliability and the availability of operating data from EPRI (The Electric Power Research Institute), a sponsor of much of the development .

Table II. Types of Entrained Flow Gasifiers

Process	Koppers-Totzek	Shell	Texaco
Development Status	Six plants in operation. Up to 600 ton/day capacity	Over 50 commercial plants operating on hydrocarbon liquids. 165 ton/day pilot pilot plant on coal	Many plants operating on hydrocarbon liquids. Several plants up to 1000 ton/day operating on coal
Raw gas Analysis (%)	CH ₄ trace H ₂ 18.7 CO 43.4 CO ₂ 6.1 H ₂ S 0.6 COS 0.1 N ₂ 0.9 H ₂ O 30.2 NH ₃ +HCN	CH ₄ trace H ₂ 30.0 CO 60.3 CO ₂ 1.6 H ₂ S 1.2 COS 0.1 N ₂ 3.6 Ar 1.1 H ₂ O 2.0 NH ₃ +HCN 0.1	CH ₄ 0.3 H ₂ 29.8 CO 41.0 CO ₂ 10.2 H ₂ S 1.0 COS 0.1 N ₂ 0.7 AR 0.1 H ₂ O 17.1 NH ₃ +HCN 0.2

B. Texaco Process

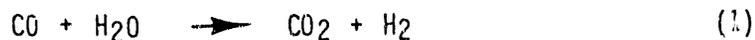
It is clear from the above discussion that there are many processes by which coal can be gasified, and numerous variable parameters within these processes. To analyze the feasibility of producing hydrogen from coal via membrane separation a process and its parameters need to be specified. Because of its simplicity, superior environmental properties, and high hydrogen and carbon monoxide composition in the gas, we have selected the Texaco coal gasification method. This process evolved from the Texaco synthesis gas generation process developed for the partial oxidation of natural gas. Later developments led to the use of petroleum refinery residues as a feedstock. The energy crisis of 1973 spurred the substitution of coal as the feed stock.

The Texaco process does not produce tars, carcinogenic compounds, or partially oxidized material which often require extensive wastewater-treatment. The technical feasibility of the Texaco process with coal has been demonstrated recently in the Montebello Pilot Plant and the Cool Water Coal Gasification Program, both in California. These two plants and many others operating on petroleum residues provide a large body of operating experience(4).

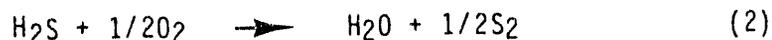
A flow diagram of the Texaco gasification process is shown in Figure 2. The major steps are optional air separation, coal gasification, water-gas shift conversion, carbon dioxide and hydrogen sulfide removal, and sulfur recovery.

The gasifier operates in the temperature range 1200-1430°C (2300-2600°F) and in the pressure range 600-1200 psig (40-80 atm). The coal-water slurry and oxygen from the air separation plant are fed into the gasifier where the combustion reactions proceed to completion in a few seconds. The gases exiting the reactor are water quenched, removing particulates and ash and cooling the stream.

The gas then flows to the carbon monoxide shift converter, where carbon monoxide is catalytically converted to hydrogen and carbon dioxide by the reaction



The process gas from the shift converter then moves to the acid gas removal system (AGR). The AGR separates H₂S and CO₂ from the gas stream. The H₂S stream is sent to a Claus unit for conversion to sulfur by the reaction



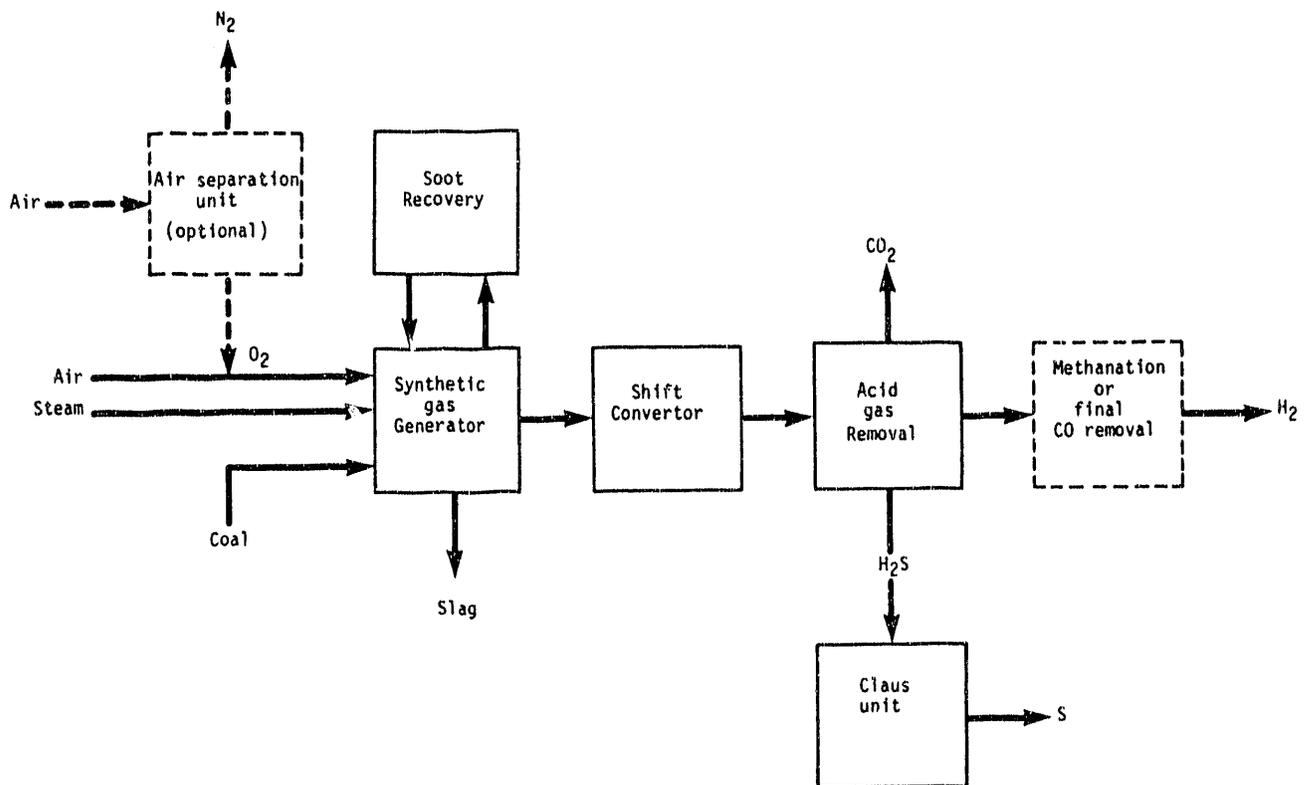


Figure 2. Flow diagram of the Texaco coal gasification process.

The CO₂ stream is treated to remove residual sulfur gases and is then vented. The H₂S and CO₂ depleted stream now consists of 97 to 98% hydrogen, 1% CO and traces of CO₂ and other gases.

In the process described above, oxygen is used as the gasifying medium. The oxygen is supplied from an air separation plant, which generally employs a standard cryogenic process with reversing flow-heat exchangers, to produce high purity (99.5% or better) gaseous oxygen. (Membrane processes to separate oxygen from air exist, but the permeate oxygen concentration is fairly low, around 35-50%.) Using pure oxygen rather than air produces a nitrogen-free product gas. This is desirable because the presence of nitrogen will substantially reduce the value of the product in most applications, and low cost methods of separating hydrogen from nitrogen have not been developed to date. It should be understood, however, that the Texaco gasifier can operate with either air or oxygen-enriched air as the gasifying medium. The use of air is not common because temperatures high enough to slag the ash cannot be attained. Data from a Texaco gasifier operating with three different gasifying media is shown in Table III(4,6). The gas produced in these processes was meant for utility boiler fuel rather than as a source of hydrogen. When air is the gasifying medium a substantial amount of nitrogen, almost 60%, is present in the gas stream. Using air enriched to 35% O₂ results in 43% N₂ in the product gas, while 100% O₂ gives only 0.5% N₂ in the product gas.

Table III. Product Gas Stream Composition with Air, 35% O₂, and 100% O₂ Used as the Gasifying Medium

Gas Stream Composition (vol%)	Oxygen content of gasifying medium		
	<u>21% O₂ (Air)</u>	<u>35% O₂</u>	<u>100% O₂</u>
H ₂	11.6	17.8	34.5
CO	19.5	23.2	41.6
CO ₂	7.7	14.6	22.0
N ₂	59.7	43.2	0.5
Ar	0.7	0.5	<0.1
H ₂ S	0.5	0.9	1.5
CO _S	<0.1	<0.1	<0.1

Conditions: Texaco Gasifier; Illinois #6 coal; temperature, 2000-2200°F; pressure, 600 psig with air, 350 psig with 35% and 100% O₂(4,6).

As described in the next section, membrane processes are able to separate hydrogen from nitrogen quite efficiently so that the use of air or oxygen enriched air in the gasifier would be possible. It is very likely that the cost of the H₂/N₂ membrane separation unit would be more than offset by elimination of the cryogenic air separation plant.

IV. PURIFICATION OF SYNTHESIS GAS BY CONVENTIONAL PROCESSES

The raw product gas that leaves the gasifier must be cleaned up regardless of whether hydrogen, low-Btu gas, synthesis gas, or methane is the desired product. The specifications to be met by the clean gas vary with the intended application.

Typically the hot gas leaving the gasifier contains coal dust, ash, HCl, NH₃ and other impurities that can be removed by a simple water quench. This quench will also cool the stream, recovering some of the heat for use elsewhere and avoiding the technical problems associated with cleaning a hot gas stream. After the water quench the primary compounds of concern in gas clean-up are H₂S, CO₂ and CO. These are removed in the shift conversion, acid gas removal, and sulfur recovery steps. Figure 3 shows the composition of the gas stream after each purification step when O₂ is used as the gasifying medium (6,7).

As shown, the water quenched process gas is first passed to a shift converter, where the CO is shifted to CO₂ for removal in the acid gas removal system that follows. The CO content of the gas entering the converter is about 42%. After full shift this level decreases to 2%(7).

The next purification step is separation of the acid gases. The goal of this separation is to remove most of the CO₂ and essentially all of the H₂S from the feed stream. The separated gases leave the process in two streams, one containing CO₂ and no H₂S, the other containing all of the H₂S and some CO₂. The CO₂ stream is clean enough to be vented without further treatment, while the H₂S enriched stream is sent to a sulfur recovery process. For the process to be most economical a system yielding an H₂S stream with an H₂S concentration of at least 15% is required. Several commercially developed systems meet this requirement. Most of them employ an absorption-desorption system in which a liquid phase selectively absorbs one or more components from the gas. The gas may simply dissolve in the liquid or it may react. After the absorption step, the pressure of the liquid-gas mixture is lowered, or the temperature raised, thereby desorbing the absorbed H₂S and CO₂ separately from the mixture and regenerating the liquid phase.

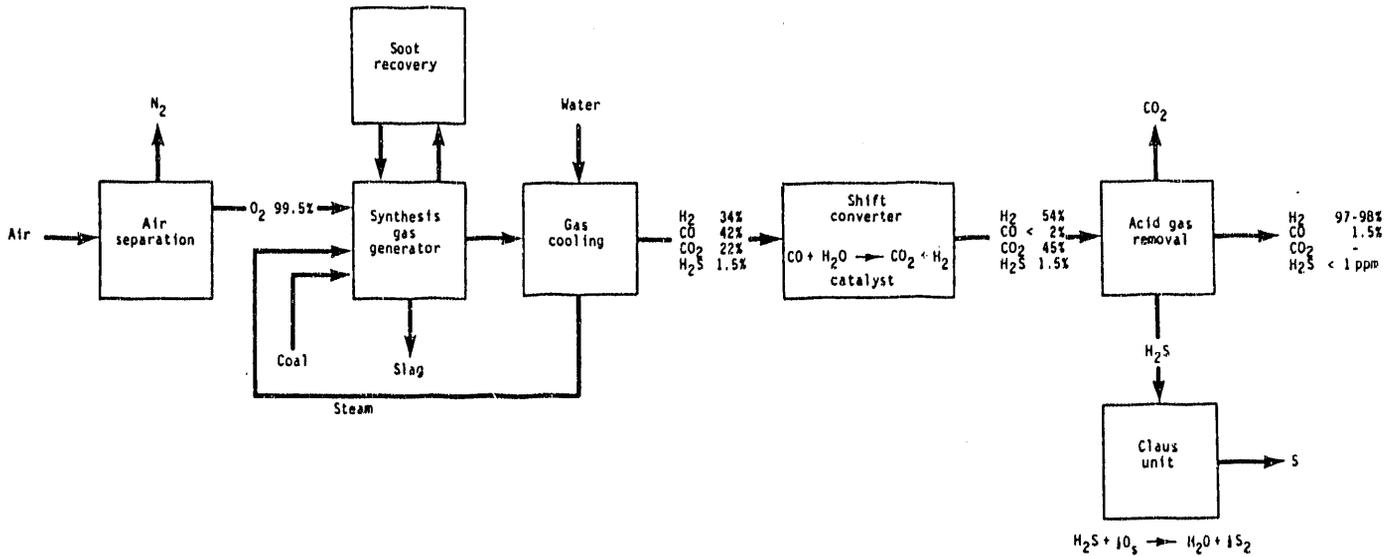
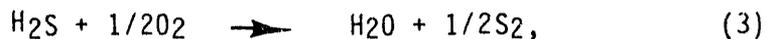


Figure 3. Approximate composition of the gas stream after each step of a coal gasification process. The numbers shown are average numbers taken from several sources and are not representative of any one particular process(4,6,7).

Three classes of acid gas removal systems are commonly used⁽⁸⁾. The first uses amine based solvents such as monoethanol amine, diethanol amine, diglycol amine, and some tertiary amines. Each amine differs in its degree of selectivity in sulfur removal. In general, amine treatment in coal processing is not as efficient or as economical as other processes because of the poor selectivity for H₂S and higher operating costs at the large operating pressures of the coal gasification process. The second class uses hot carbonate solutions to selectively remove the CO₂. A proprietary process is usually employed and a reasonable degree of selectivity is obtained. A two-stage system will generate a sulfur-rich stream that is sufficiently concentrated for further recovery in a Claus unit. Physical solvent systems comprise the third group, and at least six processes, among them the Rectisol, Fluor and Selexol processes, have been commercialized. These systems utilize higher solubility of certain solvents for H₂S and CO₂ than for the other fuel gas species. In most solvents the H₂S is significantly more soluble than the CO₂, allowing for a good separation of the two gases.

The choice of sulfur recovery process used to treat the H₂S stream from the AGR system will depend on the concentration of H₂S in the stream. The Claus process, which recovers the sulfur according to the reaction



is most effective with H₂S concentrations around 15% or above. Alternative sulfur recovery techniques such as adsorption onto solids, activated carbon, or the Stretford process are used if the sulfur feed concentration is below 10%.

Together, these gas separation processes account for a large portion of the capital and operating costs of a coal gasification facility. A precise statement of actual separation system costs is difficult to make because of the variability of the gasification processes and the operating parameters. However, Billings⁽⁷⁾ gives a breakdown of the capital costs for a Winkler gasification process, as shown in Table IV. The coal gasification step represents only 20% of the total plant capital costs while the combined purification steps represent some 34%. Clearly a reduction in gas separation costs would have a dramatic affect on the overall cost of the hydrogen produced.

Table IV. Capital Costs of the Purification Process for a Winkler
Coal Gasification Plant Producing H₂(7)

Item	% of Capital Cost
Coal handling & preparation	13.8
Coal gasification	20.5
CO shift	9.6
Acid gas removal and sulfur recovery	16.7
Gas compression	7.7
Waste water treatment	4.3
Oxygen plant	17.2
Off-site & miscellaneous	10.2
TOTAL	100 %

In summary, there are four potential membrane applications in gasification processes as illustrated in Figure 4.

1. The separation of oxygen from air.
2. The separation of hydrogen from carbon monoxide before the shift reaction.
3. The separation of hydrogen from carbon dioxide after the shift reaction.
4. The separation of hydrogen from nitrogen after the AGR removal step in an air blown gasifier process.

The separation of oxygen from air is outside the scope of this program and will only be discussed briefly in the following section. This project will concentrate on the three hydrogen separation processes.

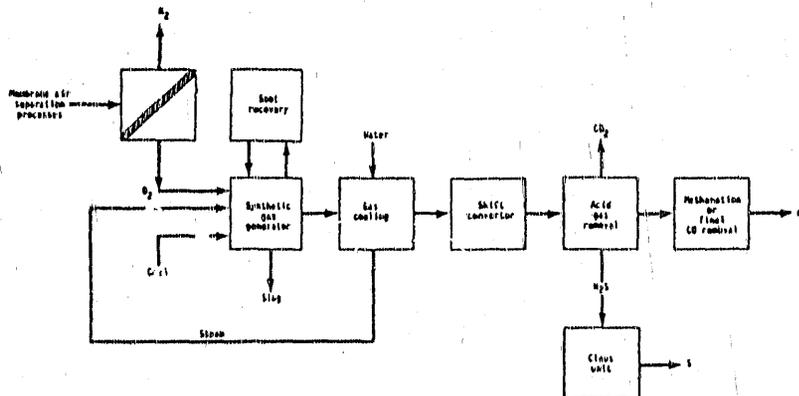
V. MEMBRANE SEPARATION PROCESSES

A. Review of Gas Separation Membranes

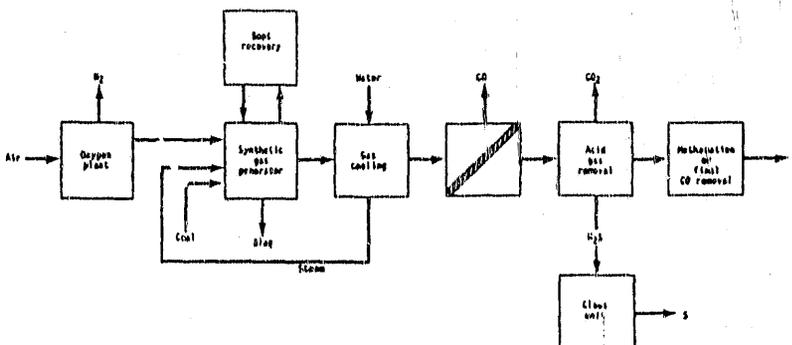
Before we discuss the potential application of membranes to hydrogen production from coal, a review of the principal types of gas separation membranes is in order.

The separation of gases by permselective membranes has a long history dating back to the work of Thomas Graham. However, the first systematic studies with polymer membranes of the type used today did not begin until the 1940s, when Van Amerongen⁽⁹⁾, Barrer⁽¹⁰⁾, and others^(11,12) laid the foundation of modern theories of gas permeation. Although progress has been made since that time⁽¹³⁻¹⁵⁾, our basic understanding of membrane science has not changed. What has changed is membrane technology. During the last decade methods have been found to

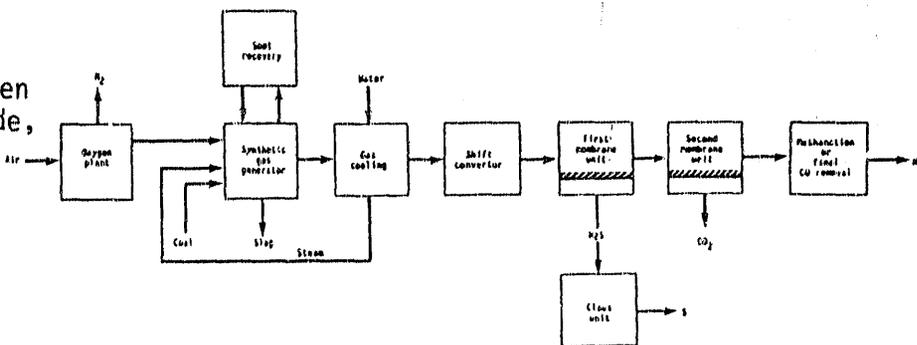
(a) Separation of oxygen from air



(b) Separation of carbon monoxide from hydrogen and carbon dioxide



(c) Separation of hydrogen from hydrogen sulfide, and carbon dioxide



(d) Separation of hydrogen from nitrogen, carbon monoxide, and carbon dioxide

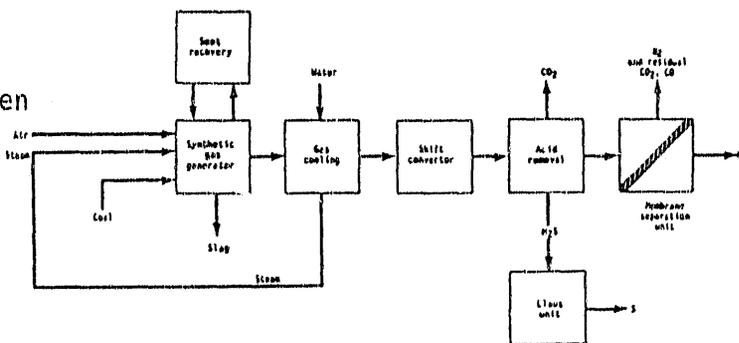


Figure 4. Examples of synthesis gas membrane separation processes

produce extremely thin (and hence high flux) membranes in compact high surface area membrane modules. As a result, there is now a surge of interest in using membranes to accomplish gas separations. These membranes can be divided into four categories: nonporous polymeric membranes, microporous membranes, facilitated transport membranes, and nonporous metal membranes.

Nonporous Polymeric Membranes: The vast majority of currently used gas separation membranes belong to this group. The permeation of gases through these membranes is generally analyzed using the solution-diffusion model, which was first proposed by Thomas Graham in 1866 and further developed in the 1940s and 50s. In this model, it is assumed that gas at the high pressure side of the membrane dissolves in the membrane material and diffuses down a gradient in concentration to the low pressure side of the membrane where the gas is desorbed. It is also assumed that the gas phases on either side of the membrane are in thermodynamic equilibrium with their respective polymeric interfaces, and that the interfacial sorption and desorption process is rapid compared to the rate of diffusion through the membrane. Thus, the rate limiting step is diffusion, which is governed by Fick's law. For simple gases, Fick's law leads to the equation

$$J = \frac{DK\Delta p}{l} \quad (4)$$

which can be further simplified to

$$J = \frac{P\Delta p}{l} \quad (5)$$

where J is the membrane flux [$\text{cm}^3(\text{STP})/\text{cm}^2\text{sec}$], D is the diffusion coefficient of the gas in the membrane [cm^2/sec] and is a measure of the gas mobility, K is the Henry's law sorption coefficient linking the concentration of the gas in the membrane material to the pressure in the adjacent gas [$\text{cm}^3(\text{STP})/\text{cm}^3\cdot\text{cmHg}$], and Δp is the pressure difference across the membrane. P is the permeability equal to the product DK and is a measure of the rate at which a particular gas moves through the membrane of a standard thickness (1 cm) under a standard pressure difference (1 cmHg). The permeability unit

$$\frac{1 \times 10^{-10} \text{ cm}^3(\text{STP})\text{cm}}{\text{cm}^2\text{sec}\cdot\text{cmHg}}$$

is often called a Barrer, after R.M. Barrer, a pioneer in membrane permeation studies.

A measure of the ability of a membrane to separate two gases (1) and (2) is the ratio of their permeabilities, α , called the membrane selectivity,

$$\alpha = \frac{P(1)}{P(2)} \quad (6)$$

The factors that determine membrane permeabilities can best be understood by considering the component terms D and K. For simple gases, the diffusion coefficient tends to decrease with increasing permeant diameter, since large molecules interact with more segments of the polymer chains and are thus less mobile. On the other hand, the sorption coefficient of gases increases with the condensability of the gas, since this is a measure of the energy required for the gases to be sorbed by the polymer. Normally, the sorption coefficient also correlates with molecular diameter, larger molecules being more condensable than smaller molecules; thus, the Henry's law sorption coefficient increases with increasing permeant diameter. The terms D and K are plotted vs. molecular diameter for natural rubber membranes and a series of gases in Figure 5.

It follows from the behavior shown in Figure 5 that a plot of membrane permeability vs. permeant molecular diameter has the form shown in Figure 6. Small molecules, such as H₂ and He, have high permeabilities because they are small and have high diffusion coefficients, while large molecules, such as CO₂, have high permeabilities because they are very condensable. Molecules such as nitrogen have relatively low permeabilities because they have both low diffusion and low sorption coefficients.

The form of the curves shown in Figures 5 and 6 is characteristic of most polymers. However, cross-linked or glassy polymers or polymers with rigid backbones generally show a more marked decrease in diffusion coefficient with increasing molecular size than more rubbery polymers. These rigid backboned polymers are therefore more selective than rubbery polymers. Unfortunately, rigid backboned polymers have lower diffusion coefficients, and are therefore much less permeable than rubbery polymers. Permeability vs. diameter curves for four polymers are shown in Figure 7(16,17). These results are typical. Silicone rubber is a highly permeable polymer, but is relatively unselective, while polystyrene and cellulose acetate are rigid, amorphous glasses with high selectivities but low permeabilities.

It is also clear from Figures 6 and 7 that H₂ is always considerably more permeable than CO or N₂ and thus easily separated from them by a polymeric membrane. On the other hand, the separation of H₂ from CO₂ is more difficult, since both gases are relatively permeable. Similarly, the separation of O₂ and N₂ is difficult, in this case because they are both relatively impermeable gases.

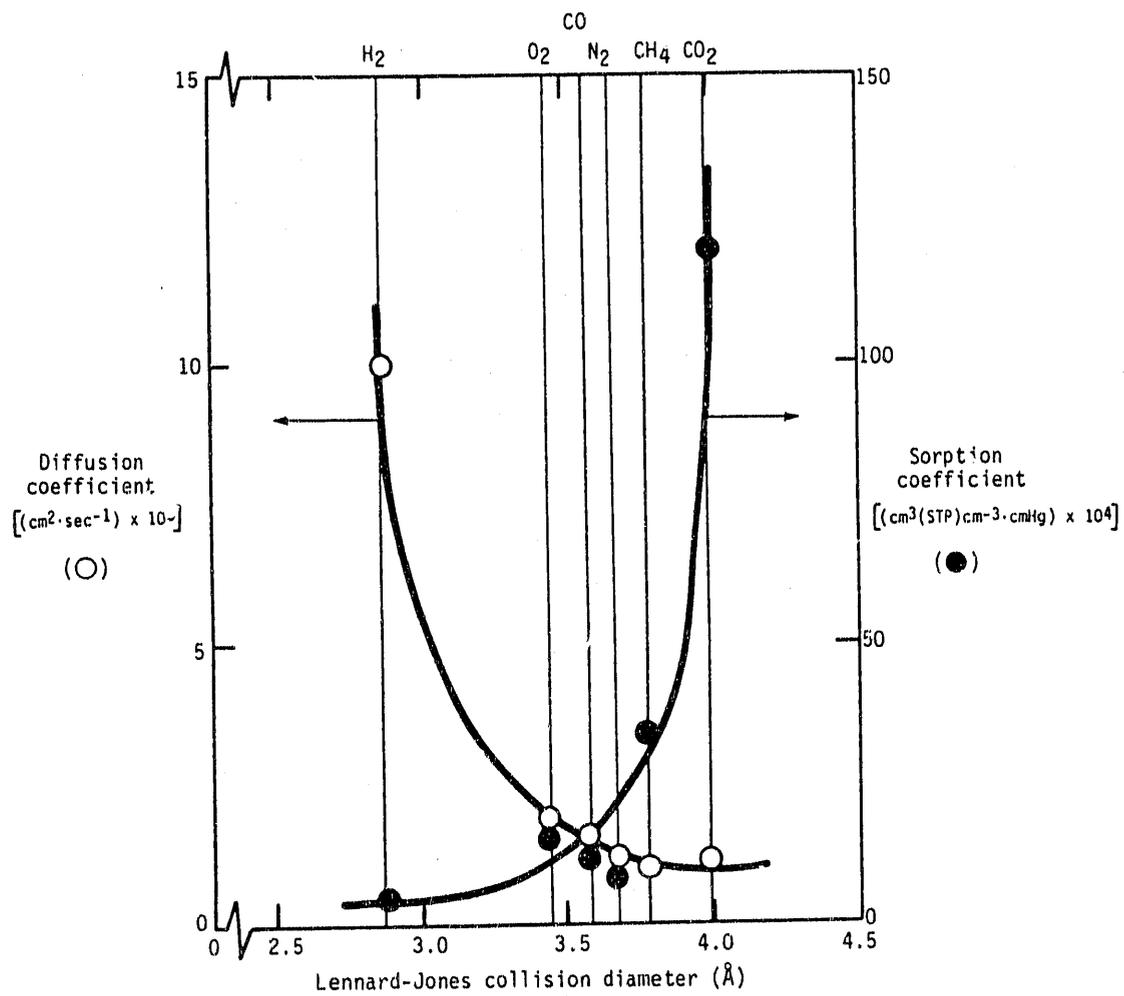


Figure 5. Gas diffusion and Henry's law sorption coefficient vs. Lennard-Jones collision diameter for natural rubber membranes.

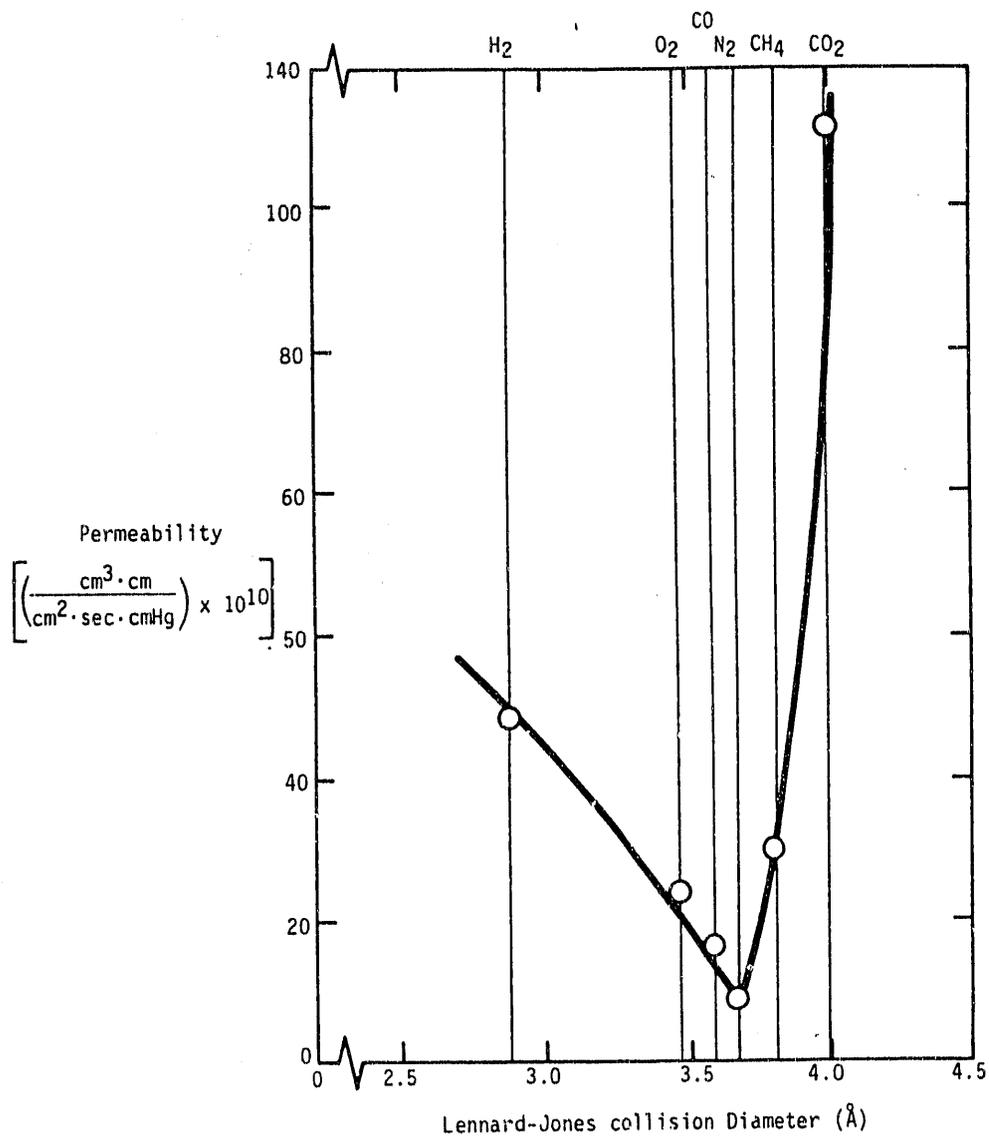


Figure 6. Permeability *vs.* Lennard-Jones collision diameter for gases in natural rubber.

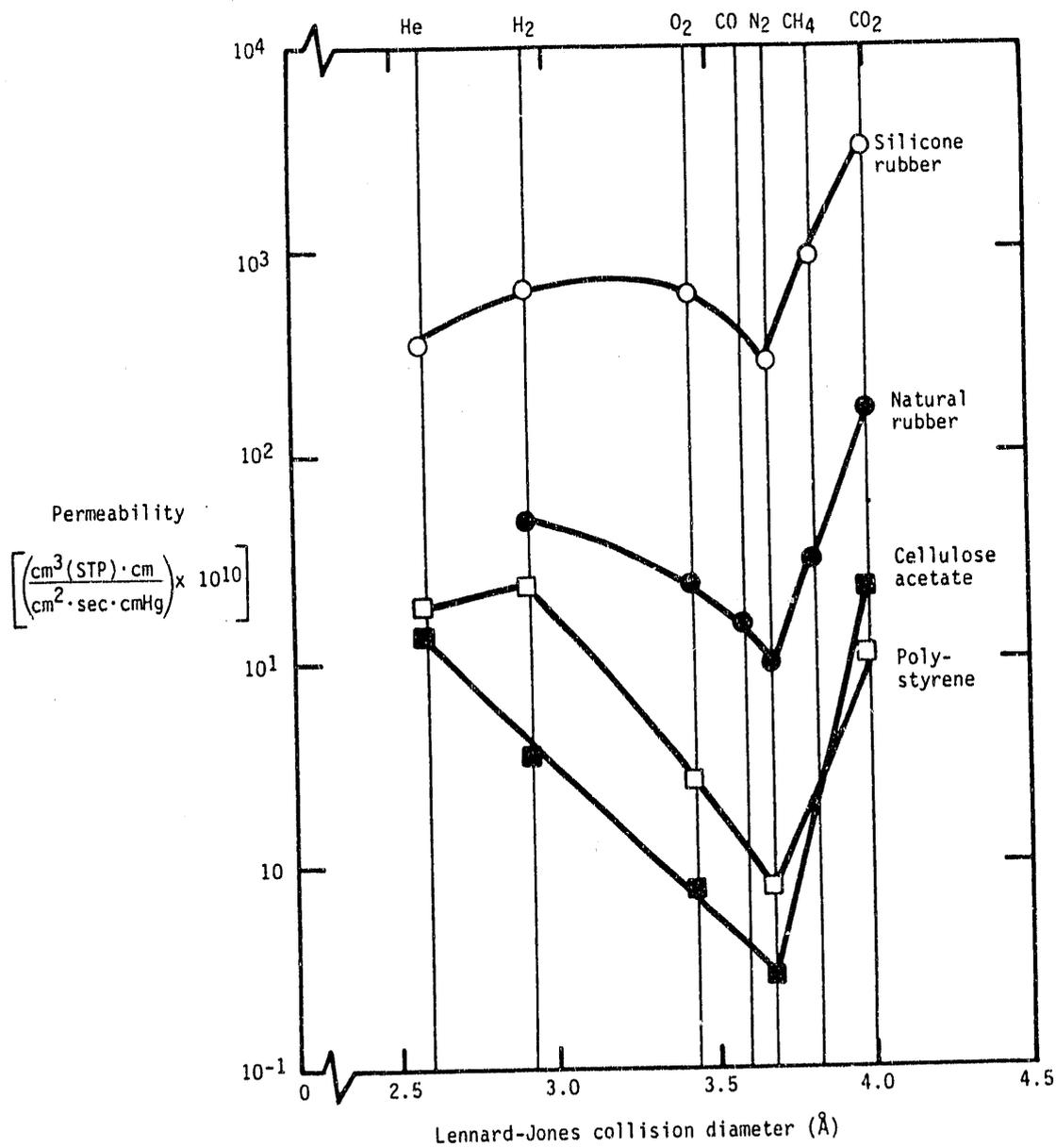


Figure 7. Permeability vs. permeate collision diameter for various polymers(6,17).

Microporous Membranes: Microporous membranes usually have high gas permeabilities, but low selectivities which prevents them from being competitive with nonporous membranes. However, we will describe this membrane type briefly, because it has a potential special application in coal gasification, for the separation of H₂ from CO₂.

Separation of gases with microporous membranes can only be achieved if the pores are very small. If the mean free path of the diffusing gas molecules is greater than the pore size, collisions between gas molecules are less frequent than collisions with the wall. This is called Knudsen flow. At every collision with the pore walls, the gas molecules are momentarily absorbed and then reflected in a random direction. Between pore wall collisions there are rarely molecule-molecule collisions and each gas molecule moves independently of all others. Hence with gas mixtures where the different species move at average velocities characteristic of their molecular weight, a separation is possible.

The gas flow in a membrane made of cylindrical right capillaries for Knudsen diffusion is given by

$$J = \frac{4r\epsilon}{3} \cdot \left(\frac{2RT}{M} \right)^{\frac{1}{2}} \cdot \frac{P(0) - P(\ell)}{\ell \cdot RT} \quad (7)$$

where M is the molecular weight of the gas, J is the flux in gm mols·cm⁻²sec⁻¹, ε is the porosity of the membrane, r is the pore radius, ℓ the pore length and P(0) and P(ℓ) are the absolute pressures of the gas species at the beginning of the pore (x=0) and at the end (x=ℓ).

Since the mean free path of gases at atmospheric pressures is in the region of 1000-2000 Å, the membrane pores must be less than 500 Å for Knudsen flow to predominate and a separation to be obtained. Using the above equation it can be easily shown that the maximum selectivity obtainable with a microporous membrane is

$$\alpha_{A/B} = \frac{\sqrt{M_B}}{\sqrt{M_A}} \quad (8)$$

where M_A and M_B are the molecular weights of the gases to be separated. The advantage of microporous membranes is the high gas permeability. It has been shown that helium and hydrogen fluxes through anisotropic porous films are 10⁴ to 10⁵ higher than fluxes through nonporous membranes(18). Microporous membranes can also be prepared from glass or ceramic materials.

These membranes can be used at temperatures up to 1000°C(19,20). The key disadvantage of microporous membranes is that their selectivity as defined by Equation (8) is usually low compared to that attainable with nonporous polymeric membranes. An exception is the separation of H₂ from CO₂, where, as discussed above, nonporous membranes are only moderately selective and the separation factor of 4.7 achievable with high flux porous membranes may be attractive.

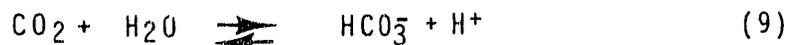
Facilitated Transport Membranes: The porous and nonporous membranes described above use polymer films as the separation barrier. Another process based on liquid membranes is being developed and in principle could lead to much higher membrane permeabilities and selectivities when compared to polymer membranes. These liquid membranes are called facilitated transport membranes.

A facilitated transport membrane for the production of oxygen is illustrated by way of example in Figure 8(21,22). The membrane consists of an immobilized liquid film held in the pores of a microporous membrane. The membrane contains a carrier which selectively and reversibly binds oxygen. Oxygen in the feed air reacts with the carrier to form an oxygen carrier complex that diffuses across the membrane and is discharged to the low pressure permeate stream. The carrier then reforms and diffuses back to the feed side of the membrane. The carrier thus acts as a shuttle, carrying oxygen across the membrane. Because of the membrane's high selectivity for oxygen over nitrogen, highly enriched oxygen permeate streams can be produced(21).

Many oxygen carriers are known, for example hemoglobin, myoglobin, and many synthetic materials, but only a few have the required properties for efficient use in facilitated transport membranes. Some of the more promising compounds are shown in Table V.

Facilitated transport membranes have been developed for a number of gases as well as oxygen. Of particular interest to us are CO₂ facilitated transport membranes. These membranes were first developed by Ward and Robb(23) and have been thoroughly investigated by Ward and others(24-27). A schematic representation of facilitated CO₂ transport is given in Figure 9. In the original work on this membrane, using a carbonate carrier, a CO₂/O₂ separation factor of 1500 and a CO₂ permeability of 750 Barrer was measured(23). This separation factor is many times higher than can be achieved with polymeric membranes.

There are two disadvantages of the carbonate based CO₂ membrane. First, the reactions



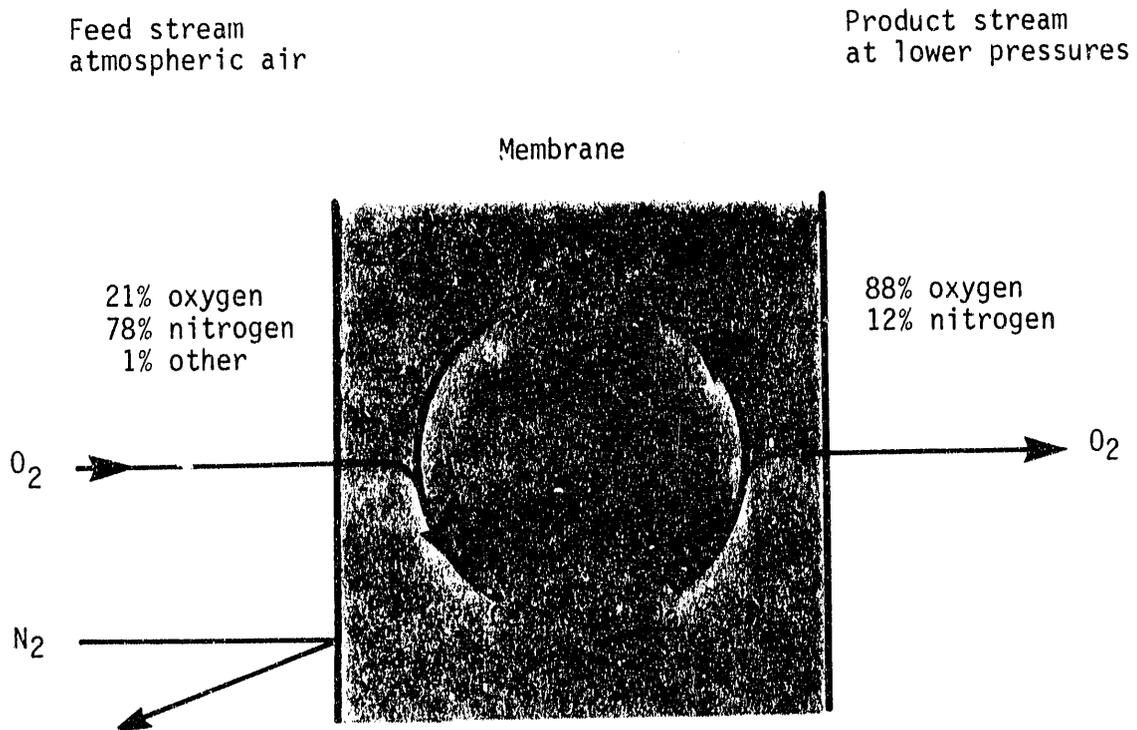
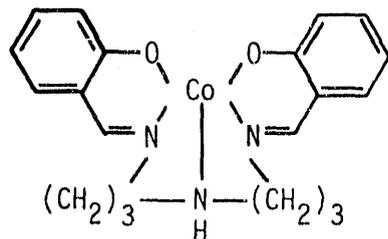
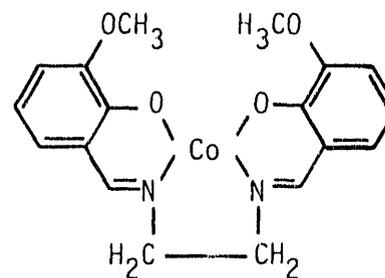


Figure 8. Production of oxygen-enriched air via carrier-facilitated transport.

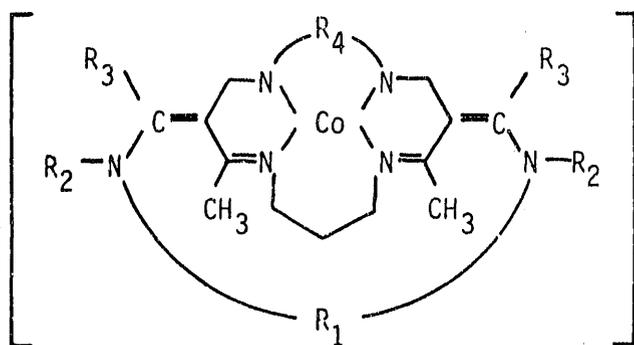
Table V. Oxygen carrier compounds for the separation of O_2 from air.



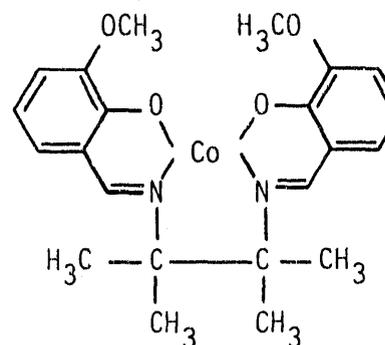
Co(salPr)



Co(3-MeOsalen)



Co(dry-cave)



Co(3-MeOsaltmen)

Membrane	O_2 Permeability ($10^{-10} \text{ cm}^3 \text{ cm/cm}^2 \text{ sec cmHG}$)	O_2/N_2 Selectivity	O_2 Content of Product Gas (%)
Co(SalPr)	1500	30	88
Co(MeOSalen)	780	11	72
Co(3MeOSaltmen)	1000	18	81
C_6 Dry Cave	610	20	84
C_5 Dry Cave	750	25	87
Silicone Rubber	500	2	40

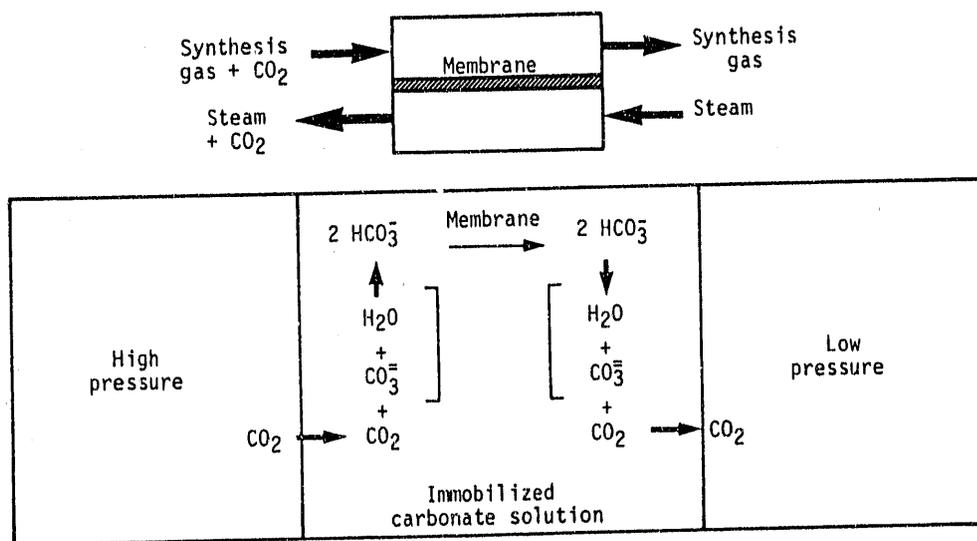
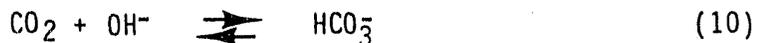


Figure 9. Facilitated CO₂ transport(27).

and



are slow; as a result the rate of CO_2 transport is largely determined by these reaction rates. Second, the permeability decreases significantly at high CO_2 pressures associated with applications in coal gasification. This is an indication of depletion of membrane reactants near the interface with the feed gas at high CO_2 partial pressure. Other CO_2 carriers have been proposed which solved these problems, for example ethylenediamine, held in a cation exchange support membrane(28).

Although the chemistry of facilitated transport membranes for O_2 , CO_2 and other gases has been worked out and a number of membranes with exceptional permeability and selectivity properties have been made, no facilitated transport membrane has yet been developed even to a bench scale process. The key problems lie in the membrane's stability. Membranes fail because of evaporation of the carrier solvent, displacement of solvent from the support membrane or chemical reaction of impurities in the gas stream with the carrier compounds. For these reasons we do not propose to explore facilitated transport membranes for our program. On the other hand, it seems reasonable to expect that these problems will be solved during the next ten to twenty years. If this occurs, facilitated transport membranes will provide serious competition both to other membrane processes and to existing cryogenic, absorption, and adsorption gas separation techniques.

Metal Membranes: The fourth class of membranes that should be considered for hydrogen separations is metal membranes. Nearly all metal films have very low gas permeabilities. An exception is the permeation of hydrogen through palladium and palladium-alloy membranes. Hence we will limit our brief description to this case. Palladium membranes are quite permeable to hydrogen and have an extremely high selectivity for hydrogen since other gases are essentially impermeable. Membrane selectivities for hydrogen over other gases on the order of 100 to 1000 can be obtained. This is orders of magnitude greater than the performance of other membranes. Palladium membranes were extensively studied during the 1950s and 60s, and this work led to the installation by Union Carbide of a plant to separate hydrogen from a refining off-gas stream containing CH_4 , C_2H_4 , CO , and H_2S (29-33). The plant was able to produce >99.9% pure hydrogen in a single pass through the membrane. Twenty-five micron thick palladium-silver membranes were used at 370 degrees centigrade and a feed pressure of 450 psi. However, because the fluxes through the relatively thick membranes used were low, the process was not sufficiently economically attractive to encourage wide use.

If thin palladium membranes could be formed the problems of low flux could be overcome. Figure 10 shows the permeability of hydrogen through palladium as a function of temperature. The hydrogen flux through palladium is proportional to the square root of the pressure drop across the membrane, so we can use the data in Figure 10 to calculate hydrogen fluxes through very thin palladium membranes at higher pressures. If the membrane thickness could be reduced, for example, to 0.5 micron, a hydrogen flux of $2.8 \times 10^{-2} \text{cm}^3(\text{STP})/\text{cm}^2\text{sec}$ would be obtained with $\Delta P = 10 \text{ atm}$ and $T = 1000\text{C}$. This is comparable with the hydrogen flux through polymeric gas separation membranes⁽³⁵⁾, and of course the selectivity should be greater by at least an order of magnitude. Membrane Technology and Research, Inc. is developing experimental ultrathin palladium membranes under a small feasibility program for the Department of the Army. The Army's interest is in pure hydrogen for phosphoric acid fuel cells. We have made small disc supported palladium membranes with membrane thicknesses on the order of 0.1 to 1 micron which have hydrogen/nitrogen selectivities greater than 700. However, a great deal of work is required to scale up the production of these membranes to a continuous process. These membranes will not therefore be used in this DOE developmental program.

B. Potential Applications of Membranes in Hydrogen Production from Coal

Based on the discussion in the previous section, it is clear that in general nonporous polymeric membranes are the preferred membranes for our gas separations. Facilitated transport membranes are promising for the separation of oxygen from air and CO_2 from H_2/CO_2 mixtures, and palladium membranes would be promising for the separation of H_2/N_2 , H_2/CO , and H_2/CO_2 mixtures. However, facilitated transport and palladium membranes are both in the early research stage and a great deal of work remains to be done before they can be made in continuous defect-free rolls for membrane module production. In the following section, therefore, we will discuss the selection of suitable polymeric membrane materials for each gas separation process in turn.

1. Oxygen from Air

As mentioned earlier, the separation of oxygen from air is an important gas separation process in the production of hydrogen from coal. Although outside the scope of our present program, a brief discussion is given below for completeness.

Virtually all polymeric materials have a higher permeability for oxygen than for nitrogen. Figure 11 shows the oxygen permeability of a large number of polymers plotted against oxygen/nitrogen selectivity. As can be seen from the figure, selectivities in the range 1 to 10 are achievable with polymeric membranes. Only a modest enrichment in oxygen concentration in

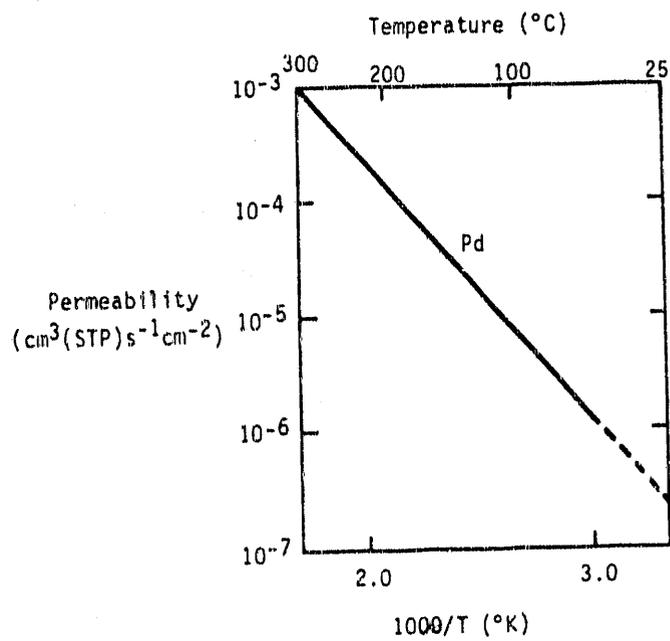


Figure 10. Permeability of hydrogen through palladium. The data are permeation rates through a $1\ \mu\text{m}$ thick film at a pressure drop of 1 atm(34).

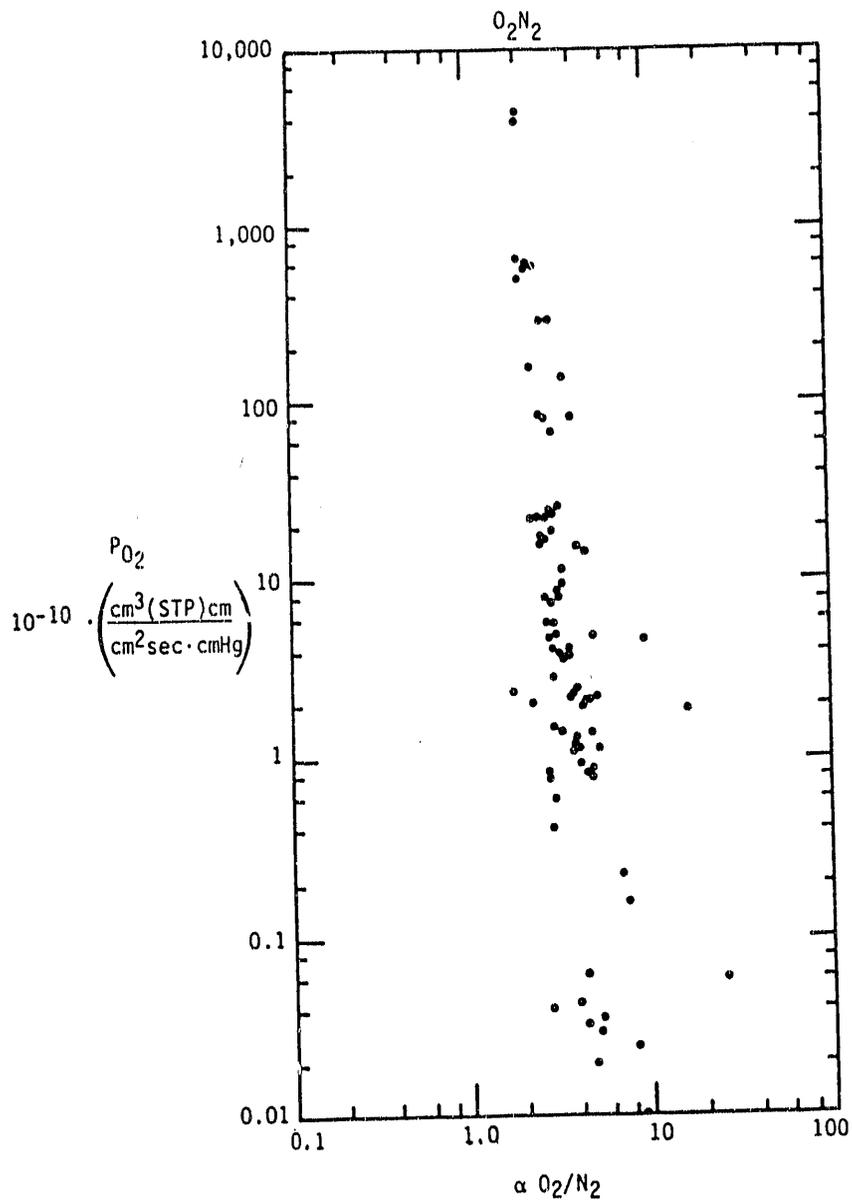


Figure 11. Oxygen permeability vs. oxygen/nitrogen selectivity (13,16,17,43).

the air is attainable in this way. The oxygen purity which can be obtained by a one stage membrane process is given by the equation

$$C(O_2) = \frac{1}{2} \cdot \frac{1}{\phi} \left[0.21 + \phi + \frac{1}{\alpha-1} - \sqrt{\left(0.21 + \phi + \frac{1}{\alpha-1}\right)^2 - \frac{0.84\phi\alpha}{\alpha-1}} \right] \quad (11)$$

where $C(O_2)$ is the oxygen concentration in the permeate, ϕ is the pressure ratio permeate to feed, and α is the membrane selectivity. Table VI shows the maximum oxygen purity which can be obtained with membranes of selectivity 2 to 10.

Table VI. Maximum Oxygen Permeate Concentration vs. Membrane Selectivity.

Membrane selectivity	2	3	4	5	6	7	8	9	10
Maximum oxygen concentration	34.8	44.4	51.5	57.1	61.5	65.0	68.0	70.5	72.7

It can be seen that state of the art polymeric membranes cannot be used to generate pure or nearly pure oxygen in a one-stage process. A multi-stage process could be used but this is then too expensive to compete with cryogenic air separation. However, if a low degree of enrichment (30 to 40% oxygen) is acceptable, for example in a combustion process, then membrane enrichment from air is feasible. It has been shown that membrane production of this grade of oxygen is cheaper than cryogenic processes(36,37).

2. Hydrogen from Nitrogen

If synthesis gas produced by an air blown gasifier is used to produce hydrogen the final product will contain large amounts of nitrogen (60 to 70% N_2). This nitrogen must be removed, but separation of hydrogen from nitrogen is a difficult process by conventional technology. As a result, oxygen blown gasifiers are used to produce hydrogen from synthesis gas. However, as shown below, the separation of hydrogen from nitrogen by membranes is relatively straightforward. The use of an air blown gasifier followed by a membrane unit would therefore be economically attractive if the cost of separating hydrogen from nitrogen with a membrane is less than the cost of separating oxygen from air in the conventional cryogenic process.

Figure 12 shows the hydrogen permeability of a large number of polymers vs. hydrogen/nitrogen selectivities. It can be seen that numerous polymers have selectivities of 30 or above; even selectivities of over 100 have been measured many times. However, not all of these highly selective polymers can be fabricated into thin films and others have extremely low permeabilities (e.g. polyvinylidene chloride, polycaprolactone). However, there exists a reasonable number of polymers with the necessary characteristics. Based on previous experience, MTR has chosen polyetherimide. The average hydrogen/nitrogen selectivity obtained at room temperature with polyetherimide samples in our laboratory was 116. The permeability varies over a range but is estimated to be approximately $3.5 \text{ cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{sec cmHg}$. From Figure 12, higher permeability membranes could be obtained but only by sacrificing selectivity. Nonetheless, we intend to develop some of these membranes to determine the optimum balance between permeability and selectivity. Our other preferred candidates are cellulose acetate, polymethylpentene, and ethyl cellulose.

The type of separation that might be obtained with a polyetherimide membrane in a hydrogen/nitrogen separation is shown in Figure 13. The membrane configuration shown is a two unit membrane system with recycle of the permeate from the second unit. Partial recycle allows a high purity product hydrogen to be obtained without losing excess hydrogen in the waste stream. This system design has not been optimized, but illustrates the separation ability of a membrane with a selectivity of 100. We have used the technique of Weller and Steiner(38) and Pan and Habgood(39) to calculate the system. As shown, >98% pure hydrogen can be produced from a feed gas of 32% hydrogen and 68% nitrogen in a single pass through the membrane. In addition, the waste gas stream contains only about 4% of the hydrogen from the feed stream. Less selective, higher flux membranes would require a smaller membrane area to treat the same gas feed but would lose more hydrogen in the waste gas stream. This type of system optimization calculation will be performed in our modeling studies Task 4.

3. Hydrogen from Carbon monoxide

Literature data on CO permeation through polymers is limited.(35,40,41). However, the permeability of carbon monoxide is normally 1.3 to 2 times higher than the permeability of nitrogen; thus we can expect a good hydrogen/nitrogen separating membrane to perform hydrogen/carbon monoxide separation well. Using this reasoning, polyetherimide, cellulose acetate, ethyl cellulose and polymethylpentene membranes will also be examined for this separation.

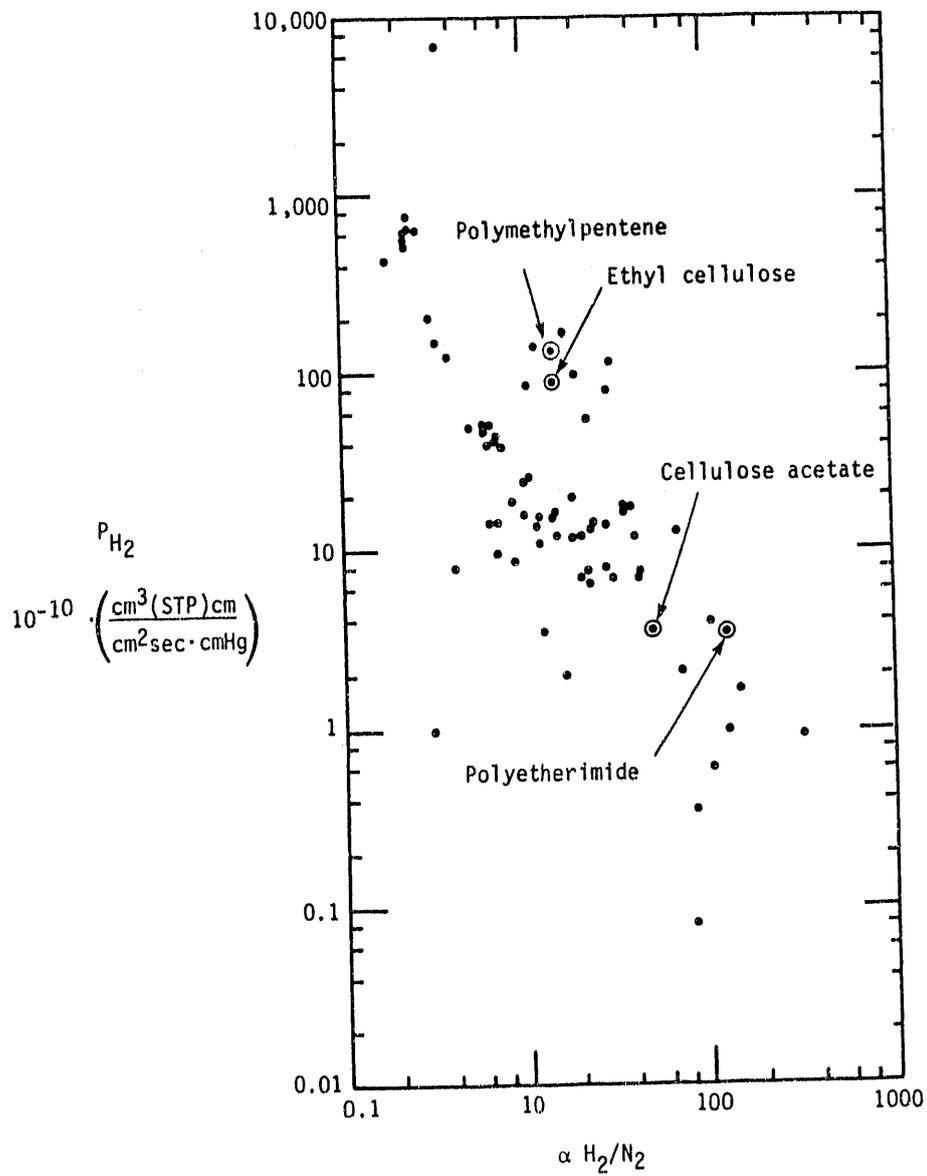


Figure 12. Hydrogen permeability *vs.* hydrogen/nitrogen selectivity(13,16,17,43).

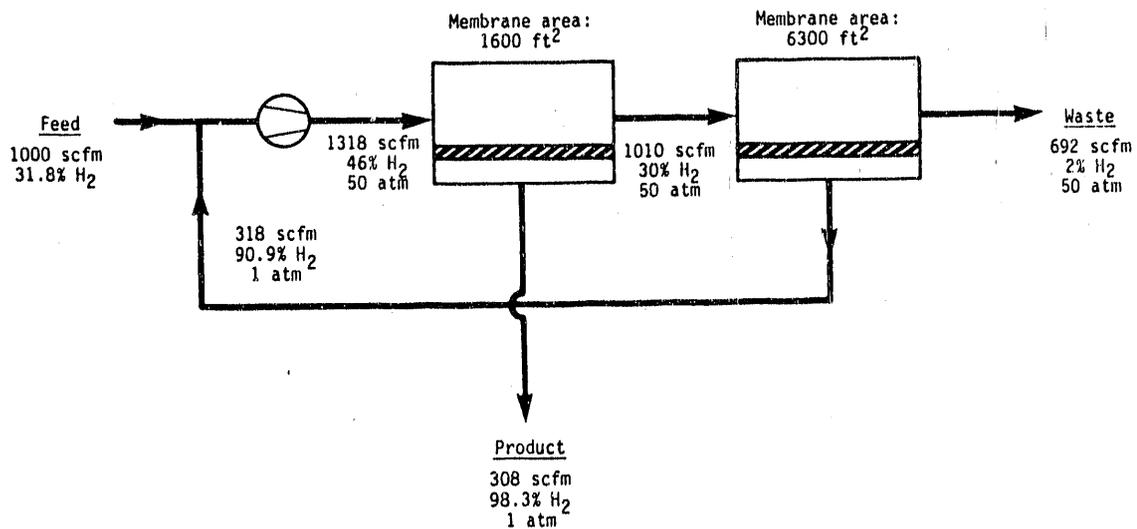


Figure 13. Example of a configuration of membrane modules for H₂/N₂ separation. (Membrane data: $\alpha = 100$, $P/\lambda(\text{H}_2) = 7 \cdot 10^{-5} \text{cm}^3/\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}.$)

4. Hydrogen from Carbon Dioxide

Figure 14 shows the CO₂ permeabilities for a large number of polymers plotted against CO₂/H₂ selectivity. Two points emerge from this figure. First, CO₂ and H₂ are quite different in their molecular diameters, yet the selectivity of most polymers is smaller than five. As discussed earlier this is because membrane permeability is a function of the mobility and the solubility of the gas in the polymer matrix. Hydrogen has both a high permeability because it is small, and a high diffusion coefficient. The larger CO₂ molecule has a high permeability because it is very condensable and has a high solubility. Owing to this low selectivity the separation of CO₂ and H₂ with membranes is much more challenging than the H₂/N₂ or H₂/CO separation.

The second point emerging from Figure 14 is that the selectivity crosses the line = 1. This means one category of polymers is more permeable to CO₂ and a second category is more permeable to H₂. Normally glassy polymers with a rigid backbone have a preferred permeability for hydrogen while rubbery polymers have a higher permeability for CO₂. As mentioned above, the selectivity of most polymers is less than 5, generally between 2 and 5, a comparable situation to the O₂/N₂ separation discussed in Section I. Thus a two or three stage membrane unit is necessary if a complete separation is to be achieved. A hybrid process using a membrane to perform a partial separation followed by a conventional process might be viable.

Of the polymeric membranes studied for the separation of hydrogen from CO₂ the work of Peterson et al.(42) stands out. They obtained selectivities between 10 and 15 working with membranes made from crosslinked methyl cellulose and methyl cellulose acetate. The best CO₂/H₂ selectivity was 40, measured with a thick film of methyl cellulose acetate. This is a remarkable value based on the permeability-selectivity data shown in Figure 14. However, this is an experienced research group and even though they had problems preparing reproducible thin film composite membranes, we believe the data is reliable and this is the best membrane to develop. MTR has considerable expertise in the preparation of thin film composite membranes and feels that further work in this area could yield worthwhile results. An alternative possibility is the application of microporous membranes. As mentioned above, the selectivity of a microporous membrane is equal to the square root of the molecules' weight ratio. Therefore the selectivity of a microporous membrane for H₂/CO₂ separation is 4.7. Most polymeric membranes have no better selectivity, and their fluxes are lower by a factor of 100 to 10,000. Our first choice then is methylcellulose acetate followed by a microporous membrane if the methylcellulose acetate membranes do not have the required selectivities.

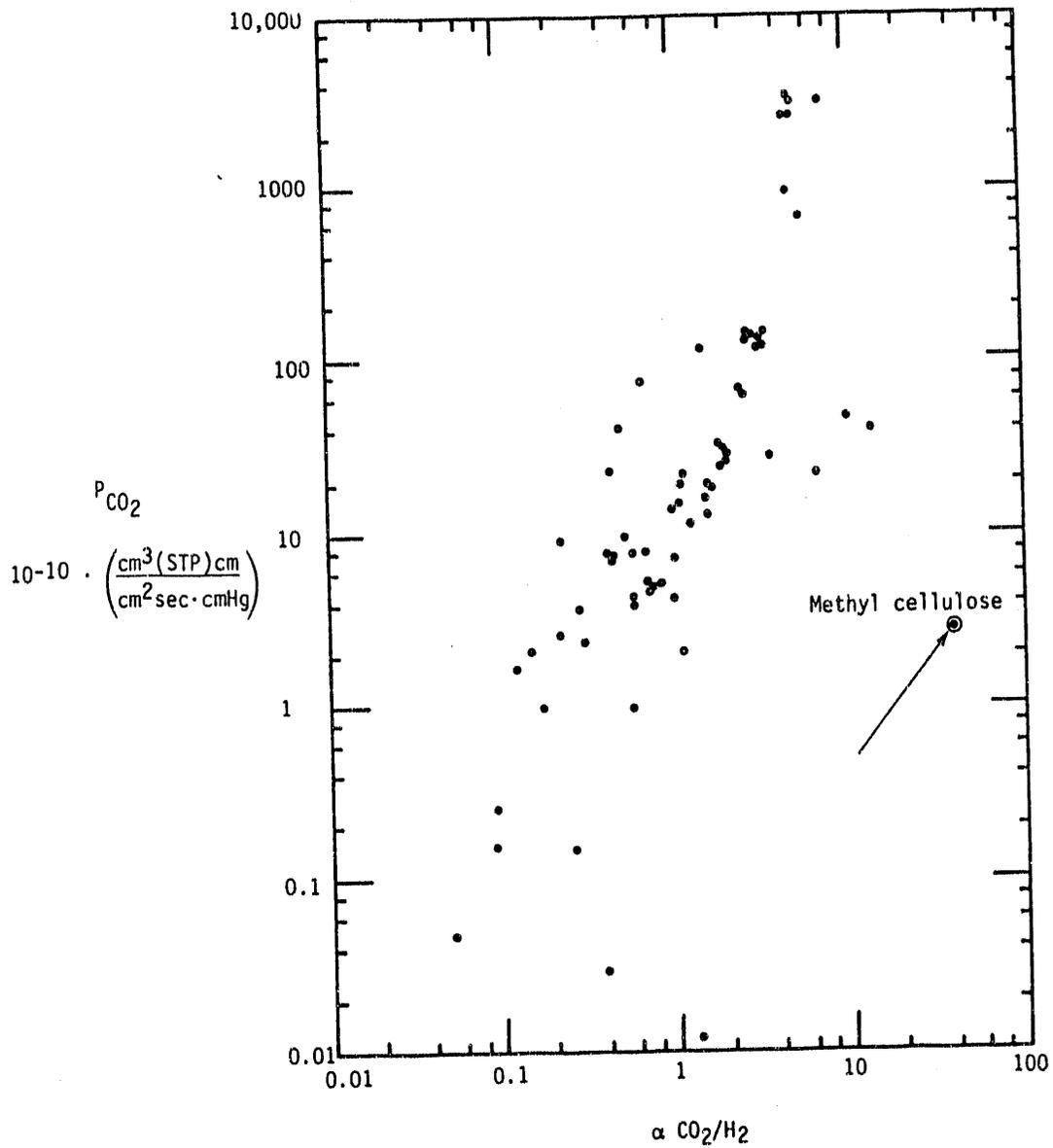


Figure 14. Carbon dioxide permeability *vs.* carbon dioxide/hydrogen selectivity(13,16,17,43).

VI. CONCLUSIONS

Membrane processes can be applied to a number of coal gasification separation problems. Potential applications are:

1. The separation of oxygen from air.
2. The separation of hydrogen from carbon monoxide before the shift reaction.
3. The separation of hydrogen from carbon dioxide after the shift reaction.
4. The separation of hydrogen from nitrogen after the acid gas removal step in an air blown gasifier process.

The separation of oxygen from air is outside the scope of this program so we have only seriously considered the last three separation processes.

A number of membranes could be used for these separations including metal membranes and facilitated transport membranes. However, these membranes are still undeveloped and in our work we propose to concentrate on homogeneous polymeric membranes.

The membranes we believe will have the best potential are, polymethylpentene, ethylcellulose, cellulose acetate, and polyetherimide, for the separation of H_2/CO and H_2/N_2 , and methylcellulose for the separation of H_2/CO_2 . The flux and selectivity data for these membranes is summarized in Table VII.

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