

GAS SEPARATION MEMBRANES AND THE GAS INDUSTRY

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In the last couple of years, membrane separations have received considerable interest. Their applications have broadened considerably and membranes are now used in a great variety of industries. In today's paper, I would like to briefly look at how membranes work, review the characteristics of membrane systems that make them desirable for certain applications, and then look at applications for gas separation membranes--in particular, the CO₂-methane separation as applied in the natural gas related industries.

Semi-permeable membranes have been used for many years but primarily in liquid applications such as reverse osmosis for desalination of water and ultrafiltration for recovery of dyes in the textile industry and cheese whey in the dairy industry. More recently, semi-permeable membranes have found commercial application in the separation of gases. Monsanto is largely responsible for the commercial success of gas separation membranes. They used these membranes for recovery of hydrogen in their own ammonia plants for several years before introducing the product to industry. Other suppliers of gas separation membranes include Separex, Envirogenics, and Dow.

Membranes also have application in the natural gas supply industry, but before we look further into the applications and limitations of membranes, let's examine just what membranes are and how they work. Basically, membranes are thin films of any one of a number of polymers which are specially prepared and suitable for a particular application. Commercially available gas separation membranes are of two types: polysulfone and cellulose acetate.

Membranes in use today for gas separations are "asymmetric membranes"; that is, the membranes are prepared so that the actual working surface--the barrier that the compounds must pass through--is a thin layer below which a thicker, porous support substrate lies (Fig. 1). A coating may be added to the surface of the membrane so that both the applied surface and the thin, active portion of the polymer act as the resistance to the compounds passing through. The polymers forming the membrane may be manufactured in either flat-sheet or hollow-fiber form. In the case of the hollow fiber, many parallel hollow fibers are packaged together in a manner analogous to a sheet-and-tube heat

exchanger (Fig. 2). Fast components in the high-pressure gases passing by the hollow fibers have the opportunity to pass through the surface and into the core. The hollow fibers are all potted in a seal at the end of the vessel, so that only gases passing through the membrane and travelling through the hollow core may exit at the one end. The high-pressure gases not passing through the membrane surface exit at the opposite end of the vessel.

In order to increase packing density, flat-sheet membranes are produced in spiral-wound modules. The polymer is cast on a support cloth to form the flatsheet membranes. Then two membrane sheets are placed back-to-back with a spacer material in between (Fig. 3). The spacer material provides channels in which gases passing through the membrane may travel, analogous to the core in the hollow-fiber type. The two membrane sheets are sealed along three edges, making a sandwich (Fig. 4). The sandwich is then attached to a product tube. Gases which permeate through the membrane are thereby routed to the product tube. The product tube is then twisted. The membrane sheets spiral upon themselves and produce a spiral-wound element (Fig. 5). Spacers are also used between the membrane sandwiches so that the feed gas may pass through the element in contact with the membrane surface. The element is wrapped with fiberglass to give it structural integrity.

The net result for either hollow-fiber or spiral-wound modules is a small package containing a large surface area of membrane. Of the four gas membrane systems available, two are hollow-fiber type and two are spiral-wound.

Hollow-fiber modules tend to be installed vertically to prevent the fibers from sagging in the middle and allowing feed gas to bypass the membranes.

Spiral-wound membrane systems tend to be oriented horizontally for ease of installation and replacement of membrane elements.

Membranes have a different resistance to different compounds, and therefore different compounds will travel through the membrane at different rates. The driving force is the difference in partial pressure for the compound from one side of the membrane to the other.

The controlling equation states that the quantity of permeate of a component i passing through a membrane is equal to the permeation rate for the component times the area of membrane available times the difference in partial pressure from one side of the membrane to the other for that component. The permeation rate for component i , R_i , is a function of the polymer being used and the thickness of polymer through which the specie must pass

$$P_i = R_i (pp_i - pp_i') A$$

P = Permeate

R_i = Rate of component i

pp_i = partial pressure component i , high.-pressure side

pp_i' = partial pressure component i , low-pressure side

A = Area

Separations are possible because different components have different permeation rates.

Since the partial pressure is constantly changing as gas travels from one end of the membrane to the other due to the selective removal of the faster species from the feed gas, this equation is applied to small increments of area producing a small increment of permeate and then integrated over the entire area available.

$$P_i = \int \Delta P_i = \int R_i (pp_i^o - pp_1') \Delta A$$

The driving force is greatly diminished as the partial pressure is reduced, and the amount of permeate produced for the same small increment of area is much less than when the partial pressure is high. With a feed gas at 500 psia and a CO₂ permeate at 50 psia, it takes almost ten times as much membrane area to allow one mole/hour of CO₂ to pass at 10% CO₂ in the feed as it does at 70% CO₂ in the feed.

On the other hand, the partial pressure and therefore driving force of the slow gas is increasing as the fast gas is removed. At low concentration of fast gas not only is more membrane area required, but the loss of other components becomes significant.

This points up the very significant characteristic of membrane systems, and that is their viability as a gas separation process is extremely high at high concentrations of fast gases but diminishes rapidly with the concentration of fast gas to where membranes are not the process of choice under normal circumstances at very low concentration of fast gases.

To overcome the potential loss of desired product, membranes may be used for bulk removal followed by a more conventional process. Staging of membranes is also possible.

Using the CO₂-methane separation as an example (Fig. 6), a gas with high concentration of CO₂ is processed in the first stage of membranes until the CO₂ concentration is reduced to some nominal level--usually 15 to 20%. The CO₂ produced as the low-pressure permeate is relatively pure. The hydrocarbon gas still containing 15-20% CO₂ is fed to a second stage of membranes where the desired low level of CO₂ is achieved. The permeate from this stage contains considerable methane but is still rich in CO₂ (50-80% CO₂). This permeate is compressed and recycled to the first stage of membranes to recover the methane and reject the CO₂. Since compression costs are related to pressure ratio rather than pressure difference, it is advantageous to produce the low-pressure permeate at some intermediate pressure (usually between 50 and 100 psia). For the same reason permeate from the first stage of membranes will also be produced at an intermediate pressure if the CO₂ is to be compressed for further use.

The economics of a second stage of membrane processing with compression should be evaluated against more conventional process alternatives.

Characteristics

Now let's look at some of the characteristics of membrane systems. They are simple. They do not have a great deal of associated hardware; there are no moving parts, and this is usually an advantage.

They are modular in nature. That is, there is no significant economy of scale, so they will tend to be more attractive when processing lower flow rates than larger flow rates. (Most conventional technologies do realize an economy of scale.)

A great deal of membrane area is typically packaged in a small volume. Therefore, the entire membrane plant usually requires less space than conventional processing.

Because membranes are simple and have no moving parts, start-up and operation of a membrane facility is rather straightforward.

Membranes are expensive; therefore, care must be taken in the design, start-up and operation, to protect membranes from contaminants, which would have a deleterious effect on the life of the membrane surface.

As we have seen, the separation carried out by membranes is not absolute. While some gases will pass through a membrane surface more rapidly than others, there is always some associated "leakage." Therefore, very pure compositions are not economically or practically attained. Membranes are most effective at bulk removal of fast gases. Care must be taken in the application of membrane technology to include combinations of membrane and other technologies to provide best overall economics.

There are differences in the characteristics of membranes available and these may come into play in the selection and design of the overall process. Cellulose acetate membranes enjoy higher selectivity between CO₂ and methane than polysulfone; therefore, a cleaner separation is possible. In other words, the methane recovery will be higher. However, polysulfone enjoys a distinct temperature advantage in that the polysulfone membrane may be operated at close to 200°F.

This is particularly important when treating associated gases with heavy hydrocarbon content.

In order to avoid condensation of heavier hydrocarbons or natural gas liquids during CO₂ removal, it is normally necessary to pretreat the gas before the membrane separation. In the case of cellulose acetate membranes, the gas may be chilled to condense out the heavier hydrocarbons and then warmed back up before feeding to the membrane unit. Another option is to heat the gas up directly so that the hydrocarbon dew point is not reached even after CO₂ removal. The problem with this approach is the temperature limitation of the membrane. With polysulfone operated at the higher temperature, the second approach is possible and advantageous. It is possible to take gas directly from the compressor discharge and feed it to the membrane separation. The higher temperature also allows more CO₂ gas to permeate the membrane since the permeation rate is a function of temperature; therefore, less membrane area will be required.

Applications

"Fast gases" will permeate the same membrane more readily than "slow gases" with an equal driving force (Fig. 7). Hydrogen, helium, and water vapor are considered very fast gases. That is, they will travel through the membrane much more rapidly than other gases. Moderately fast gases include the acid gases, carbon dioxide and hydrogen sulfide. Slow gases which tend to remain behind and not permeate the membrane include the aliphatic hydrocarbons, nitrogen, and argon. It is, therefore, not surprising that the first applications of these gas separation membranes have been the recovery of hydrogen, a fast gas, from purge streams in the production of ammonia which contain nitrogen and argon, slow gases; and in refinery applications where hydrogen is recovered from hydrocarbon streams.

On the surface, it would appear that dehydration would be another excellent application for membranes. However, most dehydration applications require water concentration remaining in the high-pressure gas to be quite low. Therefore, there is little driving force (partial pressure of water) and considerable slippage of other components cannot be economically avoided. The use of membranes for moderate dehydration, followed by other conventional techniques, is certainly a possibility and dehydration concurrent with another separation may be taken advantage of. Also, where the loss of other components is an acceptable expense and the space savings afforded by membranes is an advantage, membranes may find use in dehydration.

One area which is an attractive potential market for membranes and of special interest to the gas industry is separation of acid gases from hydrocarbon streams, specifically the separation of CO_2 from methane. Let's look at some of the applications for this separation.

Certain type gas and oil wells are suitable for increased production by fracturing. In the fracturing process high-pressure fluids are injected into the well reservoir to swell and fracture the formation. Next, a slurry of sand is fed into the well to fill the fracture. This forms a highly porous channel for gas and oil to flow to production wells. Recently, carbon dioxide has found use as the pressurizing fluid for gas and oil well fractures.

Fracture treatments using CO_2 are boosting production from tight oil and gas sands in North Louisiana, South Arkansas and East Texas. The increase in production, after fracs, has averaged 6 times for oil wells and 3-4 times for gas wells. The payout time for a CO_2 frac project averages one-and-a-half months. The associated gas immediately following CO_2 fracture necessarily contains large concentrations of carbon dioxide. The concentration diminishes rather rapidly so, for example, in one project the initial CO_2 concentration one day after the fracture was 50 to 70% CO_2 . Within a week the concentration of CO_2 had reduced to approximately 10% and more slowly thereafter until reaching levels suitable for pipeline transmission.

Membranes are excellent for treating these associated gases because of their modular nature and portability. Immediately following a CO_2 frac, membranes may be used to remove CO_2 from methane in the associated gas and as the CO_2 content comes back down, the membranes may be removed and

used elsewhere. Separex reports at least two portable membrane systems are in use for this application and one of these has already been used at three sites. The CO₂ has some methane in it and is typically burned for fuel or flared.

One of the newer sources of methane gas comes from landfill and also digester gas. Both these gases are approximately 50% carbon dioxide and 50% methane. This high CO₂ concentration and low volume of gas lends itself well to membrane processing. In fact, Monsanto reports one plant has already been sold in Alabama. This plant treats 100,000 SCFD and upgrades the gas from 600 BTU/SCF to 960 BTU/SCF. Other landfill and digester gas applications are being considered.

Sometimes gas will be produced which is not acceptable for pipeline transmission, but if the CO₂ concentration can be reduced slightly the gas can be blended with other sources and meet specifications.

Let's look at the case where 2 MMSCFD of gas containing 8% CO₂ must be treated to at least 6% CO₂. A small amine plant could be used to treat a portion of the gas.

In this case, about 375,000 BTU/Hr would be required for the regeneration of the amine. This represents 10 MSCFD of methane product if methane is used to supply the heat. This would be a very small plant.

Alternately membranes can be used.

As the material balance in Fig. 8 shows, the CO₂ rich stream will contain 60% methane and will have a heating value of approximately 3 MMBTU/Hr. This stream contains 70 MSCFD methane but may be used as local fuel, in which case there would be no energy penalty for the process. In any case, the simplicity and modular nature are advantageous for small-scale applications such as this.

The largest potential application for gas separation membranes today is in the processing of gases associated with CO₂ miscible flood for enhanced oil production.

Once the easy oil has been removed and secondary incremental oil has been removed through recovery techniques such as water flooding, tertiary methods may be used to aid in the recovery of oil still in place. Carbon dioxide injection is one of the most widely accepted forms for tertiary oil recovery.

Figure 9 shows how the viscosity of the oil underground is reduced dramatically with carbon dioxide. The top curve represents the viscosity of oil as it exists in a typical California reservoir. The lower curve represents the same oil once it has been saturated with carbon dioxide. You will note the viscosity at the reservoir pressure has been reduced by a factor of almost 10. Once the viscosity has been reduced the oil can flow much more readily through the formation to the production well.

Use of carbon dioxide has been evaluated for enhanced oil recovery by most of the major oil companies. Confidence in the ability of CO₂ to enhance oil recovery has matured to where several major oil companies are embarking on large projects.

Three major pipelines are in place to supply CO₂ to EOR projects in West Texas (Fig. 10). The SACROC project receives 100-200 MMSCFD of CO₂ by pipeline from several natural gas-treating plants. The Sheep Mountain pipeline owned by ARCO, Amerada Hess, and Exxon is capable of delivering 500 MMSCFD of CO₂ from naturally occurring CO₂ wells in Colorado and New Mexico. The most recently completed pipeline, the CORTEZ pipeline, owned by Shell, Mobil and Continental Resources, will deliver 650 MMSCFD to 1.0 MMSCFD of CO₂ from New Mexico to West Texas, and AMOCO recently announced their commitment to construct their own CO₂ pipeline from New Mexico into West Texas. The CO₂ from this pipeline will be used for several AMOCO EOR projects under way.

Here in California, Long Beach Oil Development Company is using CO₂ for an immiscible flood at the Wilmington field in Los Angeles County. Eleven to thirteen MMSCFD of vent gas from a nearby refinery hydrogenation unit containing 82% CO₂ is used.

Champlin Petroleum has started a \$20 million expansion of its CO₂ flood at the Wilmington field. CO₂ is purchased from a nearby ARCO refinery and they are currently negotiating for additional CO₂ from other companies.

The evidence is clear CO₂ injection for enhanced oil recovery is a reality today.

The gases associated with this stimulation technique vary greatly in composition and volume over the life of the project.

In many instances, existing gas processing facilities for acid gas removal and NGL recovery are available but incapable of handling the increased volume and high CO₂ concentration.

The carbon dioxide concentration in the associated gases can increase to levels as high as 90 percent in as short a period as 6 months, although carbon dioxide breakthrough within 3 to 5 years is more likely. This means the gas processor will have to contend with gases containing 80-90 percent carbon dioxide and 5 to 10 times the volume of gas in the space of 2 to 3 years! This rise in gas volume will have a profound effect on gas gathering and treatment.

As we have seen, membranes are excellent for removing carbon dioxide from methane at the high concentration levels. Also, due to their modular nature, membranes can be added, as required, as the CO₂ concentration rises. The CO₂ can be produced at intermediate pressure to reduce compression costs for reinjection. Therefore, membranes can be effectively used for bulk removal of CO₂ so that the remaining gas can be processed in existing equipment. In fact, this option is already being chosen by several CO₂ flood operators.

Union Texas Petroleum has begun injection in Texas with 10 MMSCFD of CO₂ purchased from the Sheep Mountain pipeline. They will be using Monsanto membranes for CO₂ removal from the associated gas upstream of an existing amine unit and cryogenic NGL recovery facility.

SACROC is the only large commercial-scale CO₂ flood project with a significant history. This CO₂ flood project has been in operation since 1972. After pilot testing membranes for over one year at the project, plans to install two hollow fiber membrane plants were announced. These two units are owned and operated by CYNARA, a Dow subsidiary. The units handle 50 MMSCFD and 20 MMSCFD of associated gas containing 40 to 70% CO₂. Membranes are used for bulk removal of CO₂ upstream of the hot potassium carbonate units. The CO₂ product from the membranes is reinjected into the field. Start-up of these units was completed early this year.

The use of membranes for gas separations is relatively new. In particular, this is so for the CO₂ methane separation. We have looked at the characteristics of membranes and how they operate. It is evident that for the separation of bulk quantities of CO₂ from hydrocarbon gases containing high concentrations of CO₂, membranes have a definite place. We have reviewed several of the commercial applications today: CO₂ well fracture, landfill and digester gas upgrading, and processing associated gas from CO₂ floods for enhanced oil recovery. The experiences gained from these initial applications of membranes are bound to encourage widespread use in other areas as well, particularly in those areas where they uniquely fit, such as where space is a problem, where the modular aspects allow portability in phasing in and out of membranes, and in the ease of separation when very high concentrations of CO₂ are present.

Today we have looked at how membranes work, what they can and cannot do, where they show an obvious advantage, and where they should be considered. It is essential to keep an open mind to see where membranes can fit an overall processing scheme. This is so not only in retrofits, but also in new grass-roots facilities as well.

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FIGURE 1

ASYMMETRIC MEMBRANE FOR GAS SEPARATION

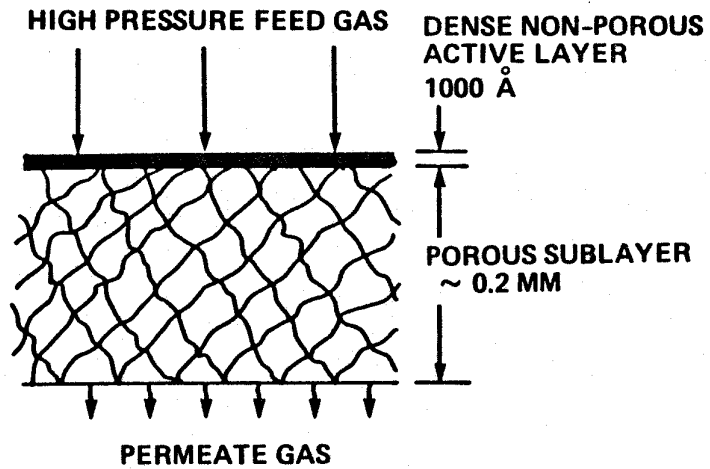


FIGURE 2

HOLLOW FIBER MEMBRANE MODULE

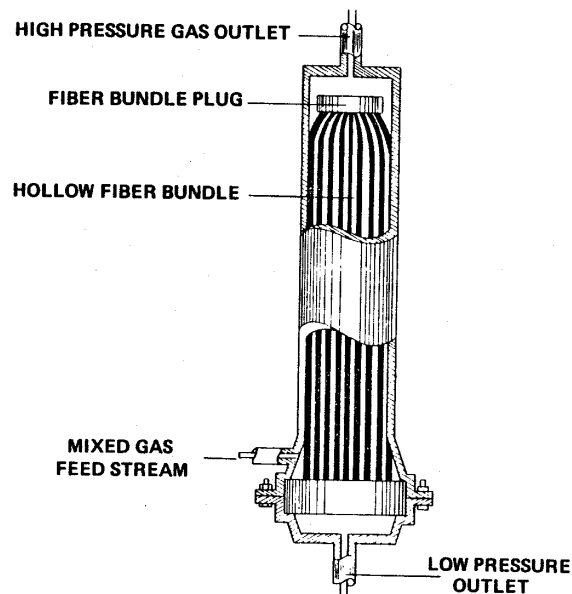


FIGURE 3

MEMBRANE SANDWICH

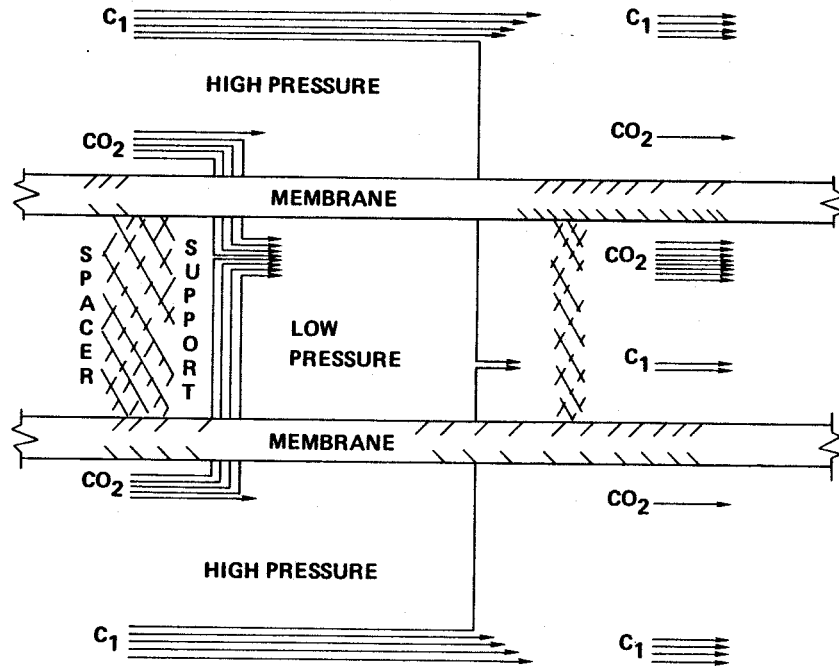


FIGURE 4

MEMBRANE SANDWICH ATTACHED TO PRODUCT TUBE

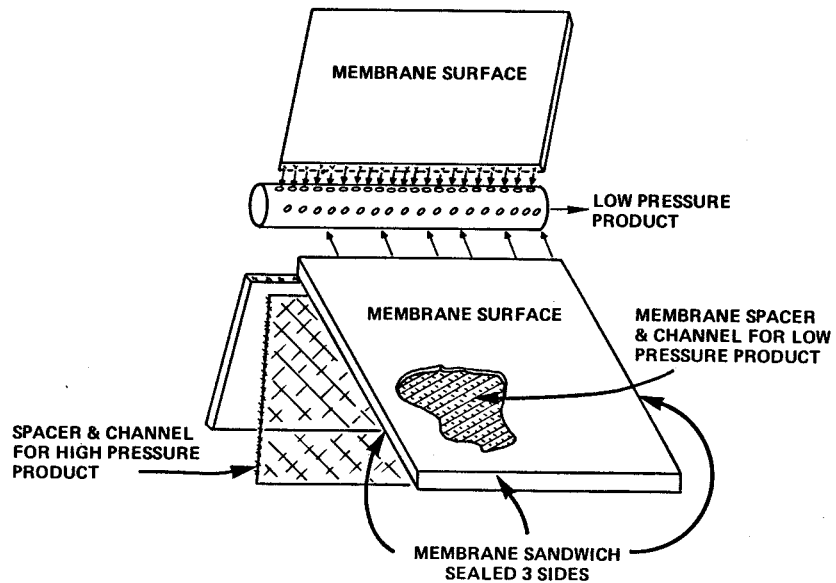


FIGURE 5

SPIRAL WOUND MEMBRANE ELEMENT

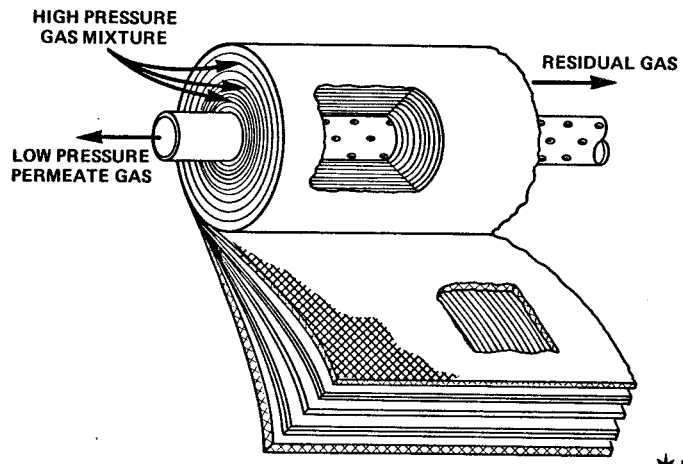


FIGURE 6

MEMBRANES 2 SECTIONS

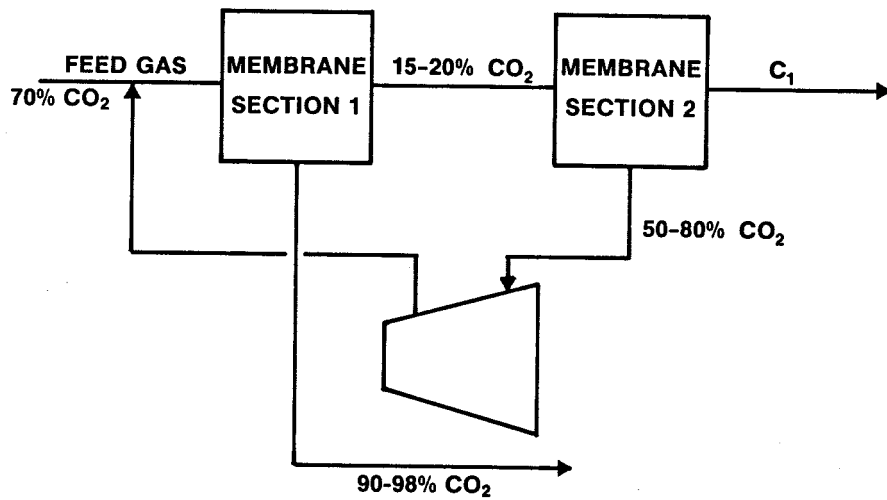


FIGURE 7

HIERARCHY OF PERMEATION RATES

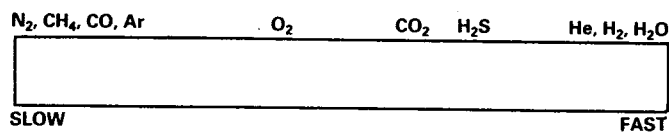
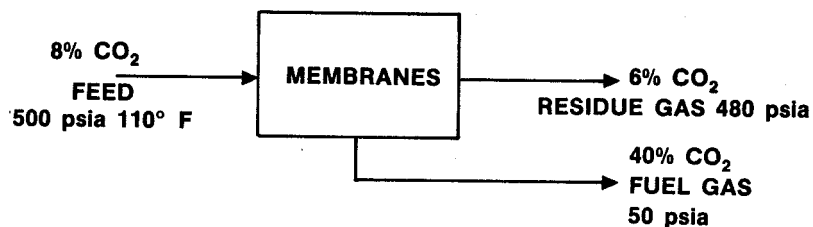


FIGURE 8

MEMBRANES FOR SMALL ADJUSTMENT OF CO_2 CONTENT



MATERIAL BALANCE

	<u>FEED</u>	<u>RESIDUE</u>	<u>FUEL</u>
FLOW (MMSCFD)	2.0	1.9	0.1
RECOVERY (% of C_1 in Feed)	100%	96%	4%

FIGURE 9

EFFECT OF CO₂ ON OIL VISCOSITY

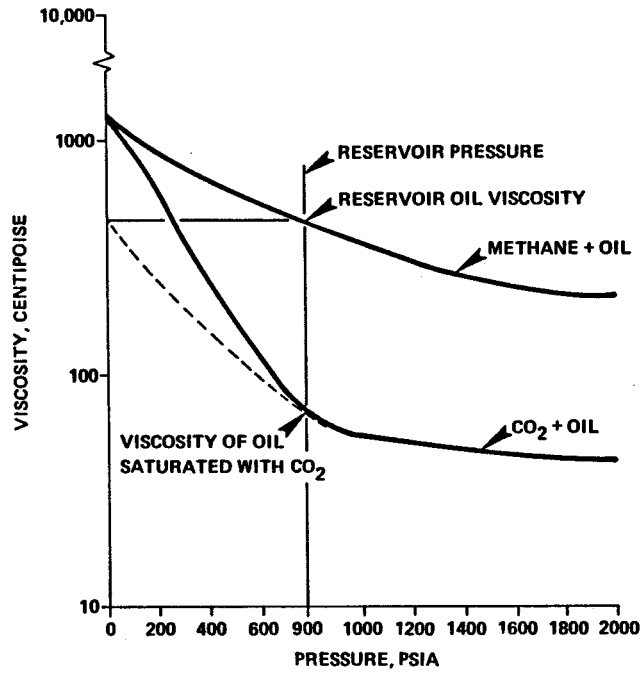
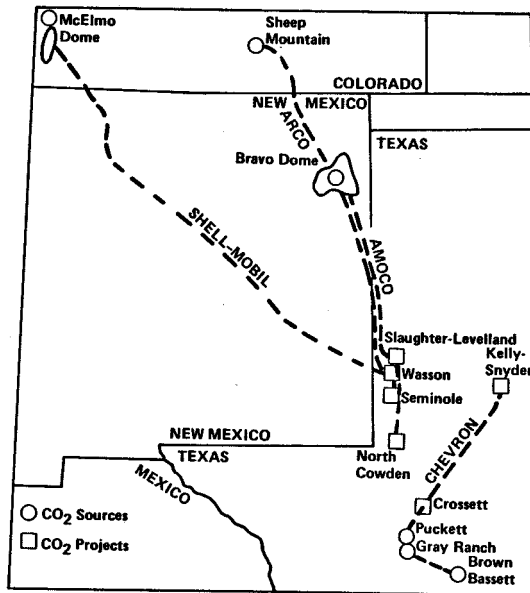


FIGURE 10



Source: New Mexico Institute of Mining & Technology