Separation of Acid Gas and Hydrocarbons

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Over the last few years, membrane applications have broadened considerably and membranes are now used in a great variety of industries. This paper reviews the characteristics of membrane systems used for gas separations, and specifically looks at applications for the CO_2 /hydrocarbon separation as applied in industry.

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. 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 commercial gas separation membranes include Dow, Dupont, Grace, and Separex, with more recent announcements by Union Carbide and Ube.

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 used for Acid Gas Separations have been primarily: polysulfone and cellulose acetate.

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. 1).

In order to increase packing density, flat-sheet membranes are produced in spiral-wound modules. (Fig.2)

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 spiralwound.

Characteristics

The driving force for permeation of the fast gas (and therefore separation of the fast gas from the other slow components) is the difference in partial pressure from one side of the membrane to the other.

The driving force is greatly diminished as the fast gas is removed and the partial pressure is reduced. The amount of permeate produced for the same small increment of area is much less when the partial pressure is low.

For example, with a feed gas at 500 psia and a CO_2 permeate at 50 psia, it takes almost ten times as much membrane area to allow one mole/hour of CO_2 to pass at 10% CO_2 in the feed as it does at 70% CO_2 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.

Therefore, very pure compositions are not economically or practically attained, and 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 are used for bulk removal followed by more conventional processes. Staging of membranes is also possible and used in smaller systems.

Membrane systems 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.

Care must be taken in the design, start-up and operation, to protect membranes from contaminants, which could have a deleterious affect on the life of the membrane surface.

There are differences in the characteristics of the commercial membranes available as well, and these may come into play in the selection and design of the overall process. Cellulose acetate membranes enjoy higher selectivity between CO_2 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. Some of the newer membranes being introduced have even higher temperature stability.

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 CO_2 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 so that the hydrocarbon dew point is not reached even after CO_2 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 CO_2 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. 3). Hydrogen, helium, and water vapor are considered very fast gases. That is, they will travel through the membrane much more readily 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. Much of the optimism for growth in the membrane industry is based on projected hydrogen usage in future years due to heavy and/or sour crude processing.

One area which is an attractive, but somewhat elusive, 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. CO_2 is only a moderately fast gas, but the volume of gas to be treated for CO_2 removal can be huge. Some of the areas where membranes have found commercial application for separation of CO_2 and hydrocarbons are reviewed below.

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. 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 CO_2 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 of these gases are approximately 50% carbon dioxide and 50% methane. This high CO_2. concentration and low volume of gas lends itself well to membrane processing. Monsanto reports one plant in Alabama which treats 100,000 SCFD and upgrades the gas from 600 BTU/SCF to 960 BTU/SCF.

Separex reports use of their membrane at a landfill operation processing 1 1/2 - 2 MM SCFD. Feed gas concentration ranges from 42-44% carbon dioxide with as much as 2-3% air. CO is removed to provide a gas with a heat content of 900-950 BTU/SCF. In this particular plant, two stages of membranes are used in series with a recycle of the permeate from the second stage to the feed compressor suction. The gas is pretreated in two beds of carbon and a coalescing filter separator before entering the first stage of the membranes. This plant has been operating since August of 1984.

Sometimes gas will be produced which is not acceptable for pipeline transmission, but if the CO_2 concentration can be reduced slightly, the gas will meet specifications.

Sun Exploration & Production Company reports membranes to be the least cost option for their operation at the Baxterville field (Mississippi, USA). They process 575,000 SCFD and reduce the CO_2 content from 5% to 2% specification.

The largest potential application for CO_2 /Hydrocarbon gas separation membranes today is in the processing of gases associated with CO_2 miscible flood for enhanced oil production.

The April 1986 Oil and Gas Journal "Production/Enhanced Recovery Report" indicates approximately 30,000 BBL/day of incremental oil production by CO_2 flood in the U.S.

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 CO_2 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 has 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 has a profound effect on gas gathering and treatment.

Membranes are an excellent candidate 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 CO_2 concentration rises. The CO_2 can be produced at intermediate pressure to reduce compression costs for reinjection. Therefore, membranes can be effectively used for bulk removal of CO_2 so that the remaining gas can be processed in existing equipment. In fact, this option is already being chosen by several CO_2 flood operators.

Union Texas Petroleum has begun injection in Texas with 10 MM SCFD of CO_2 purchased from the Sheep Mountain pipeline. They use Monsanto membranes for CO_2 removal from the associated gas upstream of an existing amine unit and cryogenic NGL recovery facility.

SACROC is the only large commercial-scale CO_2 flood project with a significant history. This CO_2 flood project has been in operation since 1972. After pilot testing membranes for over one year at the project, two hollow fiber membrane plants were installed. These two units are owned and operated by CYNARA, a Dow subsidiary. The units handle 50 MM SCFD and 20 MM SCFD of associated gas containing 40 to 70% CO_2. Membranes are used for bulk removal of CO_2 upstream of the hot potassium carbonate units. The CO_2 product from de membranes is reinjected into the field. Start-up of these units was completed early 1984, and the units continue to operate satisfactorily.

AMOCO is using Monsanto membranes at their Central Mallet Unit in the Slaughter field. Membranes are used to remove approximately 60% of the CO_2 from produced gas which is expected to reach a volume of 100 MM SCFD and a concentration of 88% CO 2. The gas is compressed and air cooled to knock out hydrocarbons and prevent condensation in the membranes before reheating to 180-190^o F. AMOCO was able to stage their capital expenditures by installing membranes eight months after initial completion.

Fluor has developed a combination process which uses both membranes and distillation to advantage. Membranes are used first to remove the bulk quantity of CO_2 and then used in a distillation scheme to remove carbon dioxide from the ethane CO_2 azeotrope. (Fig. 4)

Use of membranes to remove CO_2 from the azeotrope is an excellent application of membranes since the concentration of CO_2 is quite high (approximately 65%), and the separation factor for CO_2 relative to ethane is substantially better than the separation factor for CO_2 in methane. The use of membranes as a bulk CO_2 removal device upstream of distillation also has an advantage in that it greatly reduces the turndown problems in operating a plant which must be designed for peak capacity, yet during early stages must be operated at a small fraction of the volume throughput.

Caveat

While it is true there have been two rather significant plants constructed and now in operation, using membranes, to process gas from CO_2 floods (the Chevron SACROC Plant and AMOCO Central Mallet Plant) and one smaller plant (Union Texas Petroleum), the competition for processing by distillation techniques (i.e., Ryan-Holmes type process) is very strong. In fact, economics lean toward the distillation process for higher volume gases. At SACROC, high capacity hot potassium carbonate units were in place and. in operation to handle relatively high CO_2 concentrations prior to the installation of the Dow membranes. The membranes were used essentially to increase capacity of an already operational plant.

The AMOCO unit was also unique in the sense that AMOCO has contractual obligations to provide hydrocarbons to an existing NGL Recovery Plant. AMOCO, as a company, is in fact using distillation at their CO_2 flood in the Wasson field and, by their own analysis, expect future plants to use distillation techniques.

A study presented in the August, 1983 issue of Hydrocarbon Processing (special membrane issue) demonstrated use of Fluor's Combination process to have economic advantage over straight distillation. However, the economic advantage was not great, and given the familiarity of operators with distillation-type equipment, and their unfamiliarity with the relatively new technology of gas separation membranes, this approach has not been used commercially.

One of the major cost items is the cost of the initial inventory of membranes themselves and their replacement. A point to be made here is processing gases from CO_2 floods may provide a very large and substantial market for gas separation membranes. However, at their current cost, straight distillation techniques will continue to be preferred except in certain special circumstances.

Even when the recovery of natural gas liquids (as in the case of associated gas from CO_2 floods) is not a factor, economies of scale can work against the use of membrane systems for separation of acid gases from hydrocarbons.

As reported in the Oil and Gas Journal (February 18, 1985), Fluor recently had the opportunity to do a screening study for Petroleum Corporation of New Zealand to evaluate gas pretreatment options.

Gas, containing approximately 44 mole percent CO 2 (Table I), is received by pipeline from raw gas conditioning facilities. The CO_2 removal system is designed to reduce the CO_2 content of gas to 5.5 mole percent. Byproduct carbon dioxide is used for methanol plant feed.

The primary processes considered were Membranes, Membranes plus Benfield and a tertiary amine, TEA.

Membranes were thought to be an excellent candidate for several reasons:

1. Leakage of methane into the CO_2 was not a deterrent since CO_2 and methane would be fed to the methanol plant together. The CO_2 increases the carbon content of the feed and improves efficiency of methanol production.

2. The relatively high concentration of CO_2 (40%) in the feed gas was typical of gases which were economically treated by membranes.

3. The client had visited the SACROC facility and was impressed by the operation of membranes there.

For more details, refer to the Oil & Gas Journal article.

Capital and operating cost estimates were prepared for the purpose of screening the cases to select one for final evaluation. Screening quality capital cost estimates were made for each case based primarily on membrane system costs from Cynara, supplier of Dow membrane systems, and Benfield and TEA system costs from Union Carbide.

Utility requirements were treated as operating costs. Membrane life was estimated conservatively at 3 years, while membrane system maintenance costs were neglected on the basis that they would be small compared with membrane replacement costs.

All cases were then compared on the basis of total evaluated cost, defined as capital cost plus four years of operating cost. A summary of the screening estimate results is presented in Table II.

The most dramatic difference is between the membrane only case (with recycle) and the combination of membranes and Benfield. This again points out the rapid decline in performance as concentration of the fast gas is reduced.

However, the study showed an advantage for TEA over even the best membrane case, (membranes followed by Benfield). Today, even further advantage can be realized by use of activated MDEA (another tertiary amine) processes offered by BASF and Union Carbide.

Published studies and studies by Fluor have shown the opposite results from the New Zealand situation when looking at gases associated with CO_2 flood projects. Differences to cause this result were identified.

1. EOR projects examined typically have a higher CO 2 content (50-90% CO_2). Membranes look more attractive at higher concentrations. TEA is at about maximum loading for this case.

2. Control of hydrocarbon dew point during CO_2 removal can contribute significantly to costs. The feed gas has already had sufficient liquids removed and dew point control is not part of this study.

3. The volume of hydrocarbons being processed is much higher for this study than in EOR cases. Membranes do not enjoy economies of scale; conventional (TEA) processing does. This factor alone could shift the results.

A sensitivity analysis was run to examine effects of certain assumptions used for this case study.

The 3-year life for membranes was extended for 5 years. Capital for the Benfield unit was reduced to take advantage of larger Benfield unit available for downstream processing and capital was added to the TEA case for final CO_2 cleanup with Benfield.

TEA still showed an advantage!

Effect of Size

Next the effect of gas volume was examined.

EOR projects studied to date have large CO_2 concentrations and volumes over 100 MM SCFD. However, if we look at hydrocarbon content, the largest projects have 5-15 MM SCFD of hydrocarbon. SACROC is larger but already committed to hot pot units in place. The study gas had about 60 MM SCFD of hydrocarbons or a factor of about 10 over typical EOR applications.

We extracted the costs and very roughly adjusted them for a 1/10 flow rate with the following factors:

Item	Factor
Membrane System	$(1/10)^{1.0}$
Compressor	$(1/10)^{0.85}$
Process Equipment	$(1/10)^{0.65}$
Initial Inventory	$(1/10)^{1.0}$

The best membrane case (membranes plus Benfield) now had a slight advantage over TEA.

The results of this study are therefore in agreement with past studies by Fluor and those published in the literature.

This study also agrees with AMOCO's design philosophy at the Central Mallet unit where gas is first processed by membranes, then by a tertiary amine (activated MDEA) before finally going to a conventional amine plant for final CO_2 removal.

Conclusion

Membranes will clearly find use for carbon dioxide/hydrocarbon separations in the areas where they fit best, namely, low volume applications, temporary or short term installations, or where size and weight savings will provide a significant premium. For moderate and larger installations, they will be used in combination with other processes. To achieve a substantial sustained growth in large volume gas processing applications, the cost of processing with membranes will have to come down. This may come from an actual reduction in price or a substantial increase in performance, so that the net system cost to the operator is reduced. Only then will they compete effectively with the distillation schemes being employed today.

When membranes are being considered for a project, they should be considered in combination with other suitable processes and not only as a stand-alone process. This can lead to a large number of options. Fortunately, membrane systems can be readily simulated on the computer for rapid screening of these options.

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