Customizing Membrane System Solutions for Gas Separation Applications

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ABSTRACT

Using semi-permeable membrane systems for gas separation, especially CO_2 removal from hydrocarbon gas streams, is definitely state of the art technology. The process is environmentally attractive and offers capital cost advantages, as well as operational advantages. The technology is commercially proven and advantageous in a multitude of applications – most notably in offshore environments where space and weight savings are primary drivers, and in applications where bulk CO_2 recovery is necessary.

Proper application of membrane systems depends on many factors. Specification of the gas separation system must be carefully evaluated, and care must be exercised to ensure the application is properly defined. Proper definition includes consideration of the pretreatment system, the proper control system, downstream processing requirements, adequate sparing, and inclusion of sufficient operating flexibility. All of these considerations are important to ensure the overall performance and life of the membranes themselves.

Choosing a membrane supplier who has significant design integration experience, and more importantly extensive operating experience, can ensure the appropriate solution is determined for each customer's individual gas processing application.

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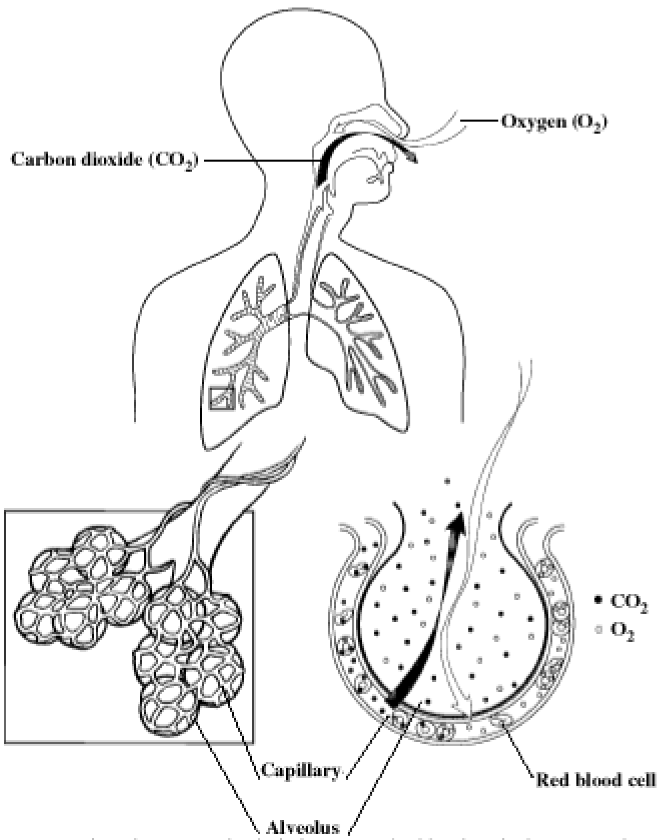
INTRODUCTION

We all are familiar with membranes and in fact we all are intimate with membranes. Our lungs are membranes and in many ways our lungs are analogous to membranes used commercially for gas separations. Our lungs put oxygen into and remove carbon dioxide from the blood stream.



Transfer of oxygen of inhaled air into the blood and of waste carbon dioxide of blood into the lungs occur in the alveolus.

Figure 1

The air that we breathe needs to be clean and free of contaminants, otherwise we require some kind of breathing apparatus (Pretreatment). The lungs also need to be kept free of fluid accumulation as much as possible since the presence of fluids make the lung membrane work much harder and contribute to premature failure. Our personal lung membrane is critical to the functioning of our body's process – if our lungs fail – we fail. The same is true with process membranes; the inlet gas needs to be properly treated, to ensure appropriate operation of the membrane to produce the results required. In many cases if the membranes fail the gas product will not meet pipeline specification and the facility is inoperable. The following is a discussion of details that must be considered to design a successful CO_2 removal process utilizing membranes.

MEMBRANE TYPES

The membranes commercially available today for CO_2 separation are Glassy Polymers such as Cellulose Acetate and Polyimide, and Rubbery Polymers such as Silicone Rubber. Figures 2a and 2b represent the two types of membrane fabrication configurations used in commercial applications, which are Hollow Fiber and Spiral wound. The membrane materials mostly used for CO_2 applications are manufactured from Cellulose Acetate polymers.

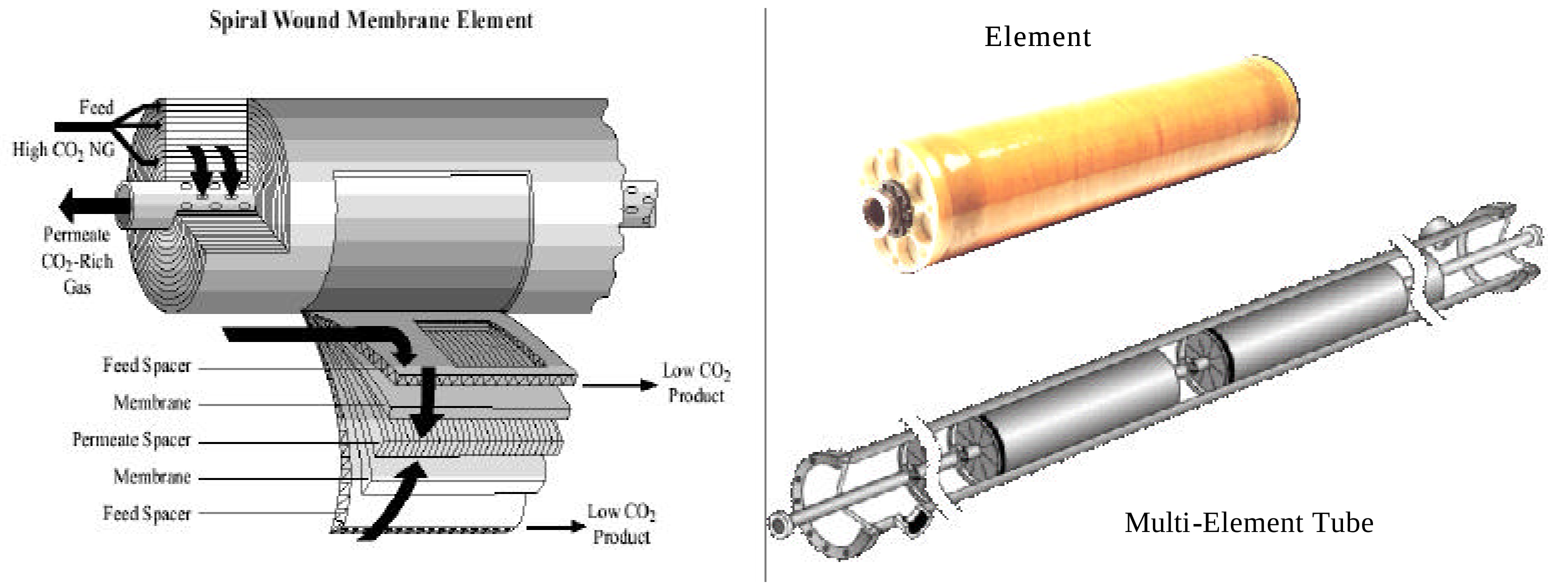


Figure 2a – Spiral Wound Membrane Device

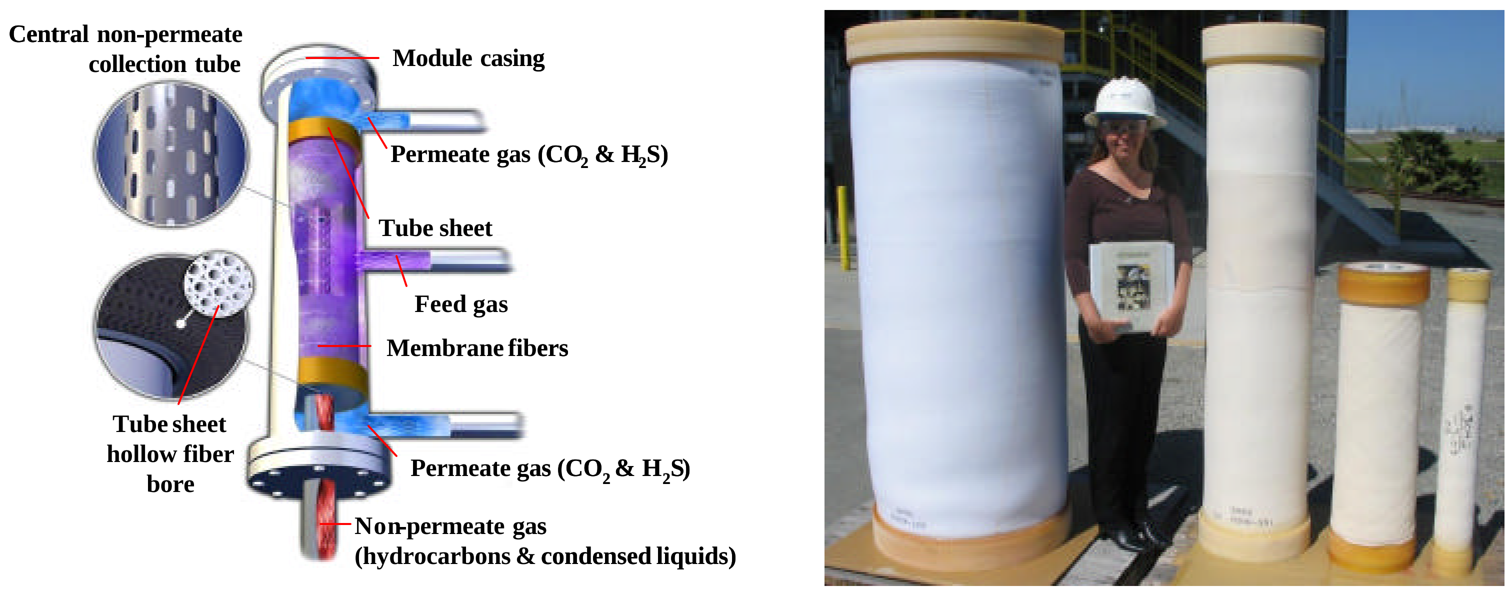


Figure 2b – Hollow Fiber Membrane Device

APPLICATIONS

Existing process applications for CO_2 removal range from a few MSCFD to over 1 BSCFD, while CO_2 Inlet compositions range from 3% CO_2 to over 90% CO_2 with product requirements down to less than 3% CO_2. There are many small membrane systems in service that are of similar design. However the larger systems should be designed specifically for the given application. Since membrane performance can be significantly affected by the operating conditions it is important that the supplier have a good understanding of the inlet conditions, outlet specifications, and other process design and equipment requirements of the project. Some existing membrane system designs and applications did not perform well initially due to poor specifications, lack of proper integration with the overall processing facility, or process design issues which required pre-treatment modifications for successful operation [1, 2, and 4]. Past experience is a good reference for future designs and their expected performance, and experienced membrane suppliers offer the best opportunity to achieve future project success.

Just as you would choose only an experienced pulmonologist (lung doctor) to take care of your personal lung membrane, the facility engineer should request only experienced membrane system suppliers with references to projects similar to the application being designed. How similar is the new facility to those in service, and is there data from actual operations or from test run on field gas that is close to the requirements of the new facility? Having a membrane supplier with good reference projects, like having a good doctor, will certainly build confidence in the ability to meet the desired facility requirements.

SYSTEM DESIGN

Defining the Application

The Scope of Supply and the definition of responsibility between vendor and customer are key elements to the successful integration of membrane systems within the overall processing facility. The facility engineers should provide the membrane supplier with a project requirement for the content of the vendor supplied system. The supply content will vary depending on the project and the membrane supplier. Key items to be considered to establish these requirements are:

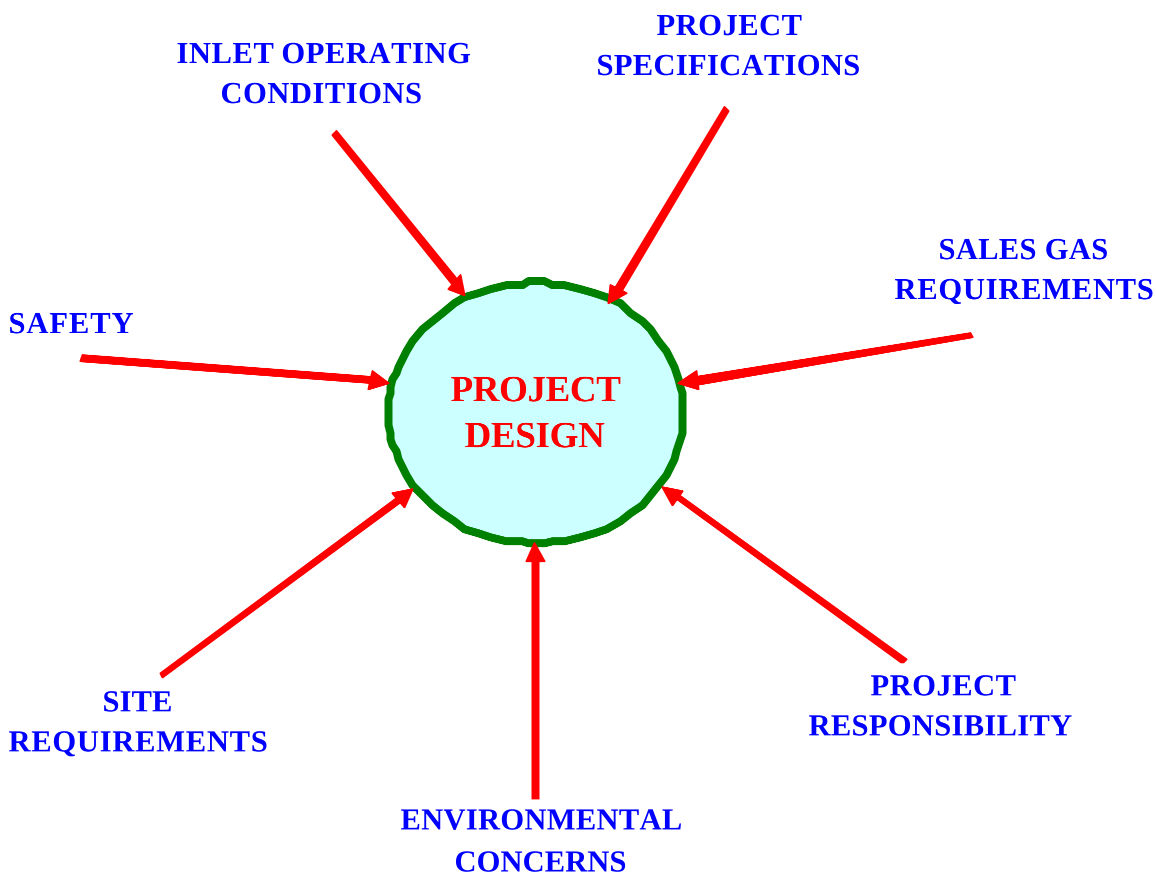


Figure 3

Project Specifications –	Process requirements, customer specifications and code requirements should be stated.
Inlet Operating Conditions –	The inlet operating conditions should be defined in detail.
Sales Gas Requirements –	Defining the sales gas specifications, condensate recovery specifications and internal fuel gas requirements.
Site Requirements –	Is the site onshore, offshore, remote, grassroots, retrofit, and what are the climate conditions, etc.

Project Responsibility – This includes scope of supply and warranty. What are the responsibilities of the groups involved in the project? And what is the warranty and who has process guarantee responsibility?

Safety Issues – Safety should be in line with the policy of the customer as well as national or international safety policy.

Environmental Issues – Environmental Issues should also be in line with the policy of the customer as well as national or international policies.

It is very important to consider the membrane system as a complete process unit and not just as another piece of equipment. The membrane unit should be evaluated as an integral and interactive part of the total processing facility. There should be coordination and communication between the facility design engineers and the membrane supplier. With the process simulation software available it is easy to jointly share process data so that the overall simulation is seamless between the membrane unit and the overall facility. This is especially important for projects involving condensing hydrocarbons or recycle streams. To successfully resolve any problem one needs to first understand the problem and the product requirements. The success of the project will depend on the completeness and accuracy of the information that defines the goals and inherent issues of the project.

Project Specifications

What are the process requirements, customer specifications and code requirements? Customer specifications and code requirements should be identified and defined as early as possible such as when a request for quotation is issued. The process requirements should be made clear and include all product requirements such as:

- CO_2 limits in the product stream.
- Other component limits such as H_2S and water.
- Product flow requirements.
- Product pressure requirements.
- Hydrocarbon dew point requirements.
- Produced liquid specifications.

Inlet Operating Conditions

The inlet operating conditions should be defined in great detail, (generally the more information the better). The following items should be known and discussed before any process design can be initiated.

1. The inlet gas pressure, temperature, flow rate, and composition are the minimum input required for design.
2. Is the inlet gas dehydrated? And if so to what level and by what means?
3. Are there known potential contaminants injected in the inlet gas such as corrosion inhibitor, or is there a lubricated compressor upstream?
4. Where is the inlet gas coming from? Is a slug catcher required?
5. What are the safety requirements? For instance, is a full flow relief valve required?
6. Will the operating conditions vary over time (pressure, composition, flow rate)?

7. Is there an extended gas analysis available? In many cases the gas analysis is not extended and all components heavier than hexane are grouped as C6+. This topic is discussed further in the next section.
8. What other impurities are present in the gas? These typically may include H_2S, mercury, and injected glycol or corrosion inhibitors.

Site Requirements

The site requirements are very important to the system design and may have a significant impact in the design. The primary factors are:

1. Is the location onshore or offshore?

   In most cases the equipment will be packaged differently for offshore applications than it will be for onshore applications. Figure 4 is a photograph of an offshore membrane application with an inlet capacity of 1.2 Bscfd.

Figure 4

Offshore requirements to consider are:

a. The space will be limited and normally there will be weight restrictions for offshore platforms.
b. Equipment maintenance requirements must be considered during design and can be very demanding. The work space is limited and there may be overhead restrictions that impact design parameters.
c. Process fluid flow considerations will vary in offshore applications due to equipment being located on different levels of the platform.
d. There may be more stringent environmental concerns regarding handling of and discharge of fluids and waste streams.
e. The safety issues will be somewhat different than for onshore facilities due to the confined and remote process facility.

2. Remote locations need to be evaluated differently than those that are easily accessible. Remote locations should be designed for unattended operation. This may require a design that is simple and include instrumentation control that allows the unit to operate with minimal operator interface. These units can also be set up to be monitored remotely if desired, when selecting a supplier that can offer this expertise. In addition, electrical power may not be available at the site. In these cases solar power may be required for instrumentation or process gas may be used for the process control instrumentation.
3. What is the climate at the location? Is it in the desert with a high ambient temperature – this can be significant for heat exchanger design. Or if it is in a cold climate, there may be a concern for liquids containing water which may freeze or form hydrates. Equipment housing and personnel protection will be additional issues.
4. Is the project "grassroots" or a retrofit addition to an existing facility? What is the interface with existing equipment? The instrumentation and equipment such as valves should be compatible for sparing wherever possible.

Scope of Supply

The scope of supply for each group involved in the project needs to be clear. What are the process boundaries and what is the scope of equipment supply? The process responsibility may include all the equipment required for the system. However the equipment supplied by the membrane vendor may not include all the equipment associated with the process system. What equipment is supplied on the process skids, what interconnects are required and by whom? What equipment will be shipped loose, including instrumentation and controls? Who is responsible for integrating the membrane control system and data acquisition network into the overall plant control system? Ineffective scope definition or reliance on assumptions can negatively affect project outcome.

Warranty

The desired warranty should be understood during the process design. Does the warranty justify the equipment and cost required to support the warranty? The warranty may have a significant effect on the project cost by adding equipment or redundancy that may not really be required to have a successful operation. Along with warranty often comes process guarantee. The guarantee needs to be well defined including conditions and time period for commissioning. In addition, the warranty and guarantee responsibilities need to be clear as to the responsible parties. What are the responsibilities of the EPC, of the vendors, sub vendors, and of the customer?

Safety and Operability Issues

Safety and operability should always be a high level concern in any facility design. What are the company specifications that will govern the membrane fabrication, equipment supplier standard or end-user specified? What national Code specifications apply, such as ASME and ANSI? The design should not only consider the membrane unit itself, but also the effects of upstream and downstream equipment. What is the pressure rating of upstream equipment? Is there a compressor upstream of the membrane unit? Is a full flow relief valve required? Is the membrane unit shut down control connected to the facility shut down? How do upsets in equipment outside of the membrane unit affect the membrane unit?

Not only should the fabrication specifications and operational issues be considered for safety, but the specific operation of the membrane unit should be understood. There should be a detailed procedure for installing and removing membrane devices from service. Purging of the membrane housing may be required. Monitoring the local ambient for H_2S may be required for some projects. All these points should be considered in a facility HAZOP review.

Environmental Issues

Environmental issues are having an increasing impact on facility design around the world. Direct environmental issues related to what is emitted to the atmosphere or what can potentially spill on the ground or into the water is paramount to consider. Since there are no chemicals required for most membrane systems, membranes are very environmentally friendly. There are no chemicals to leak in operation or in transport or storage. This is very important in areas such as offshore, the Arctic, and other environmentally sensitive areas.

There are other environmental and safety issues that do need to be addressed however, such as contamination of the membrane elements by components in the gas stream. Some of these issues are also safety issues, such as H_2S that is vented when the system is opened for maintenance for example. In South East Asia there is usually significant mercury in the gas stream. Special precautions are required when any process equipment is opened for maintenance, and must be accounted for in the design.

There are indirect environmental issues to be considered for any CO_2 removal processes such as reducing the amount of direct venting of CO_2 off gas. The CO_2 can either be used for enhanced oil recovery or for sequestration, either of which require compression to relatively high pressure. The power required for the CO_2 compression can be significant and can be a dominating factor in the total facility cost. The compression of the CO_2 off gas should be included in the process evaluation. Membrane processes can have a significant advantage over solvent type processes for EOR or sequestration by producing the CO_2 at higher pressures, thus reducing the power required for CO_2 compression. The higher the Inlet CO_2 composition the more advantageous membranes become because they can operate with high permeate pressures thus reducing the power required to compress the CO_2 for enhanced oil recovery or sequestration.

Analyzing and Developing the Process Solution

Once the application has been defined and the system requirements understood, the solution can be studied and developed. There have been problem membrane projects in the past which were mainly due to misapplication of membranes to the process. The key to developing a good process solution is to understand the Inlet gas characteristics, operating conditions and product requirements. Many of the problem projects could have been avoided by properly understanding the inlet gas characteristics and the changes in these characteristics due to removal of CO_2.

When working with gas streams containing hydrocarbon components heavier than hexane, care should be taken to properly handle the condensation that may occur due to the heavy hydrocarbons. It is important to have a complete analysis of the heavy hydrocarbon components if possible because there may be a significant difference in the gas characteristics if the heavy components are not defined in detail. For example Table 1 is a high CO_2 gas stream with a total of 0.47 % C6+ components. The Table shows two columns, "Inlet Gas Itemized" and "Inlet Gas C6+". "Inlet Gas Itemized" itemizes the components heavier than hexane, while "Inlet Gas C6+" groups the hexane and heavier components as C6, the gas streams are identical except for the grouping of these heavy components.

	Inlet Gas Itemized	Inlet Gas C6+
	Mole Fractions	Mole Fractions
CO2	0.716001	0.716001
Nitrogen	0.007194	0.007194
Methane	0.242557	0.242557
Ethane	0.010789	0.010789
Propane	0.005047	0.005047
i-Butane	0.002609	0.002609
n-Butane	0.004008	0.004008
i-Pentane	0.002238	0.002238
n-Pentane	0.002948	0.002948
n-Hexane	0.001499	0.004763
Mcyclopentan	0.000599	0.000000
Benzene	0.000801	0.000000
Cyclohexane	0.000249	0.000000
n-Heptane	0.001003	0.000000
Mcyclohexane	0.000190	0.000000
Toluene	0.000190	0.000000
n-Octane	0.000040	0.000000
E-Benzene	0.000030	0.000000
m-Xylene	0.000014	0.000000
o-Xylene	0.000002	0.000000
n-Nonane	0.000103	0.000000
124-MBenzene	0.000001	0.000000
n-Decane	0.000031	0.000000
n-C11	0.000009	0.000000
n-C12	0.000002	0.000000
n-C13	0.000000	0.000000
n-C14	0.000000	0.000000
n-C15	0.000000	0.000000
H2S	0.000021	0.000021
H2O	0.001825	0.001825

Note: Column B is the same composition as Column A.
The total of C6+ components are grouped as C6.

Table 1

Many applications group the hexane and heavier components as C6+, which is acceptable for rough estimates, but extended analysis should be used when actual bids and designs are required.

Figure 5 is a plot of the phase envelopes for the Inlet gas stream of Table 1. This plot shows how the grouping of the C6+ components affect the phase envelope. The phase envelope for the Inlet gas with the C6+ components itemized and the phase envelope for the Inlet gas with the C6+ components grouped as C6 are plotted on the same chart. Note the only difference in the compositions is the grouping of the C6+ components. There is a difference in the hydrocarbon dew point of approximately 30°F. If the composition with the C6+ grouping is used for the pretreatment design without considering liquid condensation there could be significant problems with the unit operation due to the unexpected liquids. These problems could range from slugging the inlet equipment and even the membrane elements with liquids. This problem will also pass downstream to create additional problems.

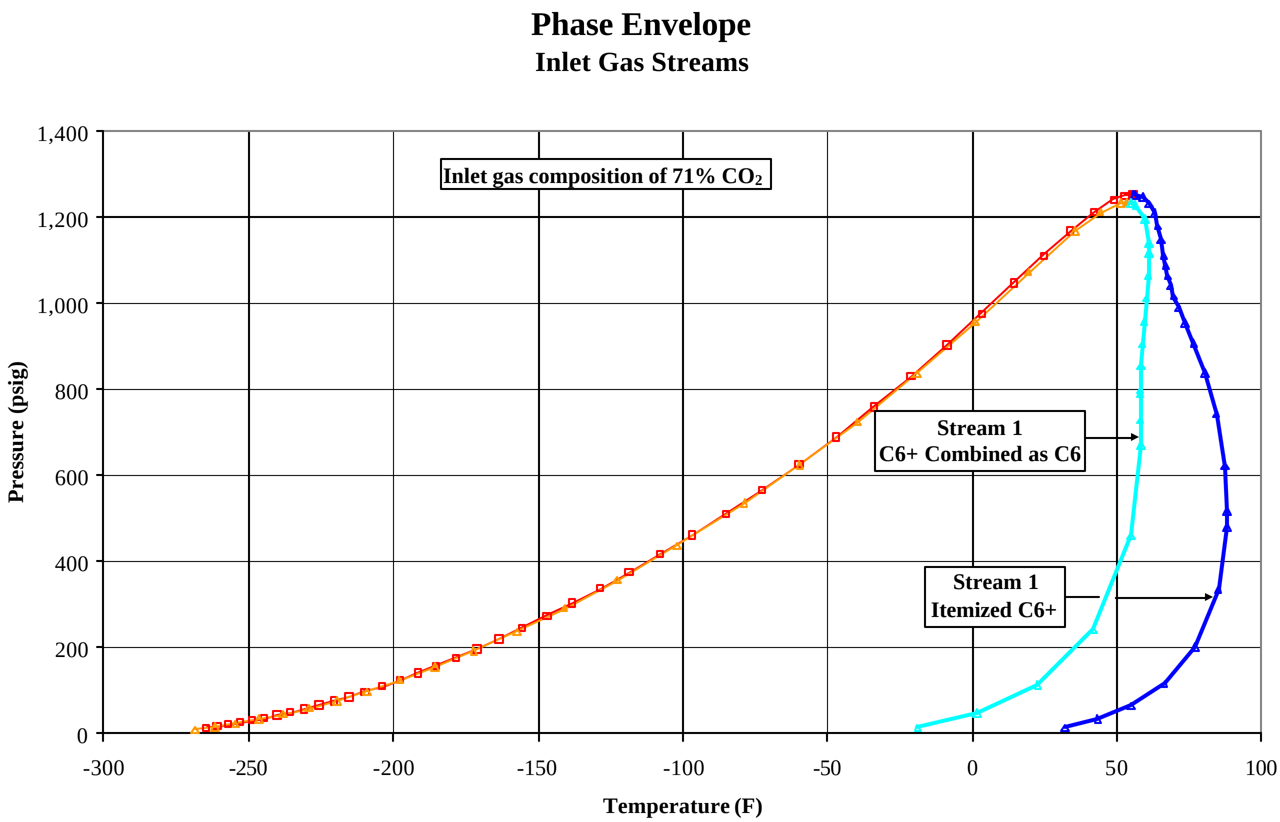


Figure 5

Care also needs to be taken with CO_2 removal for high CO_2 compositions such as the one listed in Table 1. The removal of CO_2 alone will change the properties of the product gas stream. As an example, reducing the CO_2 composition of the gas stream in Table 1 to 10% CO_2 by removing the CO_2 only, will cause a significant change in the properties and phase envelope. The removal of CO_2 with membranes will not only remove CO_2, some of the hydrocarbon components will permeate also, however the basic result of this comparison will be the same.

The method for handling condensing gas streams is different based on the membrane's specific characteristics, membrane supplier design preference, and the processing objectives of the facility. Some suppliers allow hydrocarbon condensation on the membrane elements and some try to avoid condensation on the membranes. Many system designs in the past have assumed that simply superheating the inlet gas would avoid condensate in the CO_2 removal process. Superheating the inlet gas to avoid condensation can be difficult and is an unreliable means to avoid condensation. The successful control of hydrocarbon condensation is usually accomplished by chilling the gas, using desiccant dry bed units, or by designing the membrane system to properly accommodate the condensation. It is very important to understand what will be the conditions of the gas (fluid) during the CO_2 removal.

Figure 6 is a plot of the Inlet gas stream from Table 1 "Inlet C6+" with the CO_2 reduced to a product of 10% by removing CO_2. Note the dew point temperature will be approximately 110°F. And one might assume that a superheat of 130°F would be sufficient to avoid condensation.

Phase Envelope
Product Gas Streams

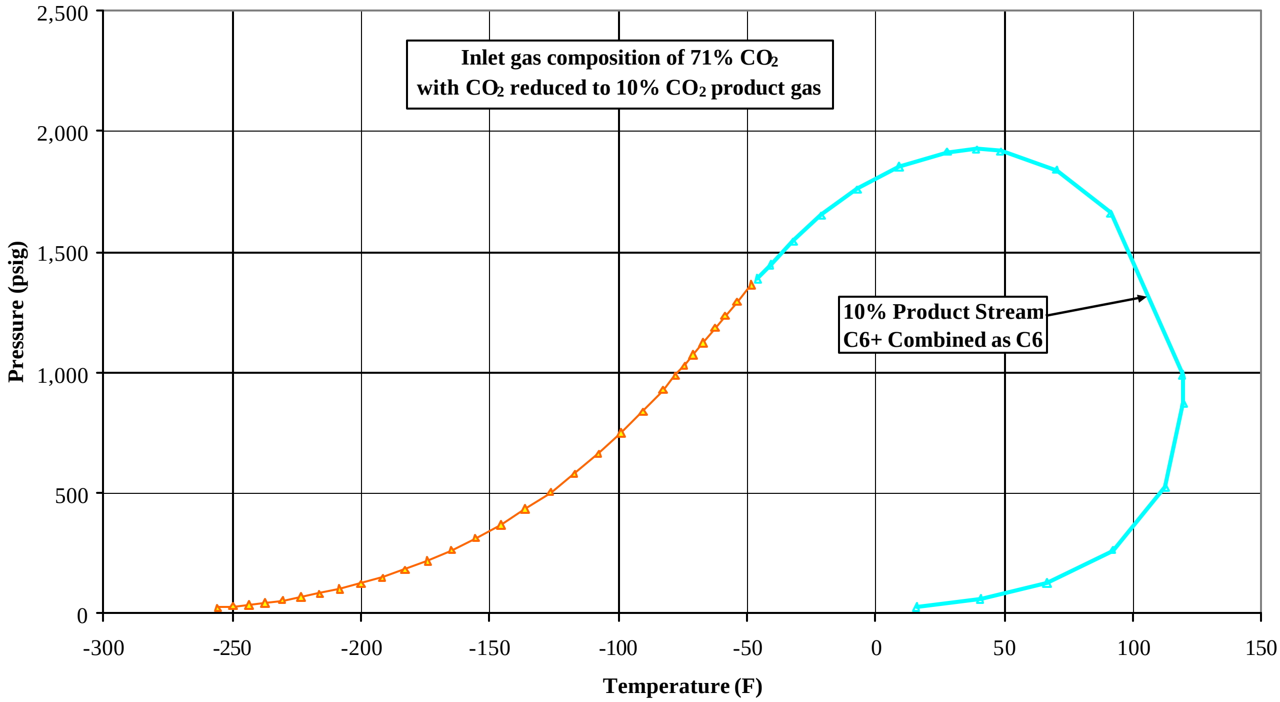


Figure 6

However if the extended Inlet gas stream "Inlet "(C6+ itemized) is reduced to 10%, the dew point temperature of the product will be approximately 150°F. Note the difference in the plot of the above phase envelop plotted in Figure 7. The control of the condensate that may result at the inlet to the membrane system or during the CO_2 removal process is very important for the operation of the membrane unit itself, and to avoid liquid problems downstream of the membranes such as pipeline slugging.

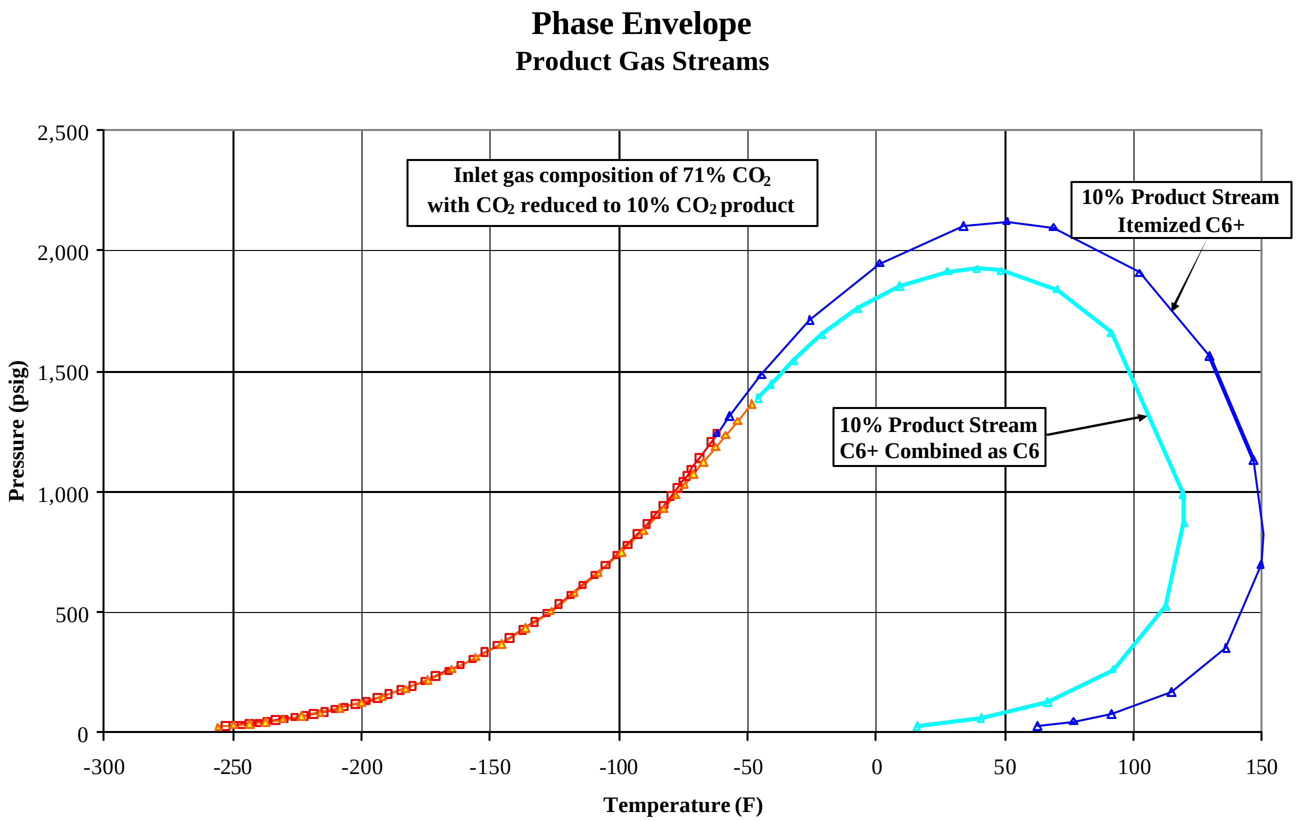


Figure 7

Optimizing the Design

Once the inlet gas characteristics are understood the process design can be completed to develop a process that delivers the required product [1, 2, 3, 4, and 5]. The completion of the process will require analyzing cost considerations to optimize a process scheme that is technically correct as well as commercially attractive. There are many options for optimizing membrane applications such as recycling permeate gas back to the inlet and utilizing secondary units to further process permeate gas for increased hydrocarbon recovery. There have been many papers presented in the past covering these options and therefore we will not discuss in detail at this time except to summarize that proper membrane system optimization is usually a trade off between hydrocarbon value and recycle compression cost, and will include a design safety margin to allow the membranes to continue to operate successfully with fluctuations in the inlet gas composition and C6+ components.

PROJECT EXECUTION

Having a proper process design does not guarantee a successful project. The execution of the design requires a coordination of efforts between the customer and the vendor. Small projects may require low level project management while large projects may require extensive project management. The more involved projects may have specifications that are complex or unfamiliar and may require engineering support that goes beyond that normally supplied. Fabrication and packaging of the membrane process equipment can be a potential problem if not done within the supplier's own facilities. The use of sub-vendors usually adds complexity to project management but may be required if the supplier does not have the capacity or capability in their own shop. Whether the packaging is within the supplier's shop or outside of the supplier's shop, quality control of the fabricated package is of greatest importance. The customer should have a good understanding of who has responsibility, from the customer down to the sub vendors. Furthermore project execution does not end with the equipment shipment. There should be assistance with training of the customer operating personnel and assistance given during site installation and startup of equipment.

SUMMARY

Although not quite the same market share as lungs in humans, membranes are widely used for CO_2 removal in process gas streams. As with trouble shooting medical problems which require analysis of the human system, CO_2 facilities require a detailed system analysis to not only determine which type of process should work best for the given project, but to establish proper design of the system for the specific project. The characterization of the inlet gas along with the required job specifications will establish the pre-treatment, configuration of membranes, and ancillary equipment requirements to produce a system that best meets the user's expectations for the project life. To design a proper, well-functioning membrane system, care must be taken in selecting a supplier with significant and relevant experience. You wouldn't trust your personal lung membranes to an unqualified or inexperienced medical professional to ensure long-term proper function of these vital components. Likewise, CO_2 gas processing facilities require properly defined processing detail and qualified providers for design and fabrication to ensure long term successful process operation.

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