Gas Treating Technologies:
Which Ones Should Be Used and Under What Conditions?

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Abstract

There are numerous types of technologies available for the treating and conditioning of natural gas streams. Unfortunately, choosing what technology to use for a specific application can be confusing and is often times not fully evaluated to determine what option will provide the most efficient and cost effective solution. The evolution of new technologies and application of old technologies in new ways has made this decision making process even more difficult. Additionally, there are more types of gas streams that need to be treated. Whether it be Coal Bed Seam Gas, landfill gas, bio-gas from dairy farms, or natural gas from gas and oil well production, most gas produced today has one or more contaminants that need to be removed before the gas can be sold into the pipeline.

In this paper we will endeavor to look at the various gas treating options available for both conventional and not so conventional gas streams and evaluate which options would be the best fit for each case, as well as the environmental impacts associated with each. This paper will also investigate the feasibility, both economically and operationally, of combining different processes to achieve the desired treating results.

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Introduction

As the demand for natural gas continues to increase, new or previously ignored areas of gas supplies are being re-visited. Many of these "new" gas supplies have been ignored in the past, due to poor gas quality and/or prohibitive costs associated with treating the gas to make it saleable. However, as gas prices have continued to rise and new gas treating technologies have been developed, the prospect of treating and selling these gas volumes has become viable.

These new gas sources include Coal Bed Seam Gas, Landfill Gas and Bio-Digester Gas, to name a few. Each of these gas streams can contain up to 50% carbon dioxide (CO_2), up to 6% oxygen, hydrogen sulfide and nitrogen, all of which need to be removed to meet pipeline specifications. Many of these gas streams also come into the plants at a relatively low pressure, requiring inlet compression.

Existing gas sources, that had been shut-in or reduced in production because of poor quality, include vacuum gathering systems and gas wells with high contaminant levels.

Despite the improving economics, the producer still wants/needs to treat their gas stream in the most efficient and cost effective manner possible. Unfortunately, time constraints often lead the producer to choose what they "think" is the best option, without considering all of the available technologies or doing a detailed evaluation of those alternatives. The author will endeavor to supply several "Rules of Thumb" that can be applied when choosing gas treating options and will illustrate, through several actual examples, how one can make the best decision for their gas processing needs.

This paper will concentrate on gas treating using amine, membranes, hydrogen sulfide (H_2S) scavengers and oxygen (O_2) removal and their application to removal of CO_2, H_2S and O_2 from raw gas streams.

Assumptions

The following assumptions are made for the discussion to follow and may vary to some extent in actual practice; however, they should be representative of what is actually seen in the field.

1. Amine will be regenerated using 1.0 lb steam generation per gallon of amine circulated (950 Btu/lb). Thus, a 100 gpm amine plant will utilize approximately 5,700,000 Btu/hr of heat input. Assuming 80% heater efficiency, fuel gas for this system will be approximately 171 MSCFD (0.12 MSCF/100gal).
2. 30 wt% DEA will remove 4 scf of acid gas/gal, while a 50 wt% amine solution will remove 5 scf acid gas/gal, without exceeding a rich amine loading of 0.45 mol/mol.
3. Depending on operating pressure, an amine plant will have an electrical power usage of 2.0 – 2.5 bhp per gallon of amine circulated (i.e. a 100 gpm plant will have an operating electrical load of 200 - 250 bhp).
4. For the purpose of this paper, membranes will only be considered for CO_2 removal, though advances are being made to also use this technology for nitrogen removal.
5. Membranes should have a minimum inlet operating pressure of at least 400 psig to operate efficiently and cost effectively, though systems have been operated as low as 125 psig.
6. When using two-stage membrane units, the first stage permeate stream will be re-compressed to the first stage inlet pressure, plus 15 psi, before entering the second stage of membranes.
7. A membrane plant will use no more than 5 kW/MMSCF, not including compression/re-compression horsepower.
8. PSA units will only be considered for N_2 removal, though recent advances indicate these may also be used in CO_2 removal applications.
9. H_2S Scavenger vessels are generally sized to maintain a superficial gas velocity of less than nine (9) feet per minute.
10. One pound of solid bed H_2S scavenger chemical, such as SulfaTreat or Iron Sponge, will recover 0.25 pounds of sulfur. The chemical has a density of approximately 93 lbs/ft^3.
11. Unless otherwise noted, all cases that follow assume a base gas composition of 84% Methane, 9% Ethane, 3% Propane and 4% Butane and heavier hydrocarbon, each adjusted proportionately to account for CO_2, H_2S and N_2 in the gas stream being treated.
12. Pipeline Gas specifications are 2% CO_2 (max); 3% Total Inerts (max); 4 ppmv H_2S (max); 20 ppmv O_2 (max) and 7 pounds H_2O/MMSCF (max).
13. Natural Gas can be sold to the pipeline for $6.50/MMBtu. Electricity can be purchased for $0.075/kW-hr.
14. Reciprocating compressors, operating at 80% efficiency and requiring a heat input of 7600 Btu/hp-hr, are assumed to be used for all compression operations.

Discussion

How do you decide which gas treating technology best meets your needs? To answer this question, you first need to define what is required and what constraints are in place. This will include knowing what contaminants are present and need to be removed, the inlet and discharge operating parameters and specifications (Pressure, Temperature, flow rate, gas composition, allowable contaminant concentration in the Sales Gas, etc.) and site location and conditions (power availability, ambient conditions, regulatory restrictions, etc.).

Once you have this information, the vetting process can begin and a preliminary evaluation can be performed. Always begin at the front of the process and work through the system, taking care to understand the effect of each contaminant on the immediate process at hand, as well as subsequent downstream processes. The evaluation process should also include a comparison of not only capital costs, but also operating and maintenance costs, material purchase and disposal costs, fuel usage cost and product losses to vents or flares.

It is imperative to understand the capabilities and limitations of the various technologies under consideration and how the different processes may compliment or conflict with one another. For example, oxygen in the gas stream will have a detrimental effect on amine, but has no impact at all on membranes. Thus, if amine is the technology of choice, an oxygen removal system, such as Newpoint's X-O_2 catalytic removal system, should be considered for installation upstream of the plant, whereas this step may not be required if membranes are used, depending on inlet O_2 concentrations and pipeline specifications. However, unlike amine, membranes are unable to attain the outlet H_2S levels required by most pipeline specifications. In those cases where H_2S is present and membranes are to be used, an H_2S Scavenger may be installed on the inlet or outlet stream, or you might follow up with an amine unit, depending on the H_2S concentration. This might also be a viable configuration when trying to minimize overall energy consumption and product losses in high contaminant concentration gas streams.

Membranes and PSA units have the reputation for being effective only for bulk removal of contaminants and always inefficient regarding the losses of hydrocarbon components, even though these drawbacks can often times be overcome for minimal cost, compared to the rest of the project cost or other technology alternatives. H_2S Scavengers, such as SulfaTreat, may seem to be an inexpensive and easy way to capture the toxic contaminant and escape environmental concerns and/or the use of a sulfur recovery unit (SRU), but operating parameters and maintenance/material costs may make this economically unattractive.

It is also helpful to know of any requirements the Operations group may have. An example of an Operational concern is the fact that some people are averse to putting sour gas through compressors and require that any H_2S removal be accomplished ahead of any compression step. Depending on the H_2S content in the gas stream, an H_2S Scavenger might first be used, followed by an amine plant after compression; or all treating might be accomplished using a single amine system.

Now, assuming that one understands all of the constraints and requirements of the system to be designed, one can use some guidelines, or Rules-of-Thumb, that can point toward the type of design to be used. For instance, when does it typically become more economical to use a membrane system instead of an amine unit? This can first be evaluated by looking at the fuel usage per MSCF of inlet hydrocarbon versus hydrocarbon losses for each system. For example, an inlet gas stream containing five (5) percent CO_2 that needs to be reduced to less than two (2) percent CO2 in the Sales Gas stream can be treated with 6 gallons of amine per MSCF of inlet gas:

1000 scf/MSCF * 0.03 scf CO_2/scf inlet * 1 gal amine/5 scf CO_2

The Fuel Gas required to operate the amine plant in this case will be approximately 0.75% of the inlet hydrocarbon content:

6 gal amine/MSCF In*0.12 MSCF FG/100 gal amine*MSCF In/0.95 MSCF HC

On the other hand, if you have inlet gas streams having 15% and 30% CO_2, and still need to meet the 2% CO_2 outlet specification, the amine and fuel gas requirements will increase to 30 gallons of amine/MSCF of inlet gas and a Fuel Gas Shrinkage of 4.25% for the 15% inlet CO_2 case and 60 gallons and 10.3% Fuel Gas shrinkage in the 30% inlet CO_2 case.

It is doubtful that a single stage membrane can ever match the hydrocarbon losses from an amine plant, even in the 30% inlet CO_2 case; however, installation of a second membrane stage can almost always keep total hydrocarbon losses, including recycle compression fuel, to less than 5%. Thus, the first Rule-of-Thumb would be to consider use of a membrane system, instead of an amine system, when the inlet CO_2 content exceeds 15% and you are only trying to reach pipeline specifications.

Additionally, the use of a membrane system in conjunction with an amine plant may prove to be a viable option. For example a 50 MMSCFD gas stream being fed to a cryogenic gas plant, but containing 30% CO_2, needs to be treated to less than 0.10% CO_2 in the treated gas stream. If treating was accomplished strictly with amine, a circulation rate of over 2000 gpm would be required.

50 MMSCFD*0.3 scf CO_2/scf inlet*1 gal amine/5 scf CO_2*1 day/1440 min

This is not only a large plant, but an energy hog. If, on the other hand, a two-stage membrane is used to reduce the CO_2 content to 2%, the amine circulation rate would be reduced to approximately 100 gpm, resulting in significant capital and operating cost savings.

Another question that often arises is when to use an H_2S scavenger instead of removing this substance in an amine plant and possibly having to install a Sulfur Recovery Unit (SRU) or Acid Gas Injection (AGI) system. In the past, it was typically thought that an inlet sulfur content of more than 300 pounds per day precluded the use of a scavenger system. This was attributed not only to the cost of replacing the chemical, but also the labor costs and potential disposal problems of the spent chemical. Specifically, Iron Sponge (iron impregnated wood chips) can be pyrophoric and this created the potential for a fire danger. However, current chemicals, such as SulfaTreat, are non-pyrophoric and the spent chemical can be used as local fertilizer without concern. Overcoming the issue of disposal of spent chemical expands the areas of application for H_2S scavengers, but does not dictate that this should be used in all instances.

The next thing to consider when choosing how to remove H_2S revolves around the inlet gas conditions (composition, flow rate, pressure and temperature) and the sales gas requirements. For example, a gas stream of 50 MMSCFD at 500 psig contains 150 ppmv H_2S and 1.9% CO_2. This gas stream already meets the Sales Gas CO_2 specification, so there is no need to remove this component. An amine system will remove 50-60% of the CO_2, resulting in an acid gas stream that is very lean in H_2S. However, the stream contains approximately 630 pounds/day of sulfur, which exceeds the previously accepted maximum. Using two 102" ID x 24'-0" S/S vessels, set in a parallel configuration, each vessel would be filled with 105,000 pounds of chemical. In this configuration, each bed will have a life of approximately 3 months, with an expected replacement cost of approximately $135,000 each time a bed is changed. This equates to a treating cost of approximately $0.068/MSCF.

630# S/day * 1# Chemical/0.25# S * $1.35/# Chemical * 1 day/50,000 MSCF

Compared to the capital and operating costs of a 100 gpm amine system and AGI system, the H_2S scavenger may be a cost effective alternative.

In contrast, if the gas stream was 5 MMSCFD with 1500 ppmv H_2S, somewhat smaller vessels could be used, but change out frequency would increase, and the cost per MCF would increase to approximately $0.68/MSCF for the H_2S scavenger, while the amine plant circulation would decrease to less than 10 gpm and the overall capital and operating costs for the two systems become more comparable.

Thus, when evaluating whether or not to use a scavenger system, do not rely solely on the amount of sulfur being recovered, but on the cost per MSCF of each available option.

Case Studies

Consider the following: A 10 MMSCFD gas stream at 1000 psig and 160F, containing 2.7% CO_2, needs to be treated to less than 2.0% CO_2 in the outlet stream. There is no H_2S in the inlet gas stream. The gas stream is located on a small platform in the Gulf of Mexico and there is no electrical power supply.

Evaluation: This is an excellent fit for a 10 gpm amine unit, except there is no electrical power source available to supply the pump and cooler motors. Though the inlet pressure is high enough, a membrane system would not typically be the technology of choice because of the "fine tuning" aspect, rather than bulk removal, required for this process. However, in this case, the lack of a power supply made the membrane system the only viable alternative.

Initially, a single stage membrane unit was proposed to perform this service. The process reduced the CO_2 content in the Sales Gas to approximately 1.8%, though it suffered a 3.2% hydrocarbon loss into the permeate stream. However, the lower capital and operating cost of the membrane unit, compared to the amine unit, made this alternative acceptable. While this was considered acceptable to the Client, MMS stated that the plant would not be allowed, unless the total hydrocarbon emissions could be limited to less than 50 MSCFD (0.5% of the inlet). It was originally thought that this limitation would kill the project and the well would be unable to produce, thus shutting in 10 MMSCFD of gas production.

Unwilling to give up on this opportunity, Newpoint suggested that the Client consider installation of a second stage of membranes to treat the permeate gas stream and reduce the hydrocarbon losses/emissions to acceptable levels (Figure 1). The new design required the first stage permeate gas stream to be compressed to the inlet gas pressure, then processed through a second stage of membrane treating. This required the customer to install approximately 160 bhp of recycle compression. The exiting, high pressure residue gas stream contained approximately 11% CO_2 and was combined with the inlet gas stream to form a first stage feed stream containing approximately 3.2% CO_2. The residue gas stream exiting the first stage of membranes (Sales Gas) still contained less than 1.9% CO_2. Also, while not a requirement for this particular project, the membranes permeated approximately 90% of the contained water vapor, giving the Sales Gas stream an outlet water content of less than 7 pounds H_2O/MMSCF.

More importantly, the second stage membrane permeate stream contained significantly less than 50 MSCFD of hydrocarbon. This second stage permeate gas stream was then vented to atmosphere.

Thus, for an increase of approximately 25% in capital cost and the monthly lease cost of compression, the Client was able to produce the gas well and increase the Sales Gas stream volume (by reducing the losses to vent) by approximately 200 MSCFD, for an increased revenue of $1300/day ($475,000/yr) on that volume alone. The overall capital cost of the two-stage membrane system, less the recycle compression, was comparable to a 10 gpm amine plant and resulted in approximately the same amount of hydrocarbon loss.

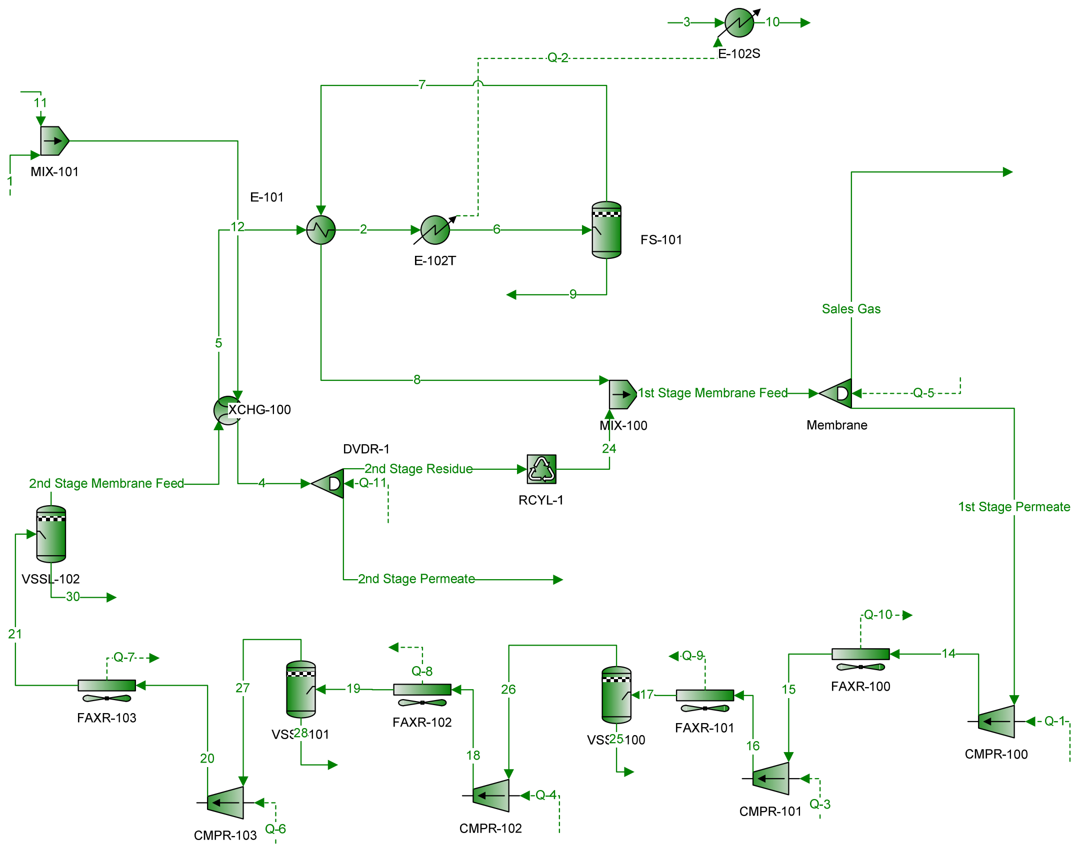

Figure 1

Consider the following: A landfill gas stream at 6 MMSCFD contains 36% CO_2, 3.2% N_2, 0.8% O_2 and 2500 ppmv H_2S (balance is methane), entering the plant at essentially atmospheric conditions. The low Btu gas stream is currently routed through an Iron Sponge for H_2S removal, compressed to 600 psig and then routed through a small Selexol unit for the removal of trace contaminants and partial dehydration before being sold; but new regulations are forcing the Client to convert to a high Btu (>900 Btu/scf) sales stream, though the new buyer will still allow up to 1% O_2 in the Sales Gas stream. The plant is located in an urban, industrial area of a major city.

Evaluation: The gas is already being treated for the removal of H_2S, is dehydrated to pipeline specification levels and the final gas stream can have up to 8% inerts and still meet the minimum Btu specification. The oxygen in the gas stream will have detrimental effects on any amine system, so a membrane system seems to be the best alternative, though reduction of the CO_2 to less than 3% in the Sales Gas stream will result in higher than acceptable hydrocarbon losses. In fact, simulations of the system indicate that over 20% of the inlet methane will be lost to the first stage permeate stream. In order to make this a profitable project, the Client believes he needs to keep the overall hydrocarbon losses to less than 5%.

Again, utilizing compression to boost the pressure of the first stage permeate stream to the first stage inlet pressure (approximately 900 bhp) and then processing through a second membrane stage results in a second stage permeate stream containing less than 3% of the total inlet hydrocarbon content (Figure 2).

The installation of the second membrane stage resulted in the savings of almost 1 MMSCFD of hydrocarbon gas that would otherwise have been lost to the atmosphere. This was not only good for the environment, but increased the gas supply and the Client's revenue by more than enough to pay for the second stage of membranes and the lease cost of the compression.

It should be noted that the membrane option was most attractive because of the allowable oxygen content in the Sales Gas stream and the presence of the existing Iron Sponge and Selexol units at the plant for removal of H_2S and contaminants such as siloxanes that are detrimental to membranes. If this had been a grass-roots operation, with more stringent product specifications, a different alternative may have been the more logical and cost effective choice.

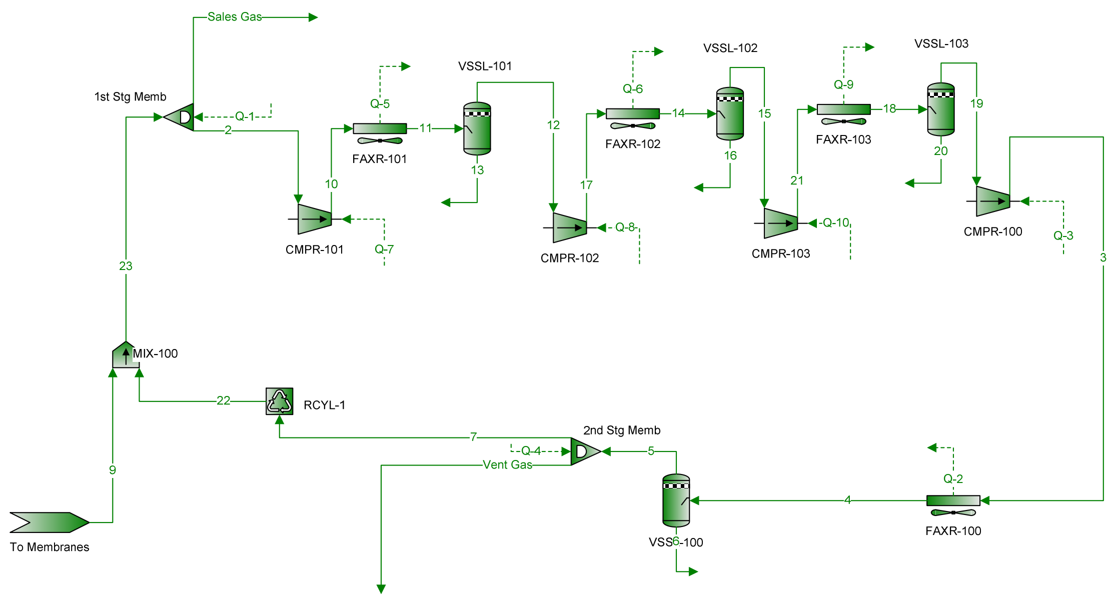

Figure 2

Consider the following: An 100 MMSCFD gas stream, at 700 psig and 100F, contains 9.5% CO_2 and 4% N_2 and 2000 ppm O_2 is being sent to a cryogenic gas processing plant for deep ethane recovery (>95%) and nitrogen rejection.

Evaluation: Due to the inlet gas composition and pressure, a PSA unit will not be considered for nitrogen removal in this case, due to the high hydrocarbon losses and excessive compression requirements. This may be a good application for membrane removal of N_2, but that technology is not being considered in this paper. Because of the plant's desire to get maximum ethane recovery, meet liquid product specifications and then reject nitrogen using cryogenics, removal of CO_2 to less than 300 ppmv should be considered. We know that a membrane unit will not allow the gas to be treated down to these levels, so we choose an amine plant for this application, ***or do we***? The oxygen content will have a negative effect on the amine system and, even without the O_2 concerns, this will require a large, energy intensive amine plant.

However, following the rule to always start at the front of the process and remove the contaminant(s) that will be detrimental to any other subsequent process, the oxygen issue is the first item that needs to be addressed. Using Newpoint's X-O_2 catalytic oxygen removal process (Figure 3), the inlet gas is first heated through cross heat exchange and then through a Gas Heater to reach the required reaction temperatures. At this point the gas enters the catalytic reactor and oxidizes a portion of the inlet hydrocarbon stream to form CO_2 and water vapor, which are contaminants that can be easily removed in downstream processes. As the oxidation process is exothermic, the gas stream rises in temperature across the reactor. The amount of temperature rise is dependent on the amount of oxygen that is contained in the entering gas stream. It should be noted that the outlet gas stream will typically have less than 10 ppmv oxygen and the reactor can be designed to deliver a gas stream containing less than 5 ppmv O_2. The hot exiting gas stream is then cooled with cross heat exchange and air cooling before going to the next treatment step.

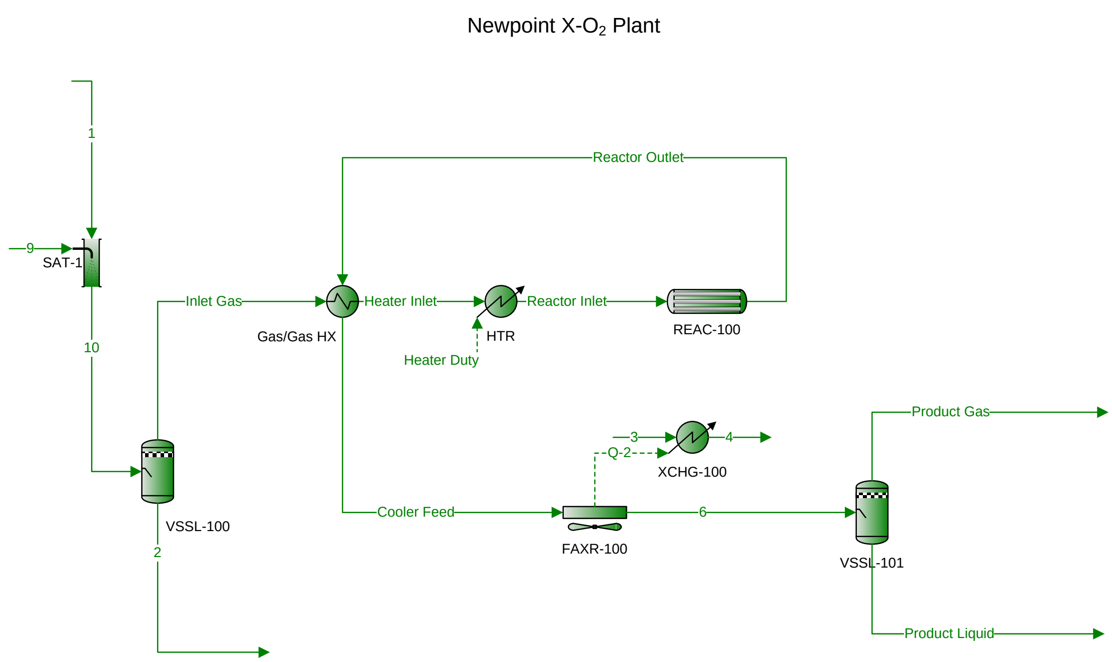

Figure 3

If, following the oxygen removal unit, we use an amine plant alone to remove the CO_2 from the gas stream, a 50 wt% mixed amine solvent would require:

100 MMSCFD * 0.095 ft3 CO_2/ft^3 Inlet *1 day/1440 minutes * 1 gpm amine/5 ft^3 CO_2 = approximately 1300 gpm of amine circulation.

This equates to a reboiler duty of approximately 74 MMBtu/hr, or a fuel rate of approximately 2.22 MMSCFD, or almost 2.5% of the inlet hydrocarbon content. Additionally, the electrical load for this plant would be approximately 2200 bhp.

On the other hand, if the gas stream is first treated using a two-stage membrane unit to reduce the CO_2 content to 5%, while keeping the hydrocarbon losses to less than 1%, the subsequent amine system could then be reduced in size to 650 gpm (Figure 4), reducing fuel and electrical consumption by 50% while still meeting the desired 300 ppm CO_2 specification in the treated gas. The treated gas can now be dehydrated and sent to the cryogenic portion of the plant for liquid product recovery and nitrogen rejection.

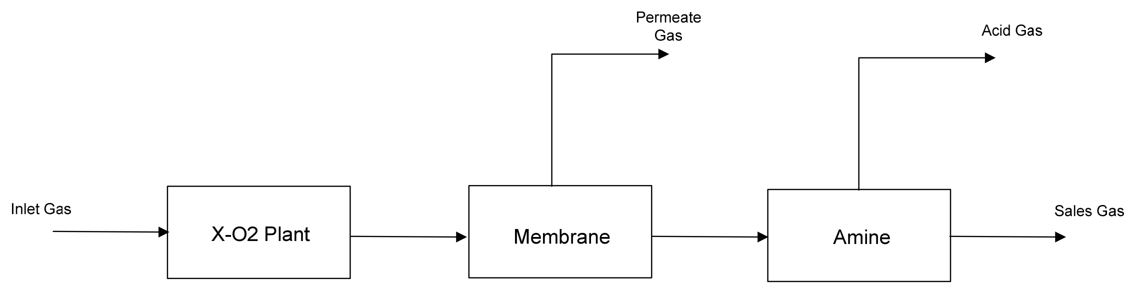

Figure 4

The membrane system requires approximately 2100 bhp of recycle compression, which will consume approximately 360 MSCFD. Thus, the net savings of using this two-stage system (membrane + amine) will be approximately 730 MSCFD of fuel gas and 2000 hp (1500 kW) of electrical power when compared to using the amine system alone. Because two systems are being utilized, the plot area for this plant will also be about double of what an amine plant would be on its own. Therefore, if plot space is limited or unavailable, use of the “two-tiered” approach may not be an option. The combination of a membrane plant and amine plant also has a slightly higher initial capital cost, but the $2,700,000 in annual operating cost savings from fuel and electricity pays for this difference in less than one year.

Conclusions

Gas treating technologies have made great strides forward in the last 10 - 20 years; and they have received a great deal more attention in the last 5 – 10 years, due to the increased energy demand throughout the world and the resultant search to exploit alternative sources that were previously considered uneconomical. It now rests upon the system designers and Operators to determine the most efficient and cost effective ways to utilize these technologies and/or develop new ways to apply them. To help in this development and evaluation process, the following Rules of Thumb can be used as a guide:

1. Understand all of the contaminants in the stream being treated and develop a process flow that will first remove those contaminants that are harmful to any subsequent downstream processes.
2. Review the proposed plant site for available plot area, utilities, etc.; these constraints may determine what types of designs are viable.
3. When only needing to meet Pipeline Specifications (2% CO_2), membranes may be a cost effective and efficient alternative to amine treating, especially if using a two-stage system.
4. When inlet CO_2 concentrations exceed 10%, the use of membranes for bulk CO_2 removal purposes may reduce the size of a subsequent amine plant by more than 50% and save a proportionate amount of fuel and energy.
5. Amine is still the only reasonable way of removing CO_2 to levels necessary for cryogenic gas processing or for removal of large amounts of sulfur. However, amine is also energy intensive, so thought should be given to using amine in conjunction with other technologies (especially if Waste Heat is not available).
6. Use of an H_2S scavenger may be the best option for low pressure and low volume streams that do not require CO_2 removal, but chemical replacement costs (material + labor) can make this option very costly as gas rates and H_2S concentration increase.