FINAL REPORT

DEVELOPMENT OF ADVANCED MEMBRANES TECHNOLOGY PLATFORM FOR HYDROCARBON SEPARATIONS

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Executive Summary

Virtually all natural gas is dehydrated during its production, transmission and storage, mostly by absorption processes. Membranes offer many potential advantages over absorption, including smaller footprints, lighter-weight packages, packaging flexibility, minimal electrical power duty, amenability to expansion due to system modularity, reduced maintenance costs, reduced emissions of heavy hydrocarbons, no liquid waste streams, and amenability to unmanned operation. The latter is particularly valuable because new natural gas sources are generally located in remote onshore and offshore sites. Most commercially-available membranes for natural gas upgrading involve high capital costs, high methane loss and performance degradation from operational upsets – all of which are barriers to their widespread adoption by the industry. The original focus of the project was to develop and demonstrate robust, high-performance membranes for natural gas dehydration. The first task completed was a user needs-and-wants study to 1) clarify the expectations of system fabricators and end users of the new separations equipment, and 2) establish the required technical and commercial targets for the membrane products. Following this, membrane system modeling and membrane development in the lab proceeded in parallel. Membrane module diameter and length, as well as and the fiber outer and inner fiber diameter, were optimized from a mathematical model that accounts for the relevant fluid dynamics and permeation phenomena. Module design was evaluated in the context of overall system design, capital costs and energy consumption, including the process scheme (particularly sweep generation), feed pretreatment, system layout, and process control. This study provided targets for membrane permeation coefficients and membrane geometry in a commercial offering that would be competitive with absorption systems. A commercially-available polymer with good tensile strength and chemical resistance was selected for membrane development. A novel dope composition and spinning process were developed, which provide a new approach to controlling membrane porosity and wall and skin morphology. A hollow-fiber membrane with an external dense “skin” was produced that has a high water vapor permeation coefficient and selectivtity, durability when in operation at 1000 psig and 70℃, and the ability to withstand aromatic and aliphatic hydrocarbon vapors for an extended period.

The fiber meets the technical requirements for a commercial product offering in gas dehydration. It can be readily manufactured with some changes in process equipment and process conditions, and is an excellent candidate for scale-up to full-size membrane modules.

1. Project Objectives

The project objectives are to develop and demonstrate a new technology for superior, robust, low-cost membrane separator systems with multiple applications, particularly those involving the following hydrocarbon separations:

a) dehydration of natural gas,
b) removal of CO_2 and H_2S from natural gas ("sweetening"),
c) dehydration of CO_2 gas,
d) pervaporative dehydration of organic liquid mixtures,
e) recovery of VOCs from vent streams, and
f) separation of hydrocarbon gases.

Of the applications listed above, natural gas upgrading has the broadest energy, economic, and environmental impact in the U.S. and worldwide. There is a strong market need for such technology since new natural gas sources, which are generally located in remote onshore and offshore sites, would be amenable to upgrading by membrane processes.

The initial focus of this project was on membranes for natural gas dehydration at the wellhead. However, using a commercially-available polymer, we have demonstrated a novel microporous membrane with high-pressure and high-temperature capabilities, a high water vapor permeation coefficient, a low methane permeation coefficient, and excellent solvent/chemical resistance. The demonstration was completed on a bench scale.

2. Background & Summary

The original focus of this project was dehydration of natural gas, for which membranes offer many advantages over present technologies including lower methane and hydrocarbon loss per unit of natural gas production, lower energy consumption, reduced maintenance costs due to fewer components, no spent glycol/mole sieve/deliquescent wastes, amenability to unmanned operation, smaller footprints, lighter-weight packages, minimal electrical power duty, and amenability to expansion due to system modularity. However, use of most commercially-available membranes for natural gas upgrading incurs high capital costs, methane loss and performance degradation from operational upsets – all of which are barriers to their widespread adoption by the industry.

Our bench-scale testing of a dehydration membrane demonstrated its commercially-viable properties. It is capable of long-term operation at 1000 psig and 70°C in the presence of heavy hydrocarbon vapors (similar to those in natural gas streams), with a high water vapor permeation coefficient and a low methane permeation coefficient. It can overcome many of the issues associated with current commercially-available gas dehydration membranes.

In the course of membrane development, we explored several leads to prepare microporous, hollow-fiber membranes from the same polymer used for the dehydration membrane. The membrane can be produced with a dense layer at the outside ("externally-skinned"), dense layer at the bore-side ("bore-skinned"), or no dense layer at all ("non-skinned"). The externally-skinned version of this membrane was demonstrated for gas dehydration.

Prior to membrane development, an industry-based, user-needs-and-wants study was conducted in order to establish and verify the technical and commercial targets for the new membrane technology. Potential customers such as system fabricators and end users were interviewed. The results were analyzed to derive a list of benefits sought and a list of technical requirements that can be used to gauge project success.

The first membrane evaluated, composed of polymer X, failed to meet targets for water vapor permeation rates. Tests were completed on a second polymer, Y, which has higher tensile strength, greater chemical resistance and is compatible with a broader range of solvent compositions compared to polymer X. The results indicate that high water vapor permeation rates are possible at commercial target values.

Another key performance and cost factor is the module design. The module diameter and length, as well as the outer and inner fiber diameter, have been optimized using a mathematical model that accounts for the relevant fluid dynamics and permeation phenomena. Module design is evaluated in the context of overall system design, capital costs and energy consumption, including the process scheme (particularly sweep generation), feed pretreatment, system layout, and process control.

Significant Accomplishments

- Conducted interviews with several oil and gas companies and compiled a list of technical and commercial requirements for success.
- Developed a spreadsheet model to simulate the effect of membrane properties on system size and weight, capex, and opex for several membrane process schemes. Summarized and presented the results to potential customers for additional feedback.

- Completed bench-scale demonstration of a membrane with adequate operating pressure and temperature capability, water vapor permeation coefficient, and solvent resistance needed to achieve commercial success.

3. Detailed Technical Report

3.1 User Needs-and-Wants Study

A user needs-and-wants study was conducted to 1) clarify the expectations of system fabricators and end users of the new separations equipment, and 2) establish the required technical and commercial targets for the membrane products. Face-to-face and teleconference interviews were used to gather “voice-of-customer” information.

Various information gathered or developed in the study is presented in the following sections: discussion details in Section 3.1.1;a technical requirements summary in Section 3.1.2; desired benefits of new product offerings in Section 3.1.3; and the results of a follow-up concept test in Section 3.1.4.

3.1.1 “Voice-of-Customer” Interview Details

The list of questions shown in Table 3.1.1 was developed for use in the customer interviews. The results of the interviews follow.

TABLE 3.1.1: Questions for VOC interviews

Are amines frequently used as corrosion inhibitors? What part of the market would we sacrifice if we knew our membrane dryer couldn’t tolerate amines?
How will you evaluate the membrane against the other technologies?
What kind of testing would you like to see on our end? What kind of evidence do you need to purchase for an offshore application? How long would the pilot test need to be?
What would acceptable methane loss be?
What do you like about the current technologies?
What problems are you looking to solve with the membrane? What are your concerns about the membrane?
What concentrations of aromatics and of methanol might the membrane expect to see?
How do you value the weight and space improvement of a membrane over other technology?
What would the acceptable pressure drop across the membrane dehydration system be?
Target pressure capabilities
How do you calculate your annual operating (maintenance plus parts) costs?
Definition for base case
Has your company actively evaluated membranes for dehydration in the past? What were the barriers to adoption?

Interview results

Company #1 is interested in technology aimed at dehydrating gas more reliably at isolated locations using remote, unattended operation for 2-3 years. Glycol dehydrators are perceived as a problematic area in offshore applications, due to unanticipated downtime and the need for attended operation. For an onshore base case, ~10 MMscfd was appropriate. The use/disposal of the permeate stream is an issue that needs to be resolved. This company also had concerns about the safety implications of the air compressor process scheme. They were interested in the case involving a vacuum pump to reduce methane loss. They mentioned that liquid ring vacuum pumps have problems and are less reliable than compressors. If permeate stream is used for fuel, it will need to be boosted to a pressure of 20-35 barg.

Company #2 noted that system weight savings via use of membranes would be very valuable offshore, where one kg of weight savings equates to 5 kg support structure savings. The process scheme that included an air compressor concerned them greatly due to issues with corrosion and explosive mixtures. Emissions regulations prevent them from venting the methane/ air mixture, even at only a 0.1% methane loss. They said that on-shore, a 3% sweep gas loss is significant. Offshore, however, where they use gas turbines to generate electricity, if they could use the permeate as fuel gas it wouldn't be a negative factor. They said 1.5-2.5 barg would be sufficient pressure for the fuel gas, and could be accomplished via a blower instead of a compressor. Company #2 thought the permeate vacuum process was attractive. They pointed out that the weight savings (in structure cost) would only be recognized on new platforms; it is prohibitively expensive to remove and replace the glycol system on existing platforms with membranes if the that system is performing well. They were very interested in comparing the capex difference to a glycol system, stating it would be attractive if the membrane capex was 20-30% less than a glycol system. Even if the membrane capex is higher than glycol, the system weight savings may justify it.

Company #3 pointed out that system on-stream time is *very* important, and rated not having to change the membranes as important. They said 0.10% methane loss was about right. They acknowledged that the most common current technology for dehydrating gas is a glycol system, but they were intrigued by the membrane possibility, especially for offshore. Footprint size is a big issue, but they could not quantify the benefit. If permeate were used for fuel gas, it would need to be boosted to 50-100 psig. The bulk of gas is dried with glycol, and resistance to technology change will be very high. Since glycol systems operate unattended and the bulk of the glycol units are installed upstream of liquids recovery, dew point-related problems could be more severe. A niche market may be the transportation market, where the flow rates are relatively low (5-20 MMscfd) and the main concern is hydrate control, not pipeline-spec dew point. For unmanned platforms, membranes will need to match glycol in terms of reliability. Glycol systems do have their issues, such as malfunctioning in cold weather.

Company #4 pointed out several general perceptions of membrane technology: it's expensive both to operate and replace membranes; has high permeate losses; fits a very small market niche; is sensitive to contamination; needs a controlled environment. They acknowledged that glycol is the incumbent technology that is well known, understood, and accepted; is forgiving with contamination; equipment failures can be fixed quickly; and for which filtration is not critical. Company #4 is looking for a membrane that can meet the following requirements: perform under non-optimal conditions, minimize the support equipment necessary for the permeate handling; work in any climate; have acceptable methane loss (<0.25%, similar to glycol or better); and can tolerate natural gas liquids and compressor lube oil carryover. Pilot tests with a new technology should last a minimum of six months so that effect of ambient temperature extremes can be determined.

Glycol dehydrators can operate unattended. The compression equipment requires the most maintenance. Glycol units can run unattended year round in remote areas. Glycol is not efficient at low pressure. If gas temperature is high then a cooler is typically used with outlet temperature of 120°F

Company #5 said that they like the glycol system because it is “old” technology, has low operating costs, and doesn’t present many operational problems for low CO_2 and low H_2S operations. However, they said a membrane product may be attractive due to reduced size and weight for offshore applications. The capital cost of a membrane system should be within at least 10-15% of that of a glycol system, but a higher cost should be justified by savings in size, weight, and maintenance. Typical pressure range for their operation is 1200-2000 psig. On their offshore platforms, which are designed for a 20-year life, shutdowns are not planned; they try for continuous operation. They don’t have spare parts on the platform because of weight considerations. For items like pumps that must have more frequent maintenance, however, they install 100% spares.

Company #6 said that membrane robustness is the main need, and that membranes must be able to tolerate operational upsets including liquid water, BTX, and liquid hydrocarbons. User perception is that membranes perform poorly under upset conditions, and that they involve a high capex cost for pretreatment, as in CO_2 applications. Pretreatment to optimize membrane performance is acceptable, but pretreatment to ensure survival is not.
Glycol systems have known problems such as foaming and flooding, and they do not like the “rock & roll” associated with floating offshore platforms. However, glycol will be hard to displace because it’s well-accepted and relatively cheap. With a membrane system, the absolute minimum acceptable membrane life between replacements is two years, with an optimum of 5 years, and maintenance would coincide with shutdowns.

Company #6 mentioned that a membrane that could be used subsea would provide an enabling technology. Some existing subsea pipelines running from wells to “gathering centers” now are up to 80 km long at a 1000 meter depth, and pipelines up 100 miles long are envisioned in the future. They have concerns about what they would do with the permeate subsea. Another potential niche for membranes would be smaller, unmanned one-well platforms. A glycol unit will generally require attended operation, although they also noted they do have unmanned platforms with glycol systems (typically 20-50 MMscfd).

3.1.2 Easy-to-Read Technical Requirements

Table 3.1.2 provides a summary of product offering requirements developed from the customer interviews.

Table 3.1.2: Technical Requirements

Benefit Sought	Technical Requirement	Measure	Target	No Go
Reduced Maintenance Over Glycol Systems	MTBF of major system components	yrs	2	
Minimum Operator Attention	Manhours required onsite for routine operation that are allocatable to our system	manhours	<glycol	
Tolerates Common Contaminants; tolerates startups and shutdowns	%CH_4 loss after two years	%of feed	0.10%	
	% loss of capacity after two years of operation at specified dewpoint	Effective system kH_2O creep rate	TBD - WAB	
	% on stream time		>99% ? Clarify	
Responsive to changes in flows, pressures, and compositions	Turndown for flow and pressure (% of capacity)	% of design capacity	10%?clarify	
	Turn up flow and pressure	% of design capacity		
	Modularity			
Wide product range/operating limits (pressure and flow)	Operating pressure range	barg	up to 90 barg	
	Operating flow range	MMSCFD	20-250 (base case 100 mmscfd)	
	Gas temp at skid edge	Deg C	20-55	
OpEx	Heavy hydrocarbon losses (base case)	% of feed	TBD	
	Environmental impact (base case)	BTX to vent or flare	0	
	Power (base case)		equal to glycol	
	Methane loss (useful)	% of feed	0.10%	0.50%
	Methane loss (waste)	% of feed to vent or flare	0	
	Pressure drop across the system	bar	<2	
	Membrane life	# years before replacement	5+	3
CapEx and Weight and Space	System capex ($/MMSCFD)		<110% of glycol	
	Membrane GP$/FT2 (weighted average of all membranes included in system)	value-add basis	$10	$5
	Footprint (base case)		<glycol	
	Weight (base case)		<glycol	
	System life without intervention	years	2.5-3	1
Lowers dewpoint of natural gas	PPM in dry gas	lb/MMSCF	2 (clarify)	

3.1.3 Customer Benefits with Rankings

Table 3.1.3 provides a ranking of the benefits of the new product offering summarized from the customer interviews.

Table 3.1.3: Benefits of the New Product Offering

Primary Benefit	Secondary Benefit	Tertiary Benefit	Customer Need	Our Rating	Competition	Goal	Improvement Ratio	Sales Point	Raw Weight	Normalized
Improves on Operational Problems	Reduced maintenance over alternatives	Remote operation	3	2	2	4	2	1.2	7.2	8.2 %
		Easy change out of separators								
		Minimal leak points								
		Capability to replace modules in field								
	Minimum Operator Attention	Low manpower required for maintenance	3	4	3	4	2	1	6	6.8 %
		Easy to operate								
		Easy to start up and shut down								
100% on stream time	Tolerates common contaminants	tolerates amine contaminants	5	3	4	5	2	1	10	11. 3%
		tolerates methanol contaminants								
		Meets CH4 loss spec over lifetime								
		Meets PDPD spec over lifetime								
		Tolerates heavy gases including aromatics								
		Can change out membrane while on stream								
		Good pretreatment; pretreatment based on fundamental knowledge of contaminant limits								
		Fiber, shell, endcaps that stand up to natural gas contaminants								
	Tolerates startups and shutdowns	Withstands starts and stops, cycling, high velocities, and phase envelope changes	4	2	3	4	2	1	8	9.1 %

Table 3.1.3: Benefits of the New Product Offering (continued)

Primary Benefit	Secondary Benefit	Tertiary Benefit	Customer Need	Our Rating	Competition	Goal	Improvement Ratio	Sales Point	Raw Weight	Normalized
Flexible Equipment Design	Responsive to changes in flows, pressures, and compositions	Flexibility to operate at different flows and pressures	3	4	2	4	1	1.2	3.6	4.1 %
		Product disturbances in flow, pressure, and temperature								
		Flexible over the life of the project (turndown)								
		80-150 barg pressure range								
		5-80 barg pressure range								
	Wide product range /operating limits (Pressure and flow)	Range of flowrates	2	2	3	3	1.5	1	3	3.4 %
		Equipment flexibility to improve current operational issues								
		Operating ranges larger than the existing technology, single technology choice for 3-150 barg								
Reduced life cycle costs vs. alternative technologies	CapEx, Weight and Space	Competitive initial purchase cost (system including pretreatment, compressors, platform structure)	4	2	4	4	2	1	8	9.1 %
		Fits easily into platform space								
		Reduced offshore platform total project cost								
		Reduced weight								
	OpEx	Methane losses competitive with current technologies	5	1	4	5	5	1.5	37.5	42.5%
		Heavy hydrocarbon loss?								
		Minimize pressure loss								
		No environmental impacts								
Lowers dewpoint of natural gas	Dewpoint depression	Pipeline spec	5	5	5	5	1	1	5	5.7 %
		Value of CO_2 removal?								

3.1.4 Concept Test Voice-of-Customer Summary

A follow-up concept test was conducted with selected customers. The various process schemes of Section 3.3 were presented, along with associated system price and respective weight. The main points from the customer interviews are summarized below:

1. The membrane option with a secondary loop and secondary compressor will always have lower reliability than a glycol system. The primary membrane-only option has the highest reliability, but always presents the issue of how to use or dispose of the permeate. A suggestion was made to use a blower to increase the permeate pressure to the required level for use as fuel (lower cost and better reliability than a compressor).

2. The membrane system without a secondary loop will have to operate at a permeate pressure higher than 4 psig or add compression to the permeate so that it can be used as fuel.

3. Deepwater offshore applications will require a lower outlet dew point, so the membrane system may not provide any footprint savings.

4. There are niche applications for this product, including small onshore remote locations, or older offshore platforms with available compression.

5. Space savings is more significant than weight. We do not provide significant space advantages or weight savings.

6. Membranes do provide operating cost advantages, but this may be of more value in certain niches.

7. Air sweep technology has issues related to safe operation. Methane permeability needs to be near zero, and leaks will be a concern.

8. Time (measured in years) will be required for market acceptance. Most potential customers will be skeptical and reluctant to try a new technology. Since resistance to change will be high, lots of hard evidence and objective data will be required. Lower initial capital costs will also help reduce the resistance.

3.2 Hollow-Fiber Membrane Development

A system technical risk analysis was conducted to identify screening and qualification tests for the fiber from a system risk viewpoint. Experimental methods and equipment for the screening tests were clarified. A prioritized list of the required tests is presented in Table 3.2, followed by a discussion of the tests themselves and the results they produced.

Table 3.2 : Membrane Screening and Qualification Tests

No.	Test outline	Functional property of fiber	Scope of test	Type of test
1	Max pressure before burst/ collapse with test loops under bore-feed/ shell-feed N2 at 80 C; first screen at 25 C	Wall strength	High P & T clean gas	Screening
2	Fiber ID creep with test loops under shell-side hydraulic pressure at 1300 psig & 80 C	ID creep	High P & T clean gas	Screening
3	k H2O and k N2 with test loops under bore-feed/ shell feed N2 at 100 psig, 25 C	k H2O, k gas	Low P & T clean gas	Screening
4	k N2 creep with test loops under shell/ bore feed N2, at 1300 psig & 80 C. k N2 measured at pressure.	k gas creep	High P & T clean gas	Screening
5	k H2O creep with test loops under shell/ bore feed N2, at 1300 psig & 80 C. k H20 measured at 100 psig.	k H2O creep	High P & T clean gas	Screening
6	k H2O and k N2 creep with test loops under shell/ bore feed N2, prewet with HC liquid on feed side, expose to 1300 psig & 80 C. k N2 measured at pressure, k H2O measured at 100 psig.	k gas, k H2O & gas creep	High P & T feed gas, fiber pre-exposed to HC liquid	Screening
7	k H2O and k N2 creep with test loops, expose under shell/ bore feed N2 with HC vapor at 1300 psig & 80 C, k N2 measured at pressure, k H2O measured at 100 psig.	k gas, k H2O & gas creep	High P & T feed gas with HC vapor	Screening
8	k H2O & k H2O creep with test loops under shell/ bore feed N2 at 1300 psig & 80 C	k H2O & k H2O creep	High P & T clean gas	Screening
9	Max pressure before burst/ collapse with test loops under bore-feed/ shell-feed N2 at 80 C; first screen at 25 C. Prewet with HC liquid on feed side.	Wall strength	High P & T feed gas, fiber pre-exposed to HC liquid	Qualification
10	Fiber ID creep with test loops under shell-side hydraulic pressure at 1300 psig & 80 C. Prewet with HC liquid on feed side.	ID creep	High P & T feed gas, fiber pre-exposed to HC liquid	Qualification
11	k N2 creep with test loops under shell/ bore feed N2, prewet with HC liquid on feed side, at 1300 psig & 80 C. k N2 measured at pressure.	k gas creep	High P & T feed gas, fiber pre-exposed to HC liquid	Qualification
12	k H2O and k N2 (initial value & creep) with test loops under shell/ bore feed N2 at 1300 psig & 80 C, k H2O & k N2 measured under operating conditions. Prewet with HC liquid on feed side.	k H2O & gas, k H2O & gas creep	High P & T feed gas, fiber pre-exposed to HC liquid	Qualification
13	k H2O and k N2 (initial value & creep) with test loops under shell/ bore feed N2 at 1300 psig & 80 C, HC vapor in feed gas at higher dewpoint than membrane temperature resulting in HC condensation, k H2O & k N2 measured under operating conditions. Prewet with HC liquid on feed side.	k H2O & gas, k H2O & gas creep	High P & T feed gas, HC liquid condensing in-situ	Qualification
14	k H2O and k N2 (initial value & creep) with test loops under shell/ bore feed N2 with HC vapor at 1300 psig & 80 C, k H2O & k N2 measured under operating conditions. Also measure k HC.	k H2O & gas, k H2O & gas creep	High P & T feed gas with HC vapor	Qualification
15	k H2O and k N2 (initial value & creep) with test loops under shell/ bore feed N2 of high CO2% with HC vapor at 1300 psig & 80 C, k H2O & k N2 measured under operating conditions. Also measure k HC and k CO2.	k H2O & gas, k H2O & gas creep	High P & T feed gas with HC vapor and high CO2%	Qualification

Dope formulation and spinning was conducted with polymer Y, which, compared to polymer X, has higher tensile strength, greater chemical resistance and a far broader range of non-solvent compositions. Both of these polymers are commercially available.

Dope formulation was studied using a variety of solvents. Screening tests were performed with the objective of producing a desirable membrane morphology and high water vapor permeation rate.

Some polymer lots received from the manufacturer had an intrinsic viscosity that was too high and caused gelling of the dopes. We identified the correct polymer QA tests to be done by the manufacturer to ensure that the final product produces good dopes.

We recognized that the two most critical success factors in producing an adequate fiber are 1) high intrinsic tensile yield strength and modulus (demonstrated by polymer Y), 2) uniformity of void distribution across the fiber wall.

Our initial attempts to produce a fiber with high k H_2O and wall strength were not successful. We produced some fibers with high k H_2O, but these fibers had macrovoids in the wall and did not survive a 70°C hydraulic test at 1000 psig.

We prepared and spun a variety of dope formulations of polymer Y at our pilot plant to solve the macrovoid issue. Several dope formulation components were tested before we arrived at a recipe that suppressed macrovoid formation. However, the conventional manufacturing process produced a final fiber with a low water vapor permeation coefficient. Changing one step of the manufacturing process increased the water vapor permeation coefficient by a factor of more than three, increasing it to a level adequate for commercial success as described in Section 3.3. The nitrogen permeation coefficient of the fiber was found to be very low. The results of a 70°C hydraulic test at 1000 psig showed a very low “creep index,” and a two-year extrapolation indicated adequate wall strength.

Post-treatment of the above fiber by a simple process produced a 50% reduction in “creep index” and ~15% reduction in the water vapor permeation coefficient.

The fiber was exposed to a mixture of aromatic and cyclo-aliphatic hydrocarbon vapors at 23°C for six days, and then subjected to a 70°C hydraulic test at 1000 psig. The results again showed a low creep index. The fiber was deemed to survive exposure to aromatic and cyclo-aliphatic hydrocarbon vapors such as those it may see in the field.

Cross-sections of the above fiber are shown in Figure 3.2.1; the previous version of the fiber is shown in Figure 3.2.2.

With this externally-skinned fiber, we achieved the necessary combination of wall strength and water vapor permeation coefficient needed for commercial success. However, the additional manufacturing process step involved will add to membrane cost. To solve this problem, we continued our search for dope additives that are capable of producing a high water vapor permeation coefficient and sufficient wall strength without the additional manufacturing process step.

Our continued formulation study resulted in a novel dope composition and spinning process which provides a new approach to controlling membrane porosity and wall and skin morphology. It therefore allows a new line of attack on the trade-off between permeation coefficient and wall strength. This new, versatile technology enables creation of a microporous wall with either an external skin or a bore-side skin.

The low polymer solids content of the dope produces a membrane with a high permeation coefficient. However, the associated low dope viscosity typically generates macrovoids in the wall. We have identified particular spinning process conditions that result in very low macrovoid density, which is the preferred wall morphology to improve the pressure capability of the membrane. The fiber has a high k H_2O without the additional processing step required for the fiber shown in Figure 3.2.1.

The latest version of the fiber meets the technical requirements for a commercial product offering in gas dehydration. It can be readily manufactured with certain modifications in process equipment and conditions, and is an excellent candidate for scale-up to full-size membrane modules.

Figure 3.2.1: Externally-Skinned Fiber of Polymer Y, Version 2

Dope contains additives to suppress macrovoids
High k H_2O, low k air via additional processing step
Survives exposure to aromatic hydrocarbon vapors with low creep at 1000 psig/ 70°C

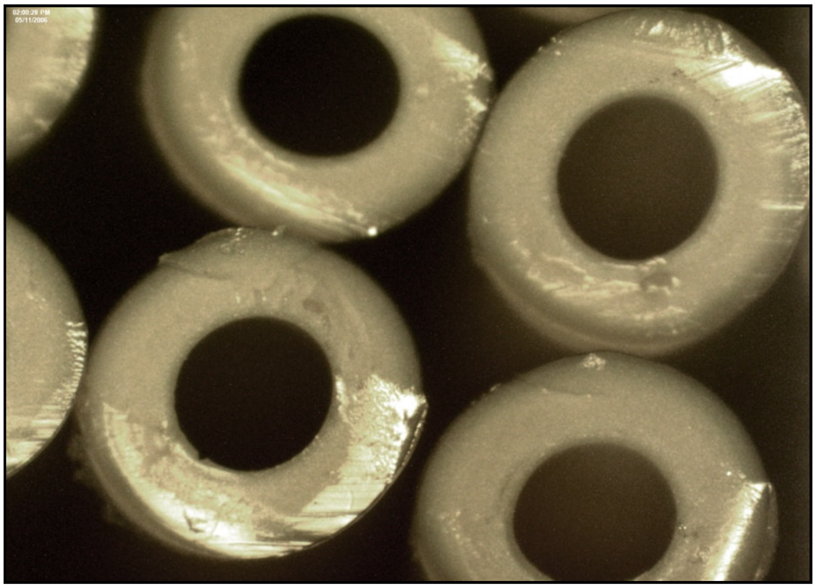
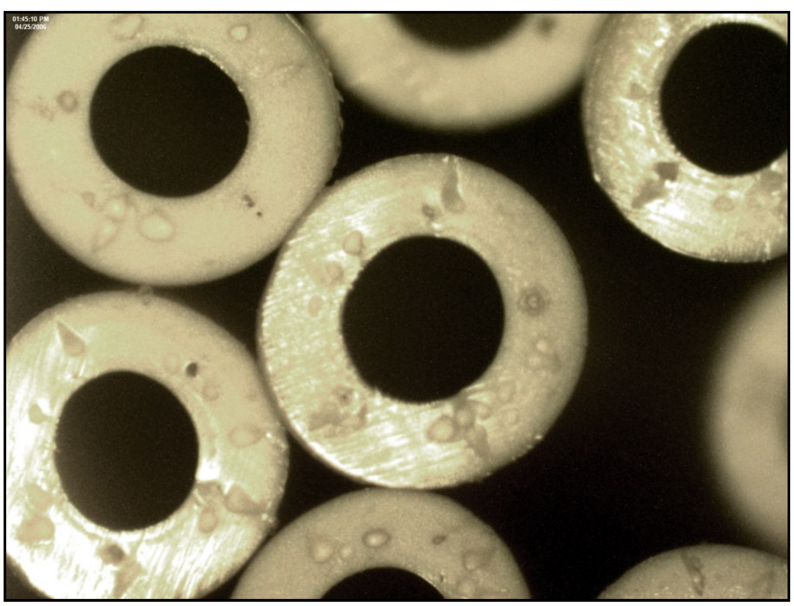


Figure 3.2.2: Externally-Skinned Fiber of Polymer Y, Version 1

Fiber wall contains macrovoids
Fiber has high k H_2O, low k air
Does not survive creep test under external pressure at 1000 psig/ 70°C



3.3 Membrane Module and System Design

The results of the customer interviews from the user needs-and-wants study were used to further quantify the technical requirements for the membrane technology. These requirements are listed below, along with several parameters that still must be quantified:

- Operating pressure <90 barg
- Operating flow range 20-100 MMscfd
- Water content of dry gas 2-7 lb/MMscf
- Typical water vapor rejection >93%
- Typical gas temperature 20-55°C at skid edge
- Methane loss: useful, <0.10%; waste = 0
- CH_4 loss <0.10% after two years of operation
- On-stream time >99%
- Flow and pressure turndown >10%
- Pressure drop across system <2 bar
- Mean time between failures (MTBF) of major components >2 years
- System capital cost <110% of the cost of a glycol system
- Modularized system
- Fewer manhours required for routine operation compared to glycol system
- Power consumption less than with a glycol system
- Footprint and weight for membrane system (base case) less than those of a glycol system
- Significantly less heavy hydrocarbon loss and environmental impact compared to a glycol system
- Parameters still to be determined: membrane system gross profit; loss of capacity after two years of operation; membrane replacement costs over the life of the project

With the above requirements in mind, a module and system optimization study was performed in order to derive target values for membrane parameters. The latter include the water vapor permeation coefficient (k H_2O), fiber outer and inner diameter, and module diameter and length.

A mathematical model of module performance was developed that accounts for various fluid flow and permeation phenomena:

a) The shell-side gas enters and exits through the perimeter of the hollow-fiber bundle; hence, the hydraulic resistance of the bundle causes the axial gas velocity to be lower at the center of the bundle compared to the outside.
b) A mass transfer boundary layer is associated with the high-pressure feed side of the membrane, causing the overall permeation coefficient to be lower than the intrinsic value for the membrane.
c) The intrinsic permeation coefficient of the membrane is related to the permeate-side diffusion coefficient and therefore is a function of permeate-side pressure.
d) The driving force for permeation is the difference in partial fugacity between the feed and permeate sides. At high pressure, the partial fugacity for water vapor is considerably lower than the partial pressure.
e) The pressure drop through the bore side of the hollow fibers is considerable and needs to be accurately estimated.

A model was also developed for the shell-side flow through the hollow-fiber bundle. This model accounts for the viscous and inertial resistance of hollow fiber in the radial and axial directions (the axial velocity variation from the outside to the center of the bundle can be estimated). The viscous and inertial resistance coefficients have been estimated using existing data at the same packing density (~50%). The results of this model were used in the performance model described above. In addition, the mass transfer boundary layer resistance (as a function of the feed-side velocity) was also obtained from existing data.
All listed effects were combined in an Aspen Plus® computer model used for optimization studies. Process and economic inputs needed for such studies include module cost or price, valuation of power consumption and methane loss, the sweep generation process scheme, and other operating costs. These inputs will be refined during the next quarter. This model was used to estimate module flow capacity and methane loss as a function of fiber dimensions, module diameter, module length, and the sweep/feed ratio at the base-case operating conditions.

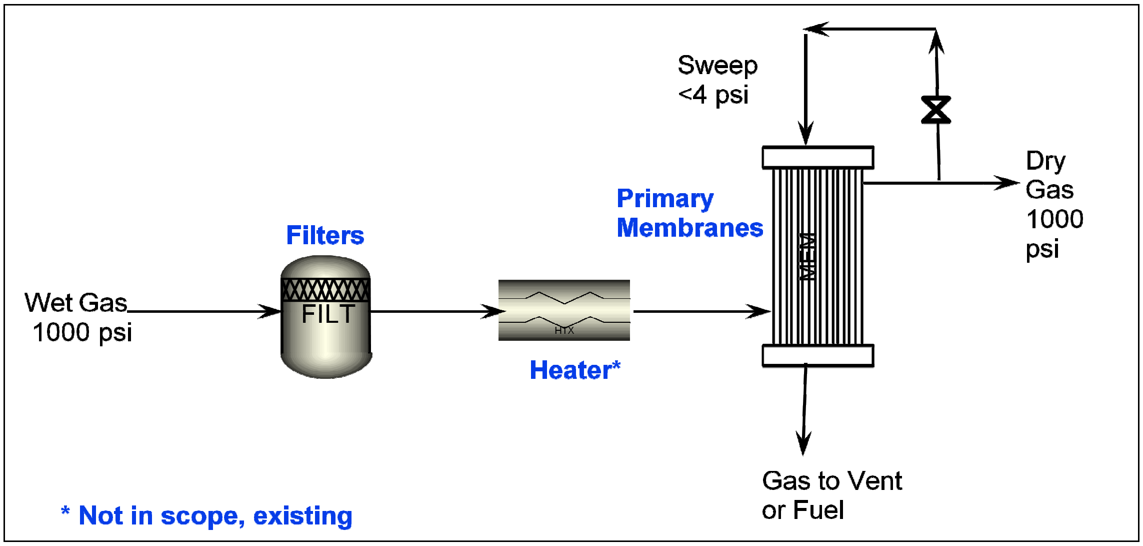
A spreadsheet model, which was developed to allow greater ease of calculations, provided results that are consistent to within a few percentage points of the computer model results. The spreadsheet model was used to conduct a module and system optimization study, which is being used to guide the hollow-fiber membrane development task.

Process and economic inputs needed for the study include module cost, system fabrication cost, feed pretreatment cost, the sweep generation process scheme, sweep compressor cost, and other operating costs. The required economic inputs were obtained by contacting equipment vendors. Several compressor vendors were contacted for information on the cost, weight and size of compressors for both sweep and recycle gas. Piston, screw, and centrifugal compressors were evaluated. Based on this information, we selected screw compressors for the sweep/secondary membrane scheme and piston compressors for recycle gas system.

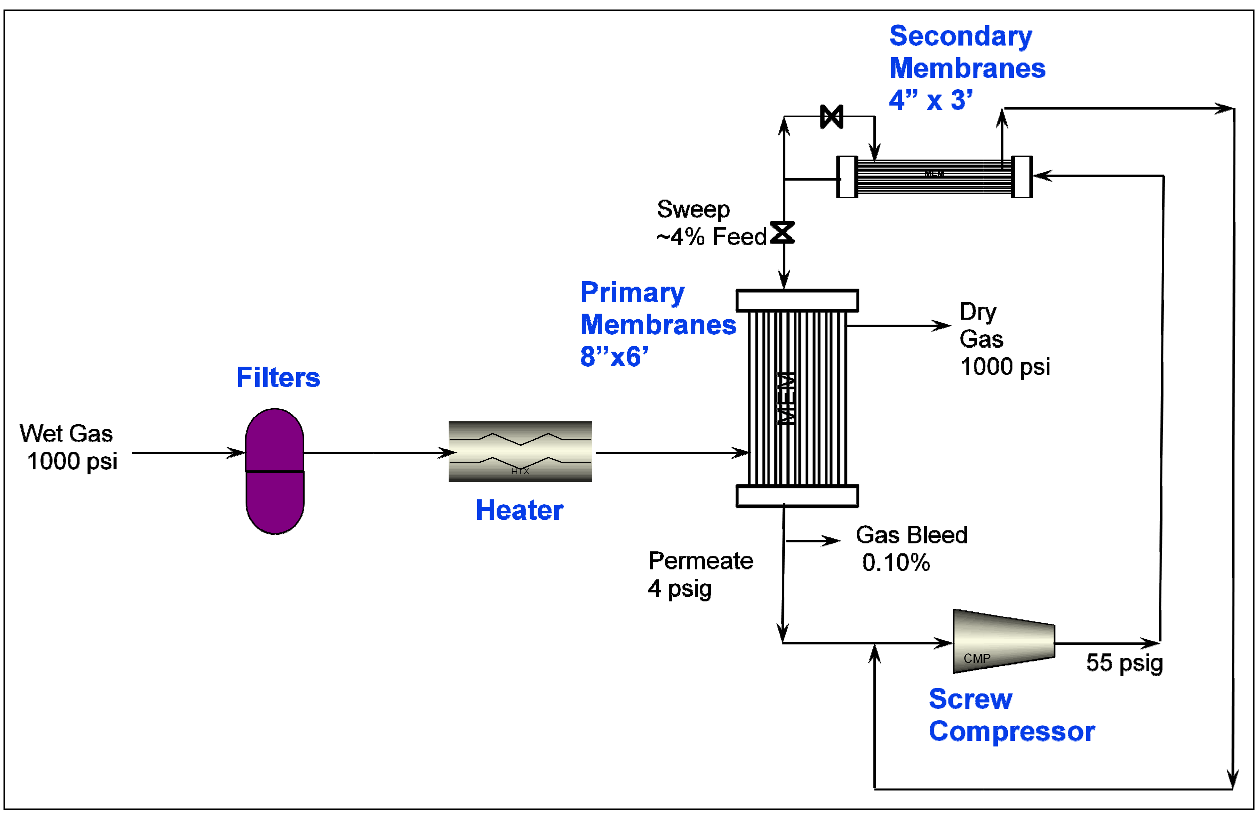
The sweep gas may be dry methane generated by compressing the sweep and drying it via a bank of secondary membrane dryers. This process is discussed in U.S. Patent 5,641,337 (1997) assigned to Air Products. Alternatively, the sweep gas may be dry air generated from compressed air via secondary membrane dryers. This simple, low-cost scheme is particularly feasible when the methane loss is very low (i.e., <<0.10%). In either case, the sweep compressor represents energy consumption, as well as capital cost, and the corresponding power needs to be minimized. This process is depicted below in Figure 3.3.1, along with three other membrane process schemes that were evaluated.

Figure 3.3.1 Process Flow Diagrams

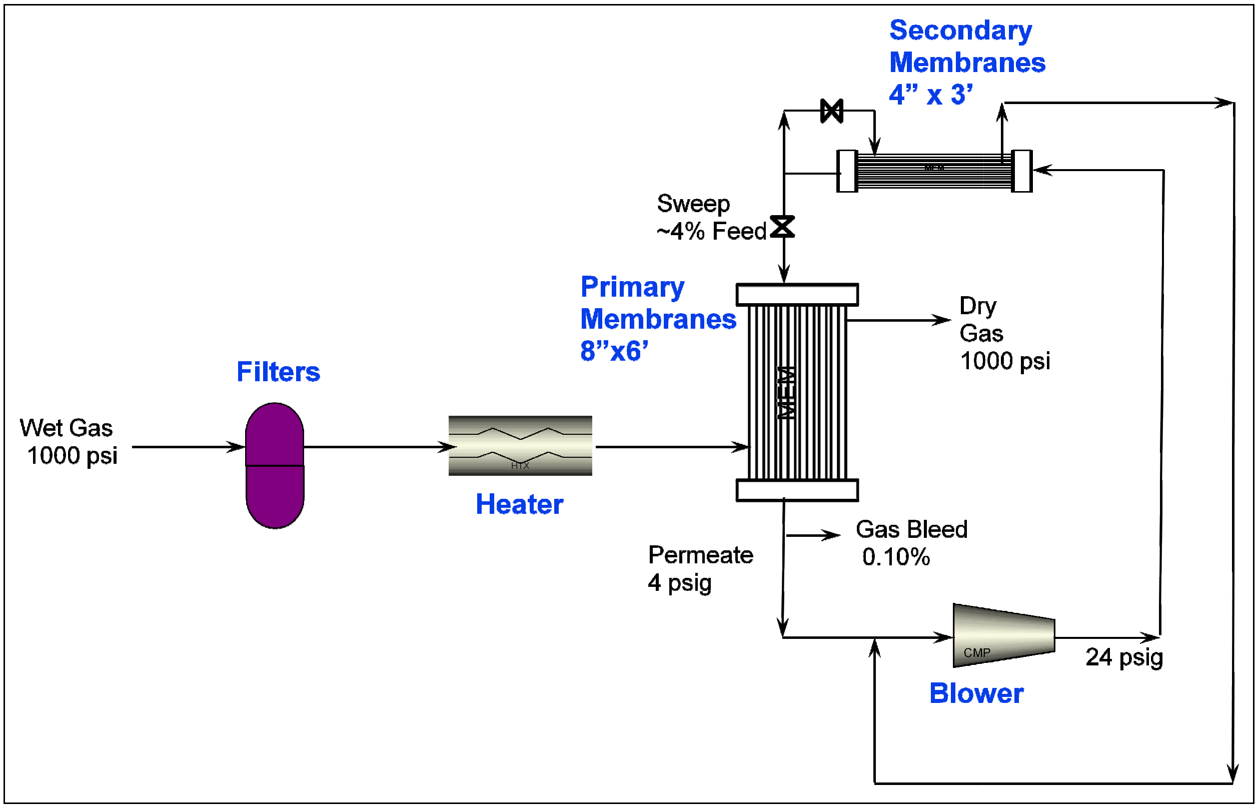
A. Process with Product Gas Sweep



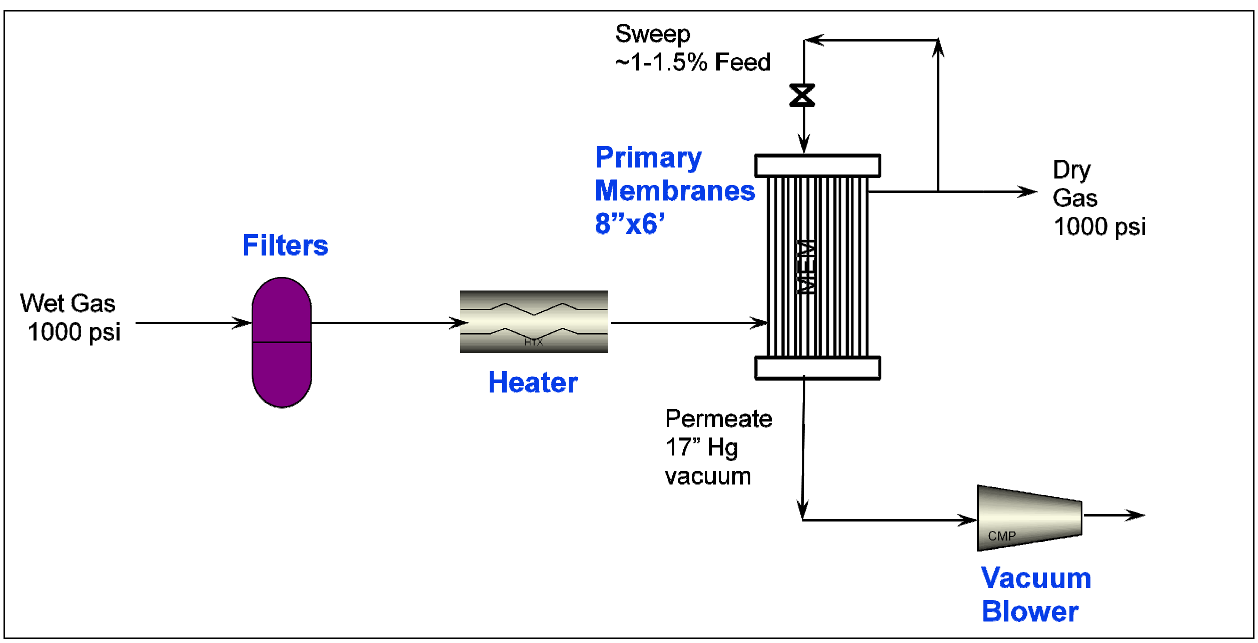
B. Process with Secondary Membranes in Sweep Loop with Screw Compressor



C. Process with Secondary Membranes in Sweep Loop with Blower



D. Process with Vacuum Blower at Permeate



The spreadsheet model was used to estimate module flow capacity as a function of fiber dimensions, the water vapor permeation coefficient, module diameter, module length, the sweep/feed ratio, and the sweep water vapor content. Methane loss was set at 0.10% by adjusting the methane permeation coefficient. By comparison, methane loss for the glycol system can be much higher -- as much as 0.26% if pressure-driven pumps are used for glycol circulation. Compressor power for the secondary loop was minimized by adjusting the pressure and water vapor content of the gas exiting the secondary membranes (i.e. the sweep gas for the primary membranes); the latter parameter affects the primary membrane performance. The optimum secondary loop pressure seems to be in the 45-55 psig range, and optimum sweep water vapor content is ~3-8X the product gas water vapor content. The corresponding power consumption is ~50% of the glycol dehydrator reboiler heat duty.

Based on the estimates, we have concluded that a module size close to our present largest commercial module -- 8" diameter x 6' length -- is adequate. Larger sizes will produce increasingly poor feed flow distribution, reducing separator efficiency, and require changes in manufacturing plant infrastructure; smaller sizes will increase the module count.

We also evaluated two other membrane process schemes: 1) using a blower (~20 psig boost) to replace the screw compressor in the secondary loop, and 2) using a vacuum blower to apply a ~17" Hg vacuum to the exit sweep, with no secondary membrane employed.

Based on these calculations, we conclude that:

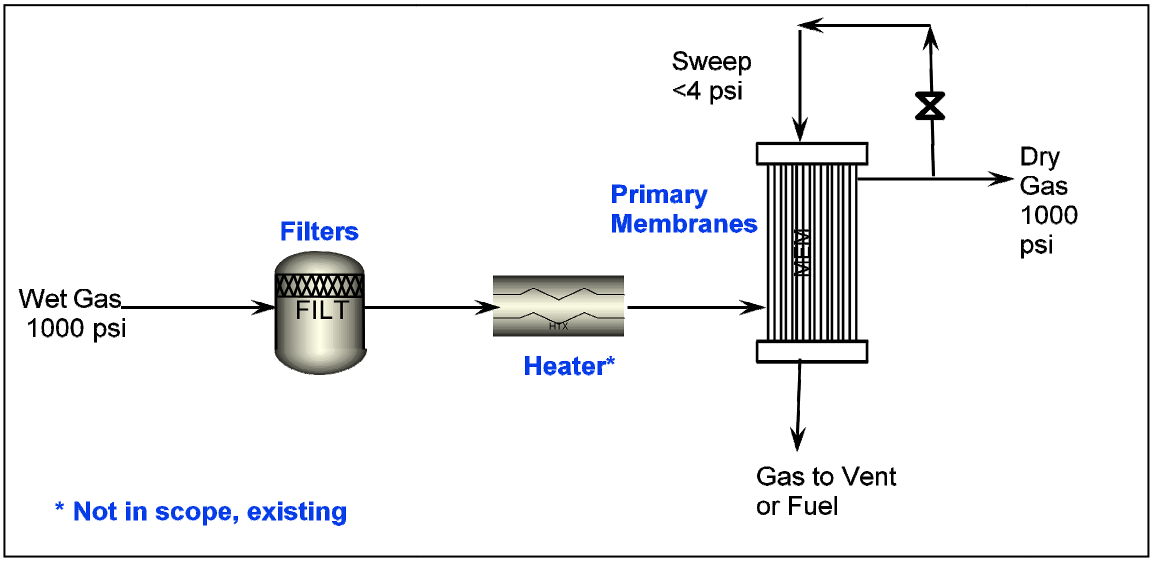
1) The simplest process involves using a vacuum blower (~17" Hg vacuum). At 100 MMscfd, the membrane system is capex-competitive with glycol and 40% lower in weight. No secondary membranes are required. About 1.3% of the dry gas is used as sweep. Because the exit sweep gas is compressed and recycled, used as turbine fuel, or otherwise integrated into existing operations, there is no hydrocarbon loss.
2) At 100 MMscfd, replacing the screw compressor (51 psig boost) with a blower (20 psig boost) in the secondary loop reduces the system weight by 5%, but increases the capex by 16% due to the increase in membrane count. One reason for evaluating this option is that blowers are generally considered to have lower maintenance needs compared to compressors.
3) At 100 MMscfd, the vacuum blower process has an 11% lower capex and 17% lower weight compared to the secondary loop/compressor process.

Figures 3.3.2, 3.3.3, and 3.3.4 show the results of the system cost and weight calculations for, respectively, the screw compressor/secondary membrane process, the blower/secondary membrane process, and the vacuum blower/no secondary membrane process. The parameters in these graphs are: "k H2O/base" or ratio water vapor permeation coefficient to base value for present commercial membranes, and, the sweep flow/ feed flow ratio.

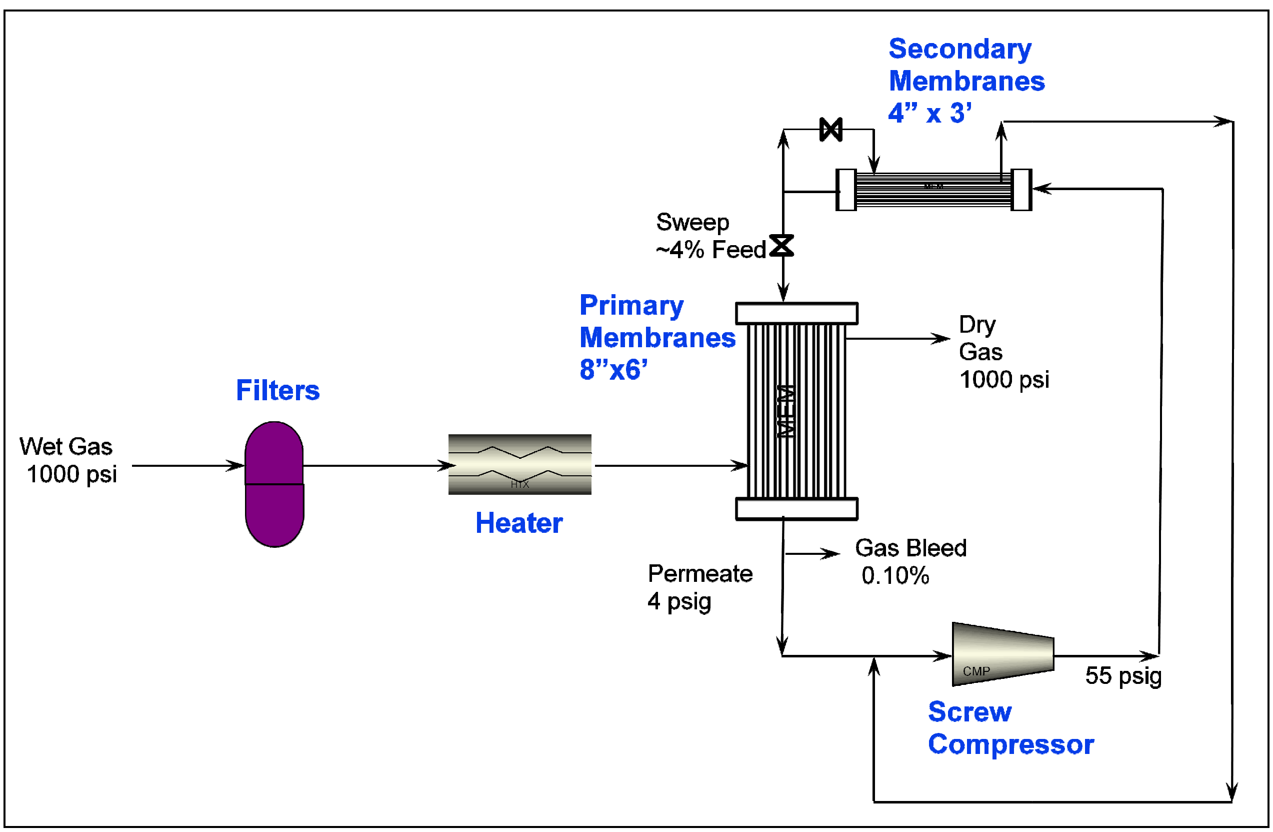
The results of the system cost and weight analysis, summarized in Table 3.3.1, show a 25-45% reduction in membrane system weight and a 7-60% price premium compared to glycol systems.

Figure 3.3.1 Process Flow Diagrams

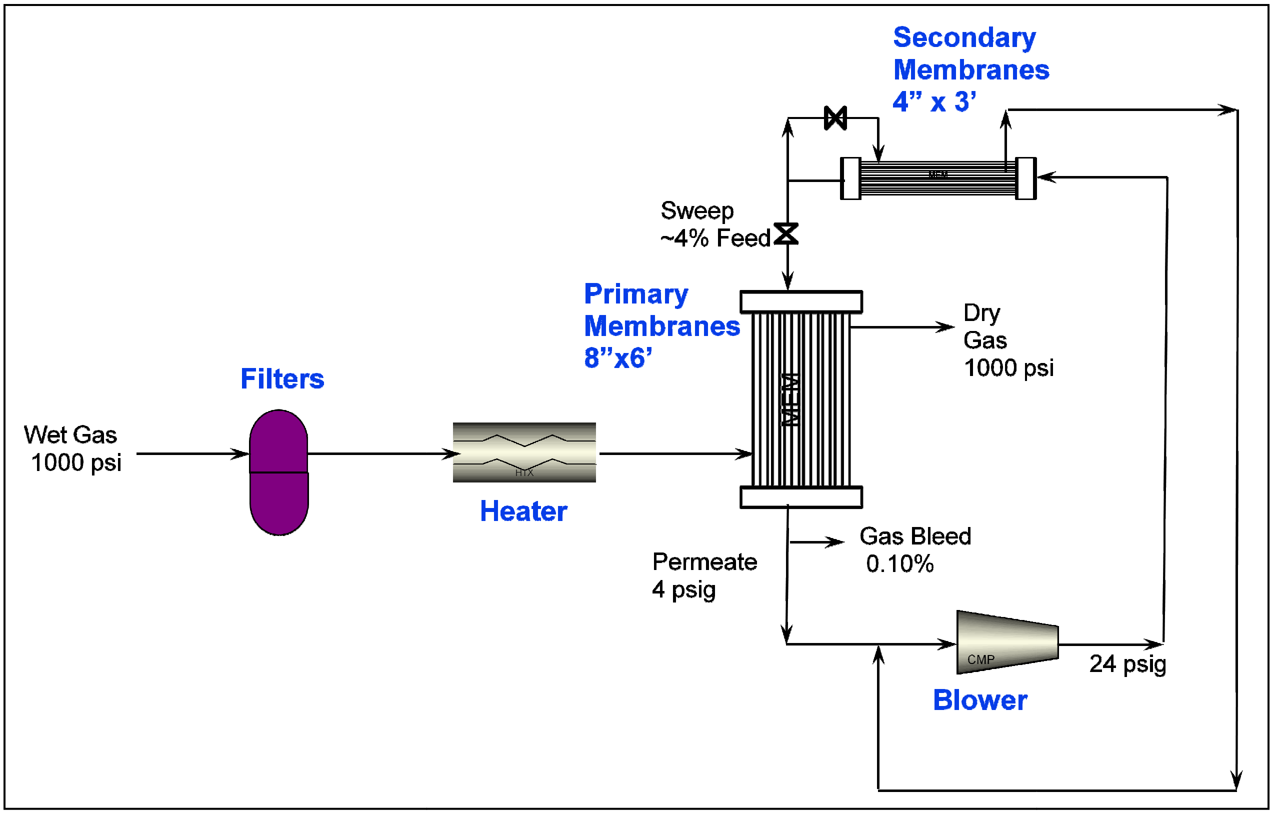
Process with Product Gas Sweep



Process with Secondary Membranes in Sweep Loop with Screw Compressor



Process with Secondary Membranes in Sweep Loop with Blower



Process with Vacuum Blower at Permeate

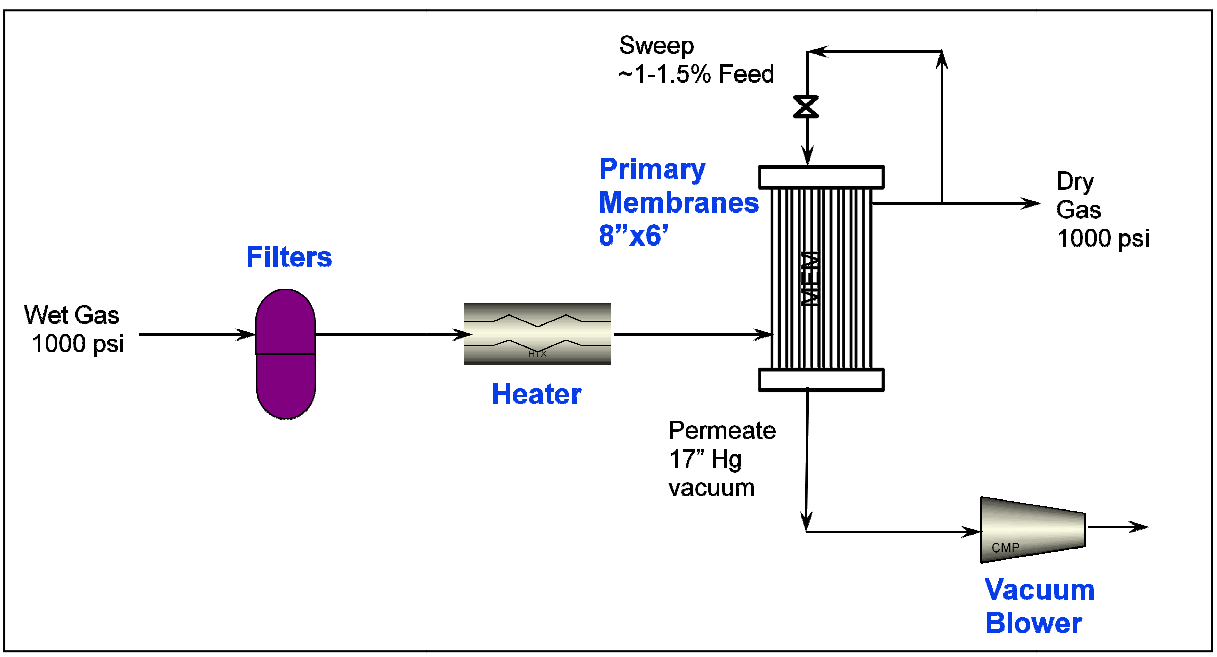


Figure 3.3.2: System Cost and Weight versus Sweep Fraction, Screw Compressor in Sweep Loop

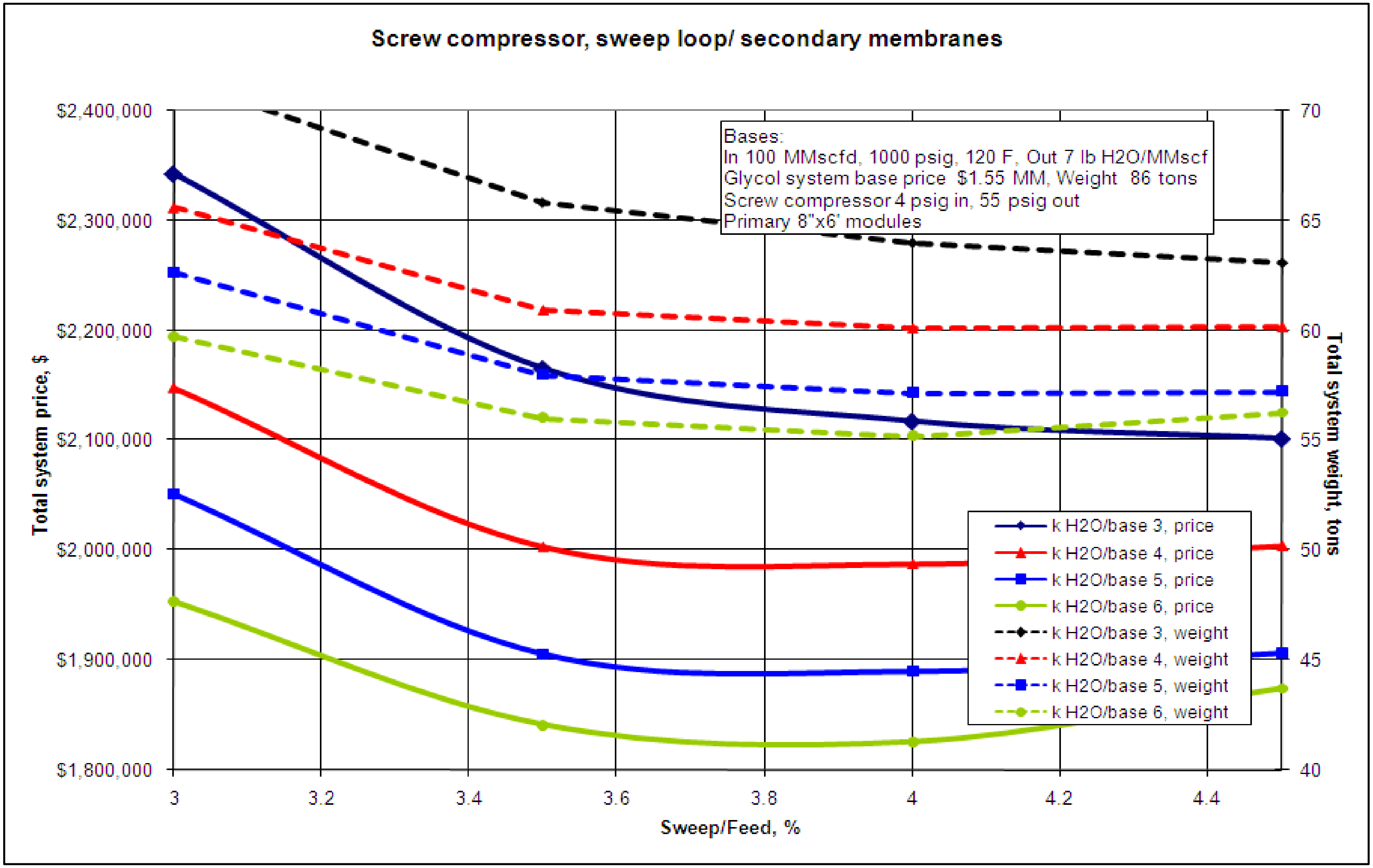


Figure 3.3.3: System Cost and Weight versus Sweep Fraction, Cycloblower in Sweep Loop

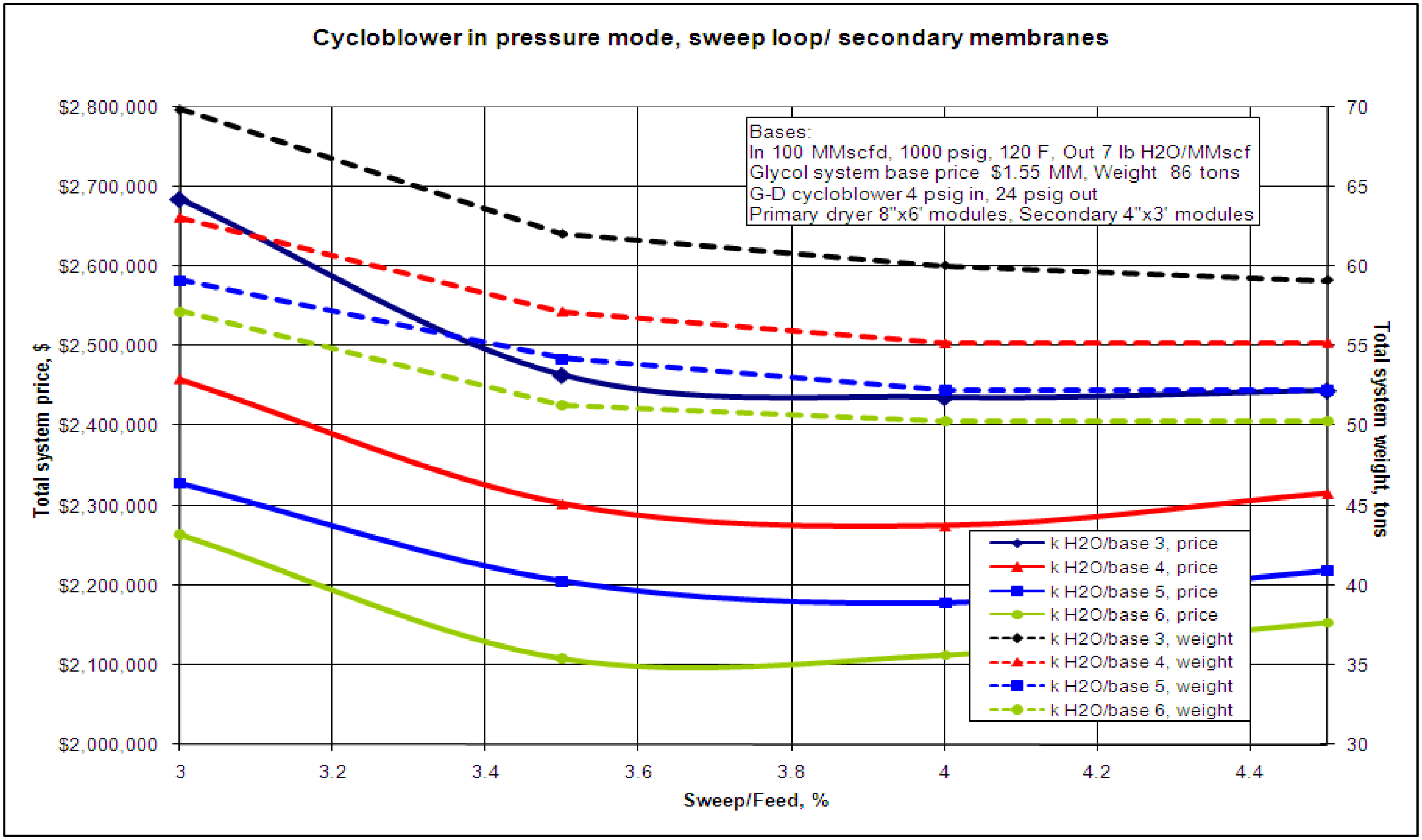


Figure 3.3.4: System Cost and Weight versus Sweep Fraction, Vacuum Blower

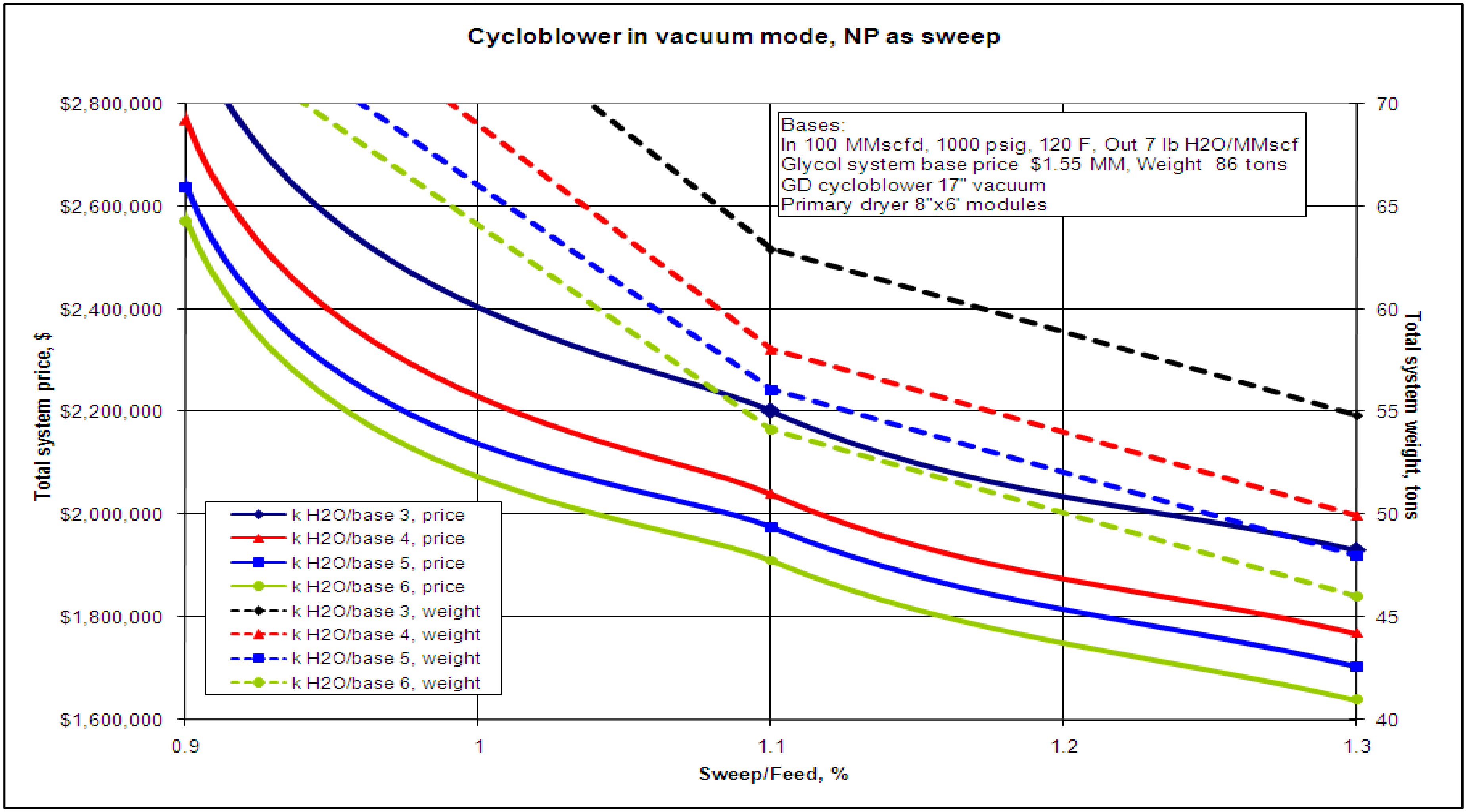


Table 3.3.1: Summary of Process Evaluation

Bases: Inlet Feed Gas 100 MMscfd, 1000 psig, 120 F, water vapor saturated, Outlet Product Gas 7 lb H2O/MMscf

Process Scheme	Ratio k H2O/ base value	Total Mem system price, $	Secondary compressor power, hp	TEG System price, $	Mem Price Premium over TEG, (Mem-TEG)/TEG, %	Primary Mems + Skid, tons	Secondary Mems + Skid, tons	Sweep Comprsr, motor drive, tons	Mem system total weight, tons	TEG system total weight, tons	Weight Diff, (Mem-TEG)/TEG%
Screw Compressor in Secondary Loop	3	$2,117,201	566	$1,534,943	38%	40.7	3.6	20.1	64	84	-24%
	4	$1,987,552	565	$1,534,943	29%	36.8	3.6	20.1	60	84	-29%
	5	$1,890,299	565	$1,534,943	23%	33.9	3.6	20.1	57	84	-32%
	6	$1,825,424	565	$1,534,943	19%	31.9	3.6	20.1	55	84	-35%
Blower in Secondary Loop	3	$2,463,883	566	$1,534,943	61%	48.5	6.6	7.5	62	84	-26%
	4	$2,302,182	566	$1,534,943	50%	43.7	6.6	7.5	57	84	-32%
	5	$2,205,161	566	$1,534,943	44%	40.7	6.6	7.5	54	84	-36%
	6	$2,108,140	566	$1,534,943	37%	37.8	6.6	7.5	51	84	-39%
Vacuum at Permeate, No Secondary Membranes	3	$1,930,374	156	$1,534,943	26%	51.5	0.0	4.5	55	84	-35%
	4	$1,768,672	156	$1,534,943	15%	46.6	0.0	4.5	50	84	-41%
	5	$1,703,991	156	$1,534,943	11%	44.6	0.0	4.5	48	84	-43%
	6	$1,639,311	156	$1,534,943	7%	42.7	0.0	4.5	46	84	-45%