CASE STUDY: MEMBRANE CO_2 REMOVAL FROM NATURAL GAS, GRISSIK GAS PLANT, SUMATRA, INDONESIA

Charles L. Anderson
Air Liquide – MEDAL, L.P.
Newport, Delaware 19804 USA
(1) 302 225-2102
charlie.anderson@airliquide.com

Anggiat Siahaan
ConocoPhillips
Jakarta, Indonesia
(62) (21) 524-1987
Anggiat.H.Siahaan@conocophillips.com

Abstract

One of the world's largest membrane systems is used for bulk removal of CO_2 from natural gas at the Grissik gas processing plant in South Sumatra, Indonesia. The membrane system processes 310 MMSCFD of natural gas, reducing CO_2 from 30% to 15%. The Grissik plant is termed a membrane plus amine hybrid which offers particularly attractive operational benefits. The membrane system has been operating for more than four years with no membrane replacement and offers the benefit of very long membrane life.

CASE STUDY: MEMBRANE CO_2 REMOVAL FROM NATURAL GAS, GRISSIK GAS PLANT, SUMATRA, INDONESIA

Charles L. Anderson, Air Liquide – MEDAL, L.P., Newport, Delaware, USA

Anggiat Siahaan, ConocoPhillips, Jakarta, Indonesia

Introduction

ConocoPhillips operates the Grissik gas processing plant on behalf of its partners, Talisman Energy Inc., Pertamina and BPMigas. The Grissik plant, located in South Sumatra, Indonesia, pictured in Figure 1, processes 310 MMSCFD of natural gas, primarily reducing CO_2 concentration from 30% in the raw feed down to 3% in the sales gas.

Figure 1. Grissik Gas Plant

Process Overview

The Grissik plant CO_2 removal process utilizes both membrane separation and amine absorption technology, termed a membrane plus amine hybrid. A simplified process flow diagram is shown in Figure 2. The Thermal Swing Adsorption (TSA) removes heavy hydrocarbons, serving the triple function of membrane pre-treatment, feed gas dehydration and sales gas hydrocarbon dew pointing.

The main attraction of the hybrid membrane/amine process is to have a single stage membrane and utilize the thermal value in the permeate stream, thereby enjoying the simplicity of a membrane separation process without the use of a recycle compressor while still avoiding hydrocarbon losses. The CO_2-rich permeate is sent to an atmospheric burner to produce steam which is used in the amine plant for regeneration.

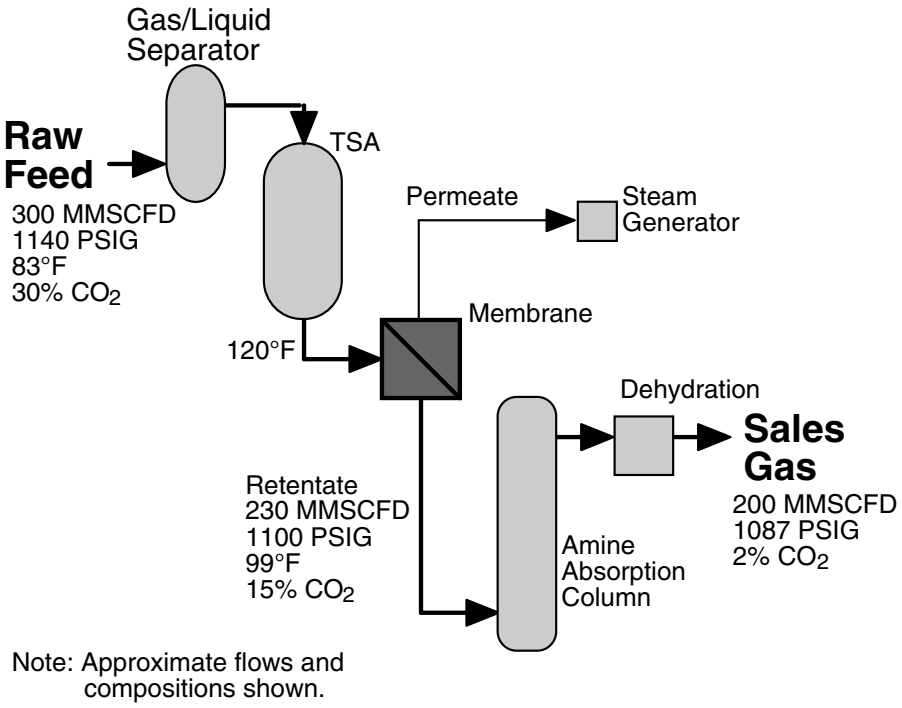

Figure 2. Grissik Process Flow Diagram

The natural gas exits the membrane under pressure with about 15% CO_2 remaining and is fed to the amine absorption column where CO_2 is removed to approximately 3% or pipeline specifications. Permeate rich in CO_2 exits the membrane close to atmospheric pressure. The final process step is dehydration.

Background

The Grissik plant was initially built and commissioned without a TSA membrane pre-treatment system, because it was believed the feed gas contained minimal amounts of heavy hydrocarbons. This was subsequently found not to be the case.

First Commissioning

The membrane was first installed by Kvaerner Process Systems with pre-treatment, consisting only of a coalescing filter and a non-regenerable adsorption guard bed. At plant startup in 1998, actual levels of heavy hydrocarbons (C_{10+}, aromatics and napthenes) were found to be higher than anticipated. This resulted in a sharp reduction in membrane capacity, declining to 20 – 30% of initial capacity within a month. During this time, and in order to maintain production capacity, membrane elements were being frequently replaced.

Installation of a TSA

ConocoPhillips responded by quickly evaluating available heavy hydrocarbon removal processes, including gas chilling and regenerable adsorption processes. The gas chilling

process was deemed ineffective at the plant operating pressure, which was near the cricondenbar of the feed gas phase envelope. The regenerable adsorption process ultimately selected was a short cycle process from Engelhard which uses Sorbead™ adsorbent (silica gel) as the adsorbent. The Engelhard process, containing silica gel material, uses multiple beds in parallel adsorption to remove the aromatics, napthenes and heavy hydrocarbons. The adsorption cycle is followed by regeneration of the silica gel at elevated temperatures. The TSA was designed to reduce the total C_{6+} components (including aromatics and napthenes) so that membrane performance can be maintained for an extended period of time.

Figure 4. Engelhard Thermal Swing Adsorption Unit

The TSA was built and installed by Kvaerner in 2000 with two separate trains, each with four adsorption vessels, pictured in Figure 4. In the foreground is the valve switching skids and regeneration gas exchangers.

TSA Design and Performance

Since the feed gas was found to contain unexpectedly high levels of heavy hydrocarbons (C_{10+}, aromatics and napthenes), the TSA has two functions and solves two problems. First, the TSA removes heavy hydrocarbons for proper membrane pre-treatment so as to yield long membrane life. Second, the removal of heavy hydrocarbons allows the sales gas to meet hydrocarbon dew point specs. Since water is more strongly held onto the Sorbead adsorbent than any of the hydrocarbons, the TSA system also dehydrates the feed upstream of the membrane unit, although this is not a particular benefit to the Air Liquide PI membrane as it is not affected by water.

TSA Process Description

Each train was designed to treat about 225 MMSCFD of feed gas and consisted of 4 adsorber towers. Each adsorber tower was internally insulated to minimize the thermal mass for the short thermal cycles.

Referring to the TSA process flow diagram (Figure 5), the wellhead feed gas, after passing through a liquid separator, is split into two parallel paths. The majority of the gas flows through the pressure drop valve and then directly to 2 towers on parallel adsorption. The cycle time of the towers is staggered by 50% to allow for a continuous flow of treated gas to the downstream membrane unit. The balance of the feed gas bypasses the pressure drop valve so as to provide the necessary flow through the towers being cooled and heated. The regeneration path contains the tower being cooled, the regeneration heater, the tower being heated, the heat recovery heat exchangers and the spent regeneration gas separator. Each tower is associated with 6 valves that allow it to change functional positions, first adsorbing, then heating/regenerating, then cooling and then back to adsorbing. Wet feed gas is used as the regeneration medium and, because of the pressure drop valve, there is no need for a compressor to boost the pressure of the spent regeneration gas.

During adsorption, water and C6+ components are adsorbed by the Sorbead adsorbent at feed gas conditions, 1100 psig and 90 to 140°F. Prior to C6+ breakthrough, the tower position is switched to heating mode and is completely heated to about 540°F. The internal insulation allows heating of the adsorbent only; hence, the mass of the heavy steel vessel wall does not have to be heated. During heating, the water and C6+ components are desorbed. This spent regeneration gas stream containing water and C6+ is then cooled, and the condensed liquids removed in the regeneration gas separator. This is the only place in the process where the heavy hydrocarbons exit the system.

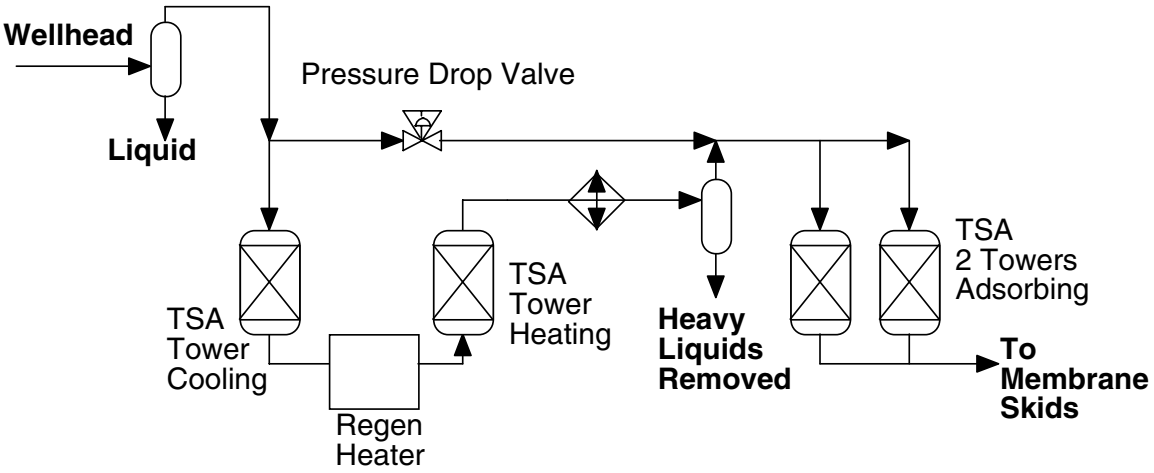

Figure 5. TSA Process Flow Diagram

Reason for 4 towers

In order to maintain an acceptable flow velocity across the adsorber bed, the number of towers used is a function of the flow rate and the tower diameter. As the maximum tower diameter was determined by transport limits, the Grissik design resulted in 4 towers with two towers in parallel adsorption. To minimize the amount of regeneration gas required, internal insulation was used. Additionally, the heating and cooling towers are in a series arrangement which also conserves the amount of regeneration gas required.

An additional benefit of having towers in parallel on adsorption is an equalized composition of the treated gas. In a single tower there is a difference in the gas composition between beginning and end of the adsorption cycle, caused by the breakthrough of the individual components. In a four tower system with two towers on adsorption, there is an offset time of half an adsorption cycle. The gas composition of the combined outlet gas is more constant than from a single tower.

Cycle times and breakthrough

The cycle times are primarily driven by the breakthrough behavior of the C6+ components in this tower design in order to meet the hydrocarbon specification of the treated gas. The cycle times finally settled on were a result of analysis and field observations. A typical cycle consisted of 2 hour adsorbing, 1 hour heating and 1 hour cooling and is further illustrated in Table 1.

Table 1. 4 Tower Mode Timing

4 Tower Mode				
Tower 1	2 h Adsorption		1 h Heating	1 h Cooling
Tower 2	1 h Cooling	2 h Adsorption		1 h Heating
Tower 3	1 h Heating	1 h Cooling	2 h Adsorption	
Tower 4	1 h Adsorption	1 h Heating	1 h Cooling	1 h Adsorption

Heat recovery between cooling/heating

In this system, which uses one tower on heating and one tower on cooling at the same time, the hot gas leaving the tower being cooled flows through the heater in order to get additional heat in. At the beginning of the cycle the gas exiting the tower on cooling is almost at the required heating temperature, resulting in nearly no make-up heat. This is because the entire tower being cooled is at the hot regeneration temperature of 540°F. During the cooling cycle, the temperature of the gas exiting the cooling tower drops so the heater has to provide the required heating gas temperature.

A gas-to-gas heat exchanger is used to capture the heat exiting the tower which is being heated. This hot gas is cross-exchanged with the gas upstream of the regeneration gas heater (see Figure 5). This exchanger is bypassed during the time when the gas exiting the tower on cooling is at a higher temperature than the gas leaving the tower in the heating step.

Regeneration heater

The Grissik TSA uses direct fired heaters. The size of the heater depends on the regeneration gas flow required to heat the adsorber bed and desorb the water and hydrocarbons within the design cycle time.

TSA Performance

After re-commissioning the plant in October 2000, good TSA performance removing the heavy hydrocarbons led to excellent membrane performance. TSA performance regarding hydrocarbon dewpoint was impressive, see Table 2 below.

Table 2. TSA Hydrocarbon Dewpoint

TSA feed gas	86°F at 1150 psig
TSA outlet gas	-22°F at 1115 psig

The corresponding phase envelopes are shown in Figure 6.

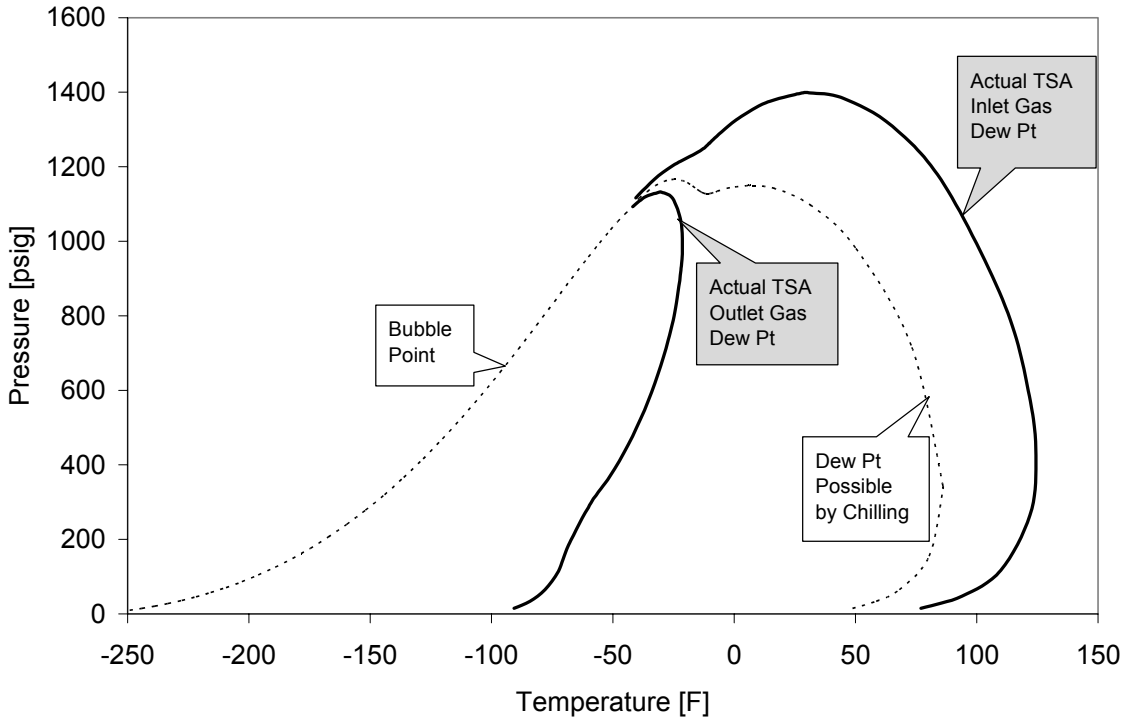

Figure 6. TSA Inlet and Outlet Phase Envelopes

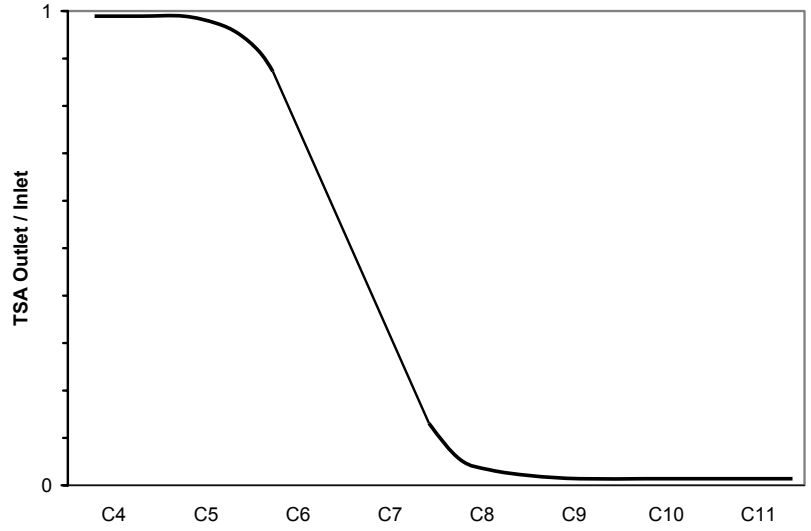

Figure 7. TSA Hydrocarbon Tail

Figure 7 shows the results of gas sampling done with a mass spectrometer where both the feed and exit streams of the TSA were analyzed dynamically. The ratio of hydrocarbon concentration in the outlet versus inlet is shown. Note the strong cutoff that occurs between C_6 and C_8. Heavier hydrocarbons are essentially completely removed.

Air Liquide – MEDAL^{TM} Membrane

The membrane technology used at the Grissik plant was provided by Air Liquide – MEDAL, L.P. The polyimide hollow fiber membrane elements (illustrated in Figure 8) provide for a high efficiency separation of CO_2 from hydrocarbon streams.

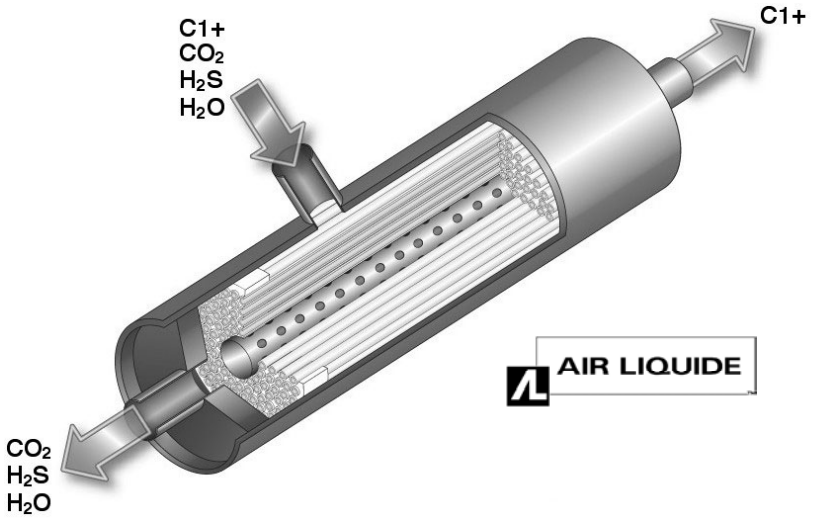

Figure 8. Air Liquide – MEDAL Natural Gas Membrane Illustration

The membrane system was fabricated as multiple skids (pictured in Figure 9) operating in parallel, each skid containing multiple horizontal tubes, with each tube containing multiple membrane elements (illustrated in Figure 10). More than 100 membrane elements are used in the Grissik plant.

Figure 9. Skid Containing Air Liquide Membrane Elements

Referring to Figure 10, multiple elements are installed in a single tube. The membrane elements are actually functioning in parallel.

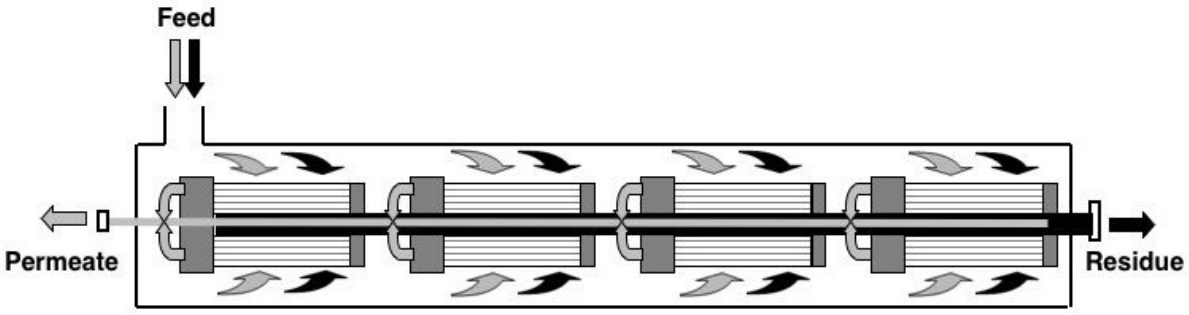

Figure 10. Multiple Membrane Element Flow Arrangement

Feed gas enters the tube near one end and flows axially to all the membrane elements by way of an annular clearance. Each membrane element is composed of several hundred thousand parallel Air Liquide proprietary hollow polyimide fibers. The feed gas enters the membrane elements on the fiber shell side and flows over the fibers, where CO_2 is removed, to

a coaxial collection tube in the center of each element (retentate). The retentate streams for each element flow axially to exit at one end of the tube. As the feed gas flows over the hollow fibers, CO_2 selectively permeates into the bore of the fibers and then flows axially to a collection point at the end of each element (permeate). The permeate of each element is then collected in the coaxial center tube and flows axially to exit the tube at the opposite end from the retentate.

Membrane Performance

Typical Operating Conditions

The membrane skids were fed directly from the output of the TSA, with feed temperatures varying roughly between 90° to 120°F. Feed pressure was typically 1100 psig. Feed gas typically contained about 30% CO_2. The permeate pressure was typically about 10 psig, flowing to the steam generator burners.

Hydrocarbon Losses vs Time

One of the main advantages of the Air Liquide polyimide membrane is its ability to maintain membrane integrity indefinitely, even when aging in the presence of heavy hydrocarbons. As illustrated in Figure 11, membrane integrity is solid and the hydrocarbon losses have actually decreased somewhat over the years since startup.

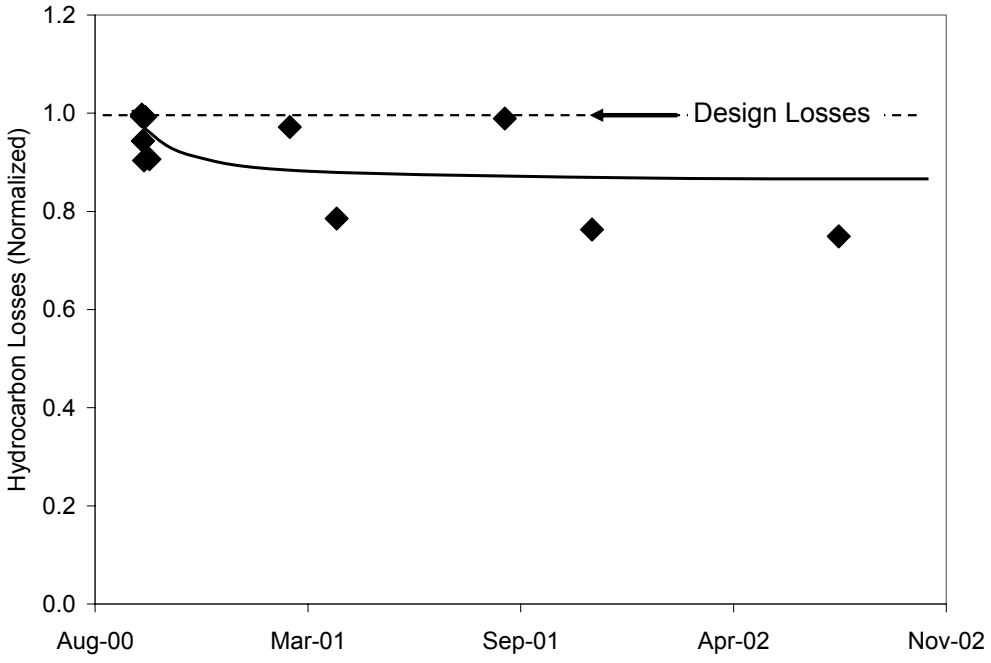

Figure 11. Membrane Hydrocarbon Losses vs Time

This trend of decreasing hydrocarbon losses indicates no loss of membrane integrity and actually shows a slight increase in apparent intrinsic membrane selectivity. Such a selectivity increase would be consistent with the change in permeability (see below).

Membrane Capacity vs Time

After the TSA was commissioned in October 2000, one membrane skid was retrofitted with new membrane elements and its performance specifically tracked. The results of this performance tracking are shown in Figure 12.

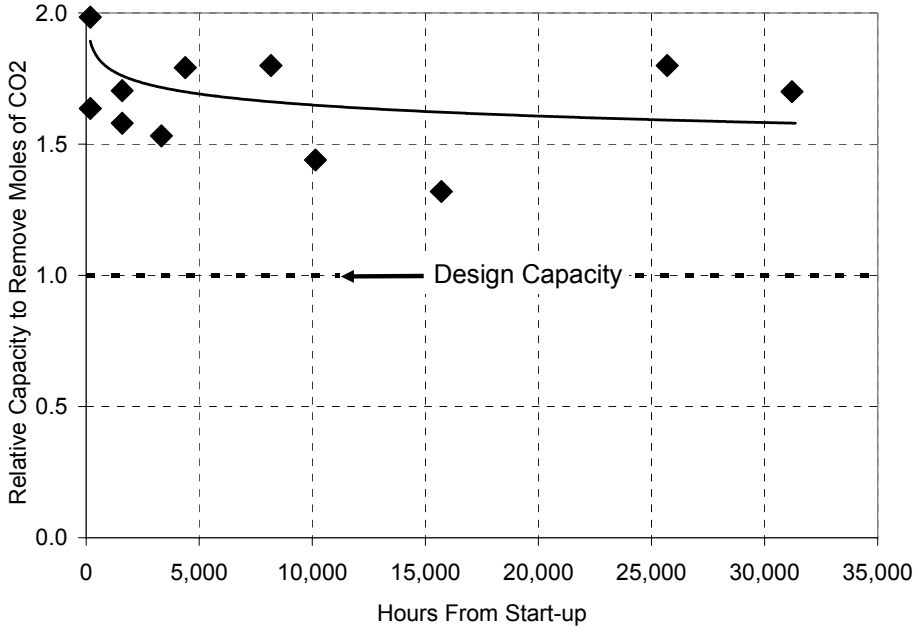

Figure 12. Membrane Capacity vs Time

The vertical axis of Figure 12 is labeled "Relative Capacity to Remove Moles of CO_2" which is in fact normalized intrinsic membrane permeability. Note the performance tracking in Figure 12 clearly shows that initial capacity was well above design and after more than 3 years of operation, capacity still remains above design. We expect the membrane life in this plant to certainly be in excess of 5 years. In fact one can see that the extrapolation of the trend in Figure 12 would suggest an indefinite membrane life. The excellent operation of the TSA and membrane by ConocoPhillips has allowed them to enjoy years of trouble free operation with zero maintenance on the membrane system, i.e. no membrane replacements. The Grissik TSA has now operated for 4 years without replacement of the Sorbead adsorbent.

During this time, the membrane skids were shut down and restarted many times for maintenance of surrounding equipment or capacity turndown. Start and stop, or pressurization and depressurization cycles have no affect on the Air Liquide polyimide hollow fiber membrane performance, although caution must be used to avoid reverse pressurization.

Permeate/Acid Gas Utilization

Two (2) Waste Heat Boiler units were installed to recover 'waste heat' available in the low Btu permeate gas stream (150 to 250 Btu/SCF) from the membrane units. Utilizing the waste heat in the permeate stream means that a single stage membrane can be used without the limitations of a 2nd membrane stage with the accompanying recycle gas compressor and still avoid hydrocarbon losses. In addition, the boilers were designed to 'incinerate' the acid gases removed by the amine gas treating system. Auxiliary fuel is utilized to make-up any inadequacy of heating value input and to stabilize the flame.

The furnace temperature is maintained above 1600 ^{O}F prior to introducing permeate fuel or acid gases. Lower temperature leads to incomplete destruction of the component and results in the emission of hazardous or flammable compound contravening limiting parameter allowed by government regulation. Waste Heat Boilers are controlled by steam header pressure that actuates pressure control valves on each steam drum. The output of the steam header pressure controller goes through flow ratio controllers of permeate gas, fuel gas and combustion air. Fuel gas flowrate is set around 10% of permeate gas flowrate while combustion air is controlled to ensure stoichiometry and complete combustion with 2-5% excess air.

The Waste Heat Boiler produces steam up to 210,000 lbs/hr at 150 psig and 358 ^{O}F. The biggest consumer of steam produced is the amine gas treating system. Condensing heat released by the steam is used to remove acid gas from amine solvent at Amine Reboilers.

Amine System

The next stage of the hybrid system is the amine system that further reduces CO_2 and H_2S to meet sales gas specification. Residue gas from the membrane unit, containing 15% CO_2, flows into the Amine Contactors and contacted with lean amine (50%-wt activated MDEA). CO_2 absorption by activated MDEA is limited to a maximum loading of 0.5 mole acid gas/mole MDEA. CO_2 content in the treated gas varies between 2-5% by volume (3%-vol average). Rich amine is then flashed at 75 psig, heated through a lean/rich amine exchanger, and regenerated by the steam heated re-boiler. The 150 psig steam used for regenerating amine is produced in the Waste Heat Boiler that burns permeate gas.

There are several common problems of amine gas treating system including reduced strength and ability to absorb acid gas, degradation, foaming and CO2 corrosion attack during acid gas breakout inside the re-boiler. Most problems found in an amine system are due to the presence of contaminant in the amine solvent, including heat stable salts, degradation products, injected chemicals, hydrocarbons and particulates. Heat stable salts and degradation products are formed by amine solvents that decompose and/or reacted with other contaminants.

Installation of the TSA and membrane upstream of the amine treating system has mitigated the above problems to an acceptable level. The TSA unit has removed heavy hydrocarbons from the feed gas and nearly eliminated the foaming risk of amine solvent. An anti-foam injection system is provided to anticipate worst case conditions.

CO_2 content reduction by the membrane unit will not only lessen CO_2 breakout in the regeneration process but also reduce contaminants that may trigger salt formation or amine degradation. Though contaminants could also be introduced by make-up water or even make-up amine, mitigating the risk from the feed process gas has significantly benefited absorption performance.

Treated gas condition at the outlet of the amine unit is normally 3%-vol CO_2 and 2-4 ppmv H_2S while sales gas contract specifies 5%-vol CO_2 and 8 ppmv H_2S. One advantage from high performance of absorption is an allowance to increase system deliverability. Increased deliverability can be achieved by bypassing some untreated gas and blending with treated gas while maintaining the sales gas specification. After development of a low CO2 gas field at Suban (average 5%-vol), a wide range of gas blending scenarios have become possible.

References

1. John Malcolm (2001), "The Grissik gas plant" by John Malcolm, *Hydrocarbon Asia*, April 2001.
2. Charles L. Anderson (2004), "Case Study: Membrane CO2 Removal From Natural Gas", *Regional Symposium on Membrane Science & Technology 2004*, Johor Bahru, Malaysia.