A NEW APPROACH TO NATURAL GAS SEPARATION

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Conventional technology of natural gas processing requires many separation steps from acid gas treating to hydrocarbon recovery, etc. The biggest drawback of the conventional gas processing is that these steps demand large usage of energy. Additionally, in the traditional technology it is rather difficult to control the emission of green house gases and toxic gases (such as methane, carbon dioxide, and hydrogen sulfide) to the environment.

The problems associated with the traditional gas processing have initiated our motivation to develop a new technology so that natural gas conditioning can be conducted in a conservative manner such that minimal energy is used, emissions to the environment are minimized, and the maximum amounts of hydrocarbons are recovered. In this work a new approach to gas processing is introduced. This new technology is adapted to a separation scheme and a model is proposed. For the scope of this project, the new technology is specifically designed to remove only acid gases (CO_2 and H_2S).

In this work, the removal of carbon dioxide and hydrogen sulfide is studied. For this project, we have conducted two case studies. In the first case study, there is only CO_2 gas present in the feed at a composition of 9%. The results show a reduction of CO_2 composition to 2%. In the second case study, we add H_2S gas to the feed to study the overall performance of this technology when both CO_2 and H_2S gases are present. The calculated results show satisfactory reductions of CO_2 from 9% to 1% and H_2S from 5% to 0.04%. PRO/II simulations provided necessary process values so that economic comparisons could be made between the amine unit and the new technology. In order to mimic a practical case in natural gas conditioning, feed gas flow-rate of 63,030 lb-mole/hr or 576 MMCF/day is used[*]. Using these conditions the total annualized cost of the amine unit and the new technology are determined to be $32.12M and $13.8M respectively for case study 1, and $39.7 and $15.8M for case study 2.

The new technology is attractive from an economic viewpoint in both case studies. The determining factor of this cost advantage is due to the energy savings in the new process. Furthermore, the new technology has the potential to have much less environmental impact because of the nature of the separation.

[*] The gas flow-rate and composition is generously provided by Williams from their Milagro gas plant.

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INTRODUCTION

The conventional gas conditioning process requires many stages of separation, which include cryogenic fractionation, gas absorption by liquid solvent, or gas adsorption by solid adsorbent, etc. Although these methods have proven to successfully separate the desired gas components, their inherent disadvantage is large consumption of energy. It would be beneficial to gas processing companies and to the environment to adopt a gas separation process that provides sufficient separation with a much lower energy demand.

In this work, we propose a process that can remove CO_2 and H_2S on an industrial scale utilizing the special property of natural gas. The advantage of this new technology is that it consumes considerably less energy and significantly reduces operation costs. Hence, this new process is an economically superior method to replace the amine unit as a means to remove acid gases from the gas stream. Additionally, the versatility of this new technology is projected to have the capability to isolate all the primary components present in natural gas.

The report is divided into two separate parts. Part 1 is an overview of the conventional gas separation process currently used in majority of plants in the US. Part 2 introduces the new technology and a comparison of its performance compared with the amine unit.

Part 1: CONVENTIONAL GAS PROCESSING

OVERVIEW OF THE CONVENTIONAL PROCESS

There are currently several step-wise processes required to isolate the many constituents of natural gas coming from the wellhead (Figure 1).

Water comes with the oil and gas when exiting the well, so the first process is the removal of the liquid water. Following flash separation, the natural gas stream is sent to an amine unit where hydrogen sulfide and carbon dioxide are removed. It is important to remove acid gases such as these due to their toxic and corrosive nature. A common side process directs the isolated acid gases to a Claus unit where sulfur can be recovered in its elemental form. The now sweetened natural gas has to be dehydrated. The next step is nitrogen removal either by pressure-swing adsorption, or cryogenic distillation. Although nitrogen is not corrosive, it is still desirable to remove because it lowers the heat value of natural gas. After nitrogen rejection the natural gas is primarily composed of hydrocarbons ranging from methane up to pentane and minor amounts of heavier hydrocarbons up to octane. Although these are typical components found in natural gas, the exact gas make-up depends highly on where the gas is obtained from. Methane is the primary component in the natural gas that is sold to consumers, so it is isolated next using a cryogenic distillation process, called a demethanizer. The methane-free natural gas liquids are then sent to an ordinary fractionation column, called a deethanizer, to recover ethane in the distillate.

In this report, we only demonstrate a new technology for the removal of carbon dioxide and hydrogen sulfide, and we compare its performance to the amine unit. Figure 2 shows the targeted task for a gas that does not contain H2S and has 9.4% CO2.

Figure 1: Conventional gas processing

Figure 1: Flow diagram for economic comparison

ACID GAS PROCESSING

The amine treating process, (Figure 3)[1], is a combination of absorption and desorption of acid gases. The "sour gas", so called due to the foul smell of hydrogen sulfide although by extension gases with only CO2 are also called like that, enters a contacting tower where it is absorbed by a liquid amine solution flowing downward. There are several types of amine solutions, but the most commonly used compounds are MEA (monoethanolamine) and DEA (diethanolamine) and MDEA (methyldiethanolamine), the solvent used in this report. The acid gases have an affinity for the amine solution, so they absorb into the liquid solution and exit the bottom of the tower in as a rich amine solution. The sweetened gas exits the top of the absorption tower free of acid gases. The rich amine solution is sent to a lower pressure stripping tower where the reduced pressure and temperature rise, provided by a reboiler, combine to act as the driving force that separates the acid gases from the amine solution. The acid gases exit the top of the stripper as vapor and the lean amine exits the bottom where it is cooled then recycled back to the absorption tower. Since it is economically favorable to recover sulfur, the acid gases are commonly sent to a Claus unit instead of being discarded. The Claus process combusts the acid gases with oxygen so that the hydrogen sulfide is converted to elemental sulfur and the remaining carbon dioxide is flared or incinerated. We do not include the Claus unit in this report.

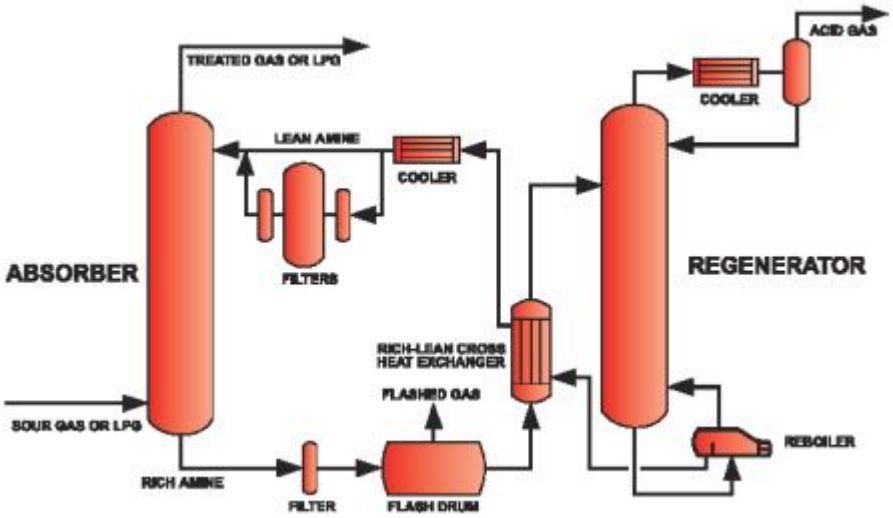

Figure 2: Amine unit schematic

DEMETHANIZER

Isolation of methane from other hydrocarbons is a process that requires very cold temperatures and a significant amount of energy input. Figure 4^2 is a simplified representation of the separation process. The feed gas is directed through a series of heat exchangers where the product stream from the cryogenic tower acts as a cooling agent. The feed gas is subsequently directed through additional heat exchanges with other streams, and lastly a refrigeration cycle. The result is a lowered feed stream temperature of roughly -120 °F so that the only component above its dew point is methane. A flash drum is then used to separate the methane pure vapor from the natural gas liquids (NGL's), which still contain a portion of the feed methane. The liquid phase from the flash drum is sent to the lower end of the distillation column. Whereas the vapor from the flash is further cooled and expanded before it is fed to the upper portion of the column as a mixed liquid-vapor stream. Almost pure methane is produced in the distillate, which is then compressed and sent as sale gas. The bottom of the column produces almost methane-free liquid hydrocarbons that are sent to the last step in natural gas processing. The turbo-expander unit uses the work produced from expanding the vapor methane to compress the sale gas. This is an attractive feature since the overall process requires large amounts of energy to operate. Another energy saving feature of this process is that refrigerant cycle costs are reduced by diverting cold liquids from the bottom portion of the cryogenic column to act as cooling utilities for the feed stream. The liquids are then fed back to a stage that corresponds with the increased liquid temperature.

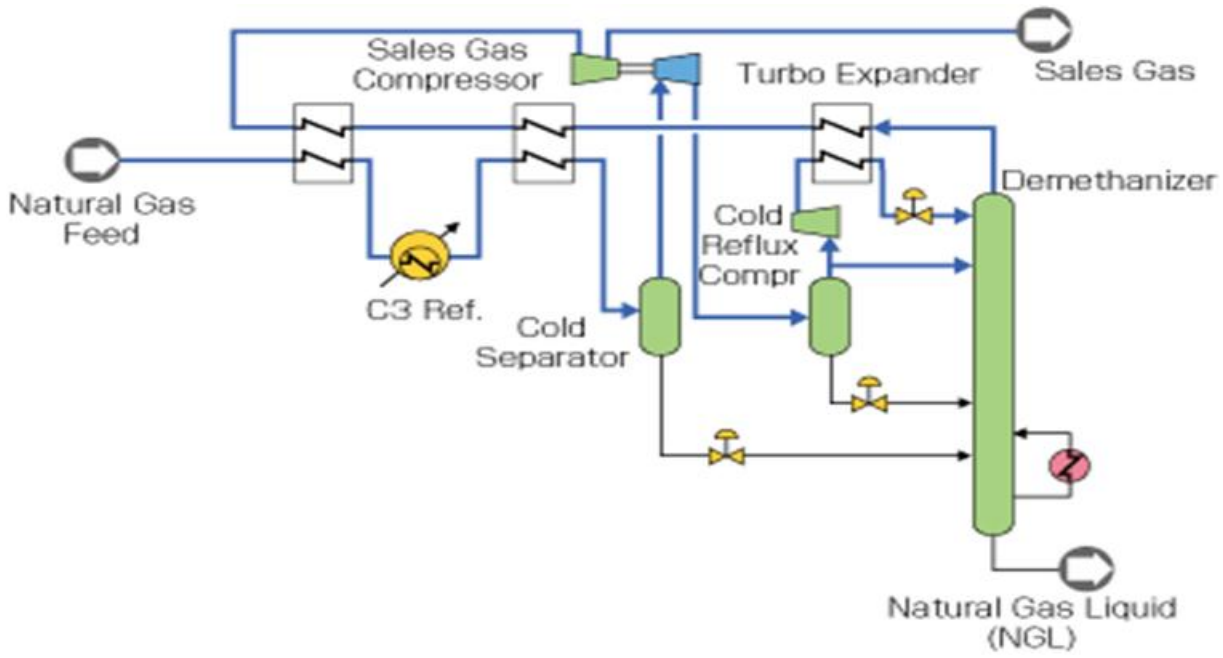

Figure 3: Demethanizer unit

NGL FRACTIONATION

Isolating ethane is a popular practice due to economic advantages in production of polyethylene over using it as an energy source. To obtain ethane an ordinary distillation column, termed a Deethanizer, is used. The distillation conditions are such that ethane exits as vapor in the distillate and the heavier hydrocarbons exit as liquid from the bottom of the column. Commonly, propane is the next component isolated for sale as a domestic heating utility, followed by isobutane for sale as household refrigerant among other applications. The leftover are pentanes and heavier components.

ECONOMICS OF THE AMINE UNIT

The majority of equipment pricing was obtained from "Plant Design for Chemical Engineer's" authored by Peters, Timmerhaus, and West. Analysis was done for two cases:

1) CO_2 is the only acid gas,

2) CO_2 and H_2S are both present.

For case 1, the feed flow rate and composition used as a basis were provided by Williams and match the properties of the gas processed at their Milagro plant. For case 2, the Williams feed composition was slightly altered to include H_2S. Since the gas composition data from Milagro contains many components currently outside the scope of this study (BTEX and others), these additional component compositions

were subtracted out and the remaining percentages were normalized. These gases are shown in Table 1.

Table 1: Case Study gases conditions

CASE STUDY 1	
Components	Composition
C1	0.897
C2	0.007
C3	0.001
IC4	0.0002
CO2	0.094
Flow-rate (lbmole/hr)	63030
CASE STUDY 2	
Components	Composition
C1	0.850
C2	0.008
C3	0.002
H2S	0.0500
CO2	0.090
Flow-rate (lbmole/hr)	63030

The process flow diagram adopted for the amine unit, depicted in Figure 5, was obtained from SimSci's PRO/II database. Tray diameter and spacing of the absorption and regeneration columns were evaluated by PRO/II. However, the Milagro plant has a capacity for large gas flow rates and consists of three contacting columns and two regeneration columns. The diameters and tray spacing obtained from PRO/II were scaled to a five column arrangement by keeping the superficial vapor velocity the same.. Column equipment costs were obtained graphically from Figure 15-11, and 15-13 in PT&W[20] based on column height and diameter with bubble cap trays. Reboilers for the regeneration towers were priced as carbon steel autoclaves with an assumed capacity equal to that of the liquid holdup on each tray from Figure 13-16. The condensers were priced as air blown heat exchangers from Figure 14-28.

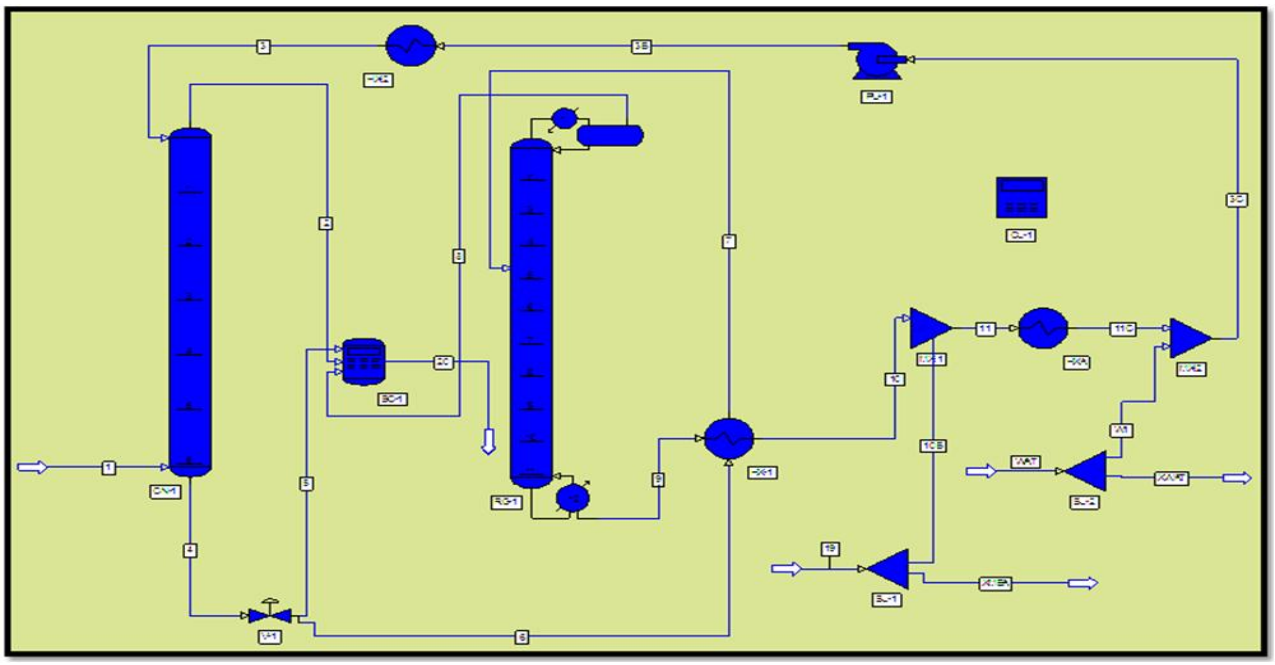

Figure 4: Amine unit simulation

Heat exchangers were priced as a function of heat transfer area. Overall heat transfer coefficients (U) were obtained from Table 14-5 in PT&W according to the type of fluids exchanging heat. Since PRO/II provides U*A values, exchanger costs were then evaluated graphically from Figure 14-17 in PT&W based on heat transfer area and a pressure adjustment factor.

The pump was priced based off capacity and outlet pressure as a cast iron centrifugal pump using Figure 12-23 in PT&W. The amine solution used in the simulation was obtained from Williams as a 50/50 water-MDEA mixture. Although this solution is recycled, the fixed cost for the first batch needs to be evaluated and this was conducted by determining the liquid hold-up of the liquid in the towers and piping. Using PRO/II data the weir heights were calculated using the Francis Weir equation and the volume of fluids on each stage were determined. An aeration factor of 0.5 was assumed so that the gas volume on each tray could be subtracted from the total volume. The volume of the pipes was determined by a correlation for optimum pipe diameter found as Equation 12-15 from PT&W. Lastly, all evaluated equipment costs were adjusted using the Marshall and Swift index provided in PT&W. The final capital investment costs are given in Table 2.

Table 2: Amine Fixed Capital

Amine unit FCI					
Case study 1_CO2 as only acid gas					
Columns		Type	No. trays	Pressure (psi)	**Cost**
3	Absorber	Bubble cap	24	920	$1,330,000
2	Stripper	Bubble cap	22	15.5	$105,000
Exchangers		MOC	Area (ft2)		
2	Cooler/Heater	3688.5373	3,500		$526,760
Pump		MOC	Flow (m^3/s)		
1	Recycle	Cast iron	0.66		$42,000
Condensers			Area (ft^2)		
2	Air blown	Carbon steel	2500		$115,000
Reboilers			Volume (m^3)		
2	Autoclave	Carbon steel	5		$125,000
First batch amine		Type			
	Solution	Water/MDEA			$596,173
Total					**$2,839,933**
Case study 2_CO2 and H2S as acid gas					
Columns		Type	No. of trays	Pressure (psi)	**Cost**
3	Absorber	Bubble cap	24	920	$1,387,189
2	Stripper	Bubble cap	22	15.5	$105,000
Exchangers		MOC	Area (ft2)		
2	Cooler/heater	3688.5373	3,500		$526,760
Pump		MOC	Flow (m^3/s)		
1	Recycle	Cast iron	0.66		$52,676
Condensers			Area (ft^2)		
2	Air blown	Carbon steel	2500		$125,964
Reboilers			Volume (m^3)		
2	Autoclave	Carbon steel	5		$137,416
First batch amine		Type			
	Solution	Water/MDEA			$708,083
Total					**$3,043,089**

From Table 2, we note that the largest portion of the fixed capital is credited to the absorption and stripping towers. Additionally, when hydrogen sulfide is added to the feed stream the capital cost is slightly elevated.

Operation costs are displayed in Table3. Unfortunately, during operation a small portion of this mixture is continuously lost to the product streams. The amount of MDEA and water needed to be replenished, provided by PRO/II, were multiplied by their associated costs to determine this operation cost. Natural gas is needed to fuel the reboiler and electricity is needed to power the pump. A value of $5 MMBTU/hr

was provided by Williams as a good estimate. Electricity was priced as self-generated electricity from Table B-1 in PT&W.

Table 3: Amine operating cost

Amine Treatment Operating Cost			
Case study 1_CO2 as only acid gas			
Process water	Flow(lb/hr)	Price ($/lb)	Cost ($ / year)
	17,100	0.02	$2,800,000
Process amine	Flow(lb/hr)	Price ($/lb)	
	32	1.54	$415,000
Natural Gas	Duty (MMBtu/hr)	Price ($/MMBTU)	
	631	5	$26,500,000
Electricity	Duty (kWh)	Price ($/kWh)	
	4,163	0.062	$2,200,000
Total			**$31,915,000**
Case study 2_CO2 and H2S as acid gas			
Process water	Flow(lb/hr)	Price ($/lb)	Cost ($ / year)
	17,100	0.02	$4,055,184
Process amine	Flow(lb/hr)	Price ($/lb)	
	32	1.54	$393,819
Natural Gas	Duty (MMBtu/hr)	Price ($/MMBTU)	
	631	5	$30,660,000
Electricity	Duty (kWh)	Price ($/kWh)	
	4,163	0.062	$4,385,876
Total			**$39,494,879**

The amine unit has large operation costs, primarily due to the above average heat duty required from the reboilers on the stripping towers. The primary effect of adding hydrogen was that the duty at the reboiler increases and the process becomes more costly. An important aspect of the amine unit is that the amount of acid gases present in the feed directly affects the required heat duty at the reboiler. As the acid gas content increases, the amount of amine solution required to achieve 2 % pipeline standards also increases. The ultimate effect is that the reboiler has to heat larger amounts of liquid and this is reflected in the heat duty. The CO_2 content analyzed in this case was 9.34 %, which is an above average amount for an amine unit to tackle alone without the help of preliminary membranes to decrease the CO_2 composition.

Part 2: NEW GAS SEPARATION PROCESS

PROCESS DESIGN*

*Technical information will be disclosed upon signing a Confidentiality agreement . Only results and economics analysis are shown in this report.

ACID GAS REMOVAL UNIT DESIGN

The scope of this project focuses on treating the acid gases that are often found in natural gas mixture such as CO_2 and H_2S. There are two case studies conducted to examine the performance of the separation using the new technology. In case study 1, CO_2 gas comprises of 9% of the feed gas, the goal is to reduce this composition of CO_2 to below 2% in order to meet the pipeline regulations. In case study 2, 5% of the feed gas is replaced with H_2S and CO_2 composition is kept at 9%. The results of the two case studies will be used to examine the feasibility of the new technology in natural gas conditioning.

Case study 1: CO_2 removal

Results: Table 4 summarizes the results of the CO_2 removal performance.

Table 4: CO2 removal unit results

Components	Feed composition	Product gas composition	Acid gas composition	Hydrocarbon recovery
C1	0.897	0.972	0.024	99.8%
C2	0.007	0.008	0.001	98.6%
C3	0.001	0.001	0.005	70.2%
iC4	0.0002	0.0001	0.0024	20.3%
CO2	0.094	0.019	0.968	
Flow-rate	63030 lbmoles/hr	58067 lbmoles/hr	4964 lbmoles/hr	

Discussion:

The new process satisfactorily reduces the acid gas composition from 9% to 2%. One shortcoming of the process is that there are some losses of propane and iso-butane. However, since the actual feed flow-rates of these two components are so small, it is hard to have an accurate assessment of this loss. Nevertheless, the resulting loss of profit is considered in the overall economic analysis of the process.

Case study 2: CO_2 and H_2S removal

Results: The results of this case study are reported in Table 5 below.

Table 5: CO2/H2S removal unit results

Components	Feed composition	Product gas composition	Acid gas composition	Hydrocarbon recovery
C1	0.850	0.977	0.039	99.4%
C2	0.008	0.009	0.001	98.4%
C3	0.002	0.002	0.001	94.0%
H2S	0.050	0.0004	0.367	
CO2	0.090	0.011	0.593	
Flow-rate	63030 lbmoles/hr	54500 lbmoles/hr	8530 lbmoles/hr	

Discussion:

The results show an even sharper separation of H_2S than CO_2. Although there is some loss of propane; this loss is smaller than that of the previous case study. Future study needs to increase the amount of propane and heavier hydrocarbon gases in the feed in order to have a more accurate assessment on the recovery of the heavier hydrocarbon gases using the new technology.

ECONOMICS

The economic analysis for the simulations is carried out in the same manner for each case, so the method will only be discussed once.

Table 6: New unit fixed costs

New unit FCI		
Case Study 1: CO2 as only acid gas		
Total		**$1,914,337**
Case Study 2: CO2 and H2S as acid gas		
Total		**$1,987,025**

When CO_2 is the only acid gas present the fixed capital is slightly smaller. This can be expected since the amine unit costs are also slightly smaller when CO_2 is the only acid gas present. Additionally, the fixed costs for the new technology are slightly lower than the amine unit costs, but still closely comparable.

Operation costs are shown in Table 7. The addition of H_2S into the feed stream affects the operation costs on a larger scale than it affects the fixed costs. The exciting aspect of the operation costs is that they are much less than the amine unit operation costs. When CO_2 is the only acid gas the operation costs for the new technology are 42% of the amine units. When both acid gases are present the new technology is only 39% of the amine unit operation costs.

One last piece of economic data of importance is the total annualized cost (TCI). In this report the total annual cost is based on lifetime of 15 years. These results are shown below for the amine and the new separation processes under both conditions.

Table 7: Novel method operating cost

Novel Method Operating Cost			
CO2 as only acid gas			
Total			$13,673,940
CO2 and H2S			
Total			$15,656,116

Table 8: Novel method operating cost

Total annualized cost			
	Amine unit	New technology	Savings
CO2 only	$32,200,000	$13,800,000	57%
CO2 & H2S	$39,700,000	$15,800,000	60%

CONCLUSION/RECOMMENDATIONS

Model calculations show that acid gases such as CO_2 and H_2S can be removed effectively using the new technology. Economics analysis reveals more than 50% savings of the total annual cost compared to the traditional amine unit; the largest reduction of cost is attributed to the energy at the reboiler.

Although the two case studies conducted in this project only focus on the removal of acid gases, the same principle could also be applied to isolate the hydrocarbon gases, and the

technology can potentially replace the demethanizer and the fractionation train. It would be interesting to examine the performance and the economics of the new technology compared with the cryogenic distillation in the demethanizer. Cryogenic distillation a costly process due to the large demand of cooling; hence, if the new process succeeds, it would be a breakthrough in the gas separation technology.

Based on the nature of the separation, the gas emission can be controlled so that the toxic gas and the green house gases can be prevented from harming the environment. However, this feature will need to be verified experimentally.

RECOMMENDATIONS

- In order to have a complete assessment of the new acid gas removal unit and also to determine the optimal conditions for the new technology, a wider range of CO_2/H_2S concentrations should be studied.
- A separate study in which the feed flow-rates of the C_{3+} gases are higher should be investigated to test the recovery performance of the new technology with the heavier hydrocarbon gases.

[1] Schematic obtained from http://www.amines.com/
[2] Schematic obtained from http://www.toyo-eng.co.jp