

Novel Method for Gas Separation

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2008

Summary

Natural gas has many impurities that must be removed to increase the worth of the natural gas. There are seven major processes that are used to efficiently separate each components of natural gas. Water must first be removed, and then acid gasses must be removed. The third step is the removal of water vapor, then mercury then nitrogen must be rejected from the stream. Finally , methane is separated, and this is the most important aspect of the process. Lastly all of the liquid natural gases ar separated.

The novel process developed has many advantages over the current method used for natural gas processing. First it is much more cost effective than the current method by having reduced operating costs. This process has the potential to have much less of an environmental impact by reducing greenhouse emissions. It can separate most of the contaminants in natural gas, and split each stream such as methane, and ethane into the separate components. The last benefit is that everything can be done using one process just with different stages. Water and mercury are not removed by using this process.

For a fair comparison only the processes that perform the same functions as the novel process were economically compared. We evaluated amine treating, demethanizing, and deethanizing processes have had the economics calculated by using a simulation program, SimSci's Proll. The economics of all of the separated process are compared to the novel process during this report.

There is uncertainty in certain parameters, so three cases were evaluated. The first case is the optimistic view that our parameters are within reasonably practical ranges and render the best economics. The second is the pessimistic view that the parameters are in feasible extremes and they render the worst economics. The last case is the average case, where parameters are between the two extremes. These parameters will be able to be determined from a few experiments that will be conducted at some point in the future. The benefit of this novel method is that all three of these cases result in a lower annualized cost than the current method used. The savings range between 50% to 80% in operating costs. Our fixed capital investment is higher.

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Introduction

Natural gas processing requires many different steps to separate out all of the contaminants, and components. These many steps can lead to extremely high operating costs, and fixed capital investment. A novel process has been developed that has the potential to reduce the operating costs by 6 fold, and only increase the fixed capital investment by less than a factor of 2. This process has an annualized cost that is 3 times less than the current method for gas processing. Technical detail must be withheld from this discussion due to intellectual property issues with the office of technology development. However this paper will discuss in detail the current method for natural gas processing, introduce the economics of this current process, then compare the economics of the current process and the novel process.

The Current Process

Natural gas has many impurities that must be removed to increase the worth of the gas. Free liquid water is first removed, along with condensate and oil. Hydrogen sulfide, mercaptans and carbon dioxide are then removed through an acid gas removal process. Hydrogen sulfide and mercaptans are what cause the gas to be sour. The gas is called sour because of the sulfuric smell associated with it. This sour

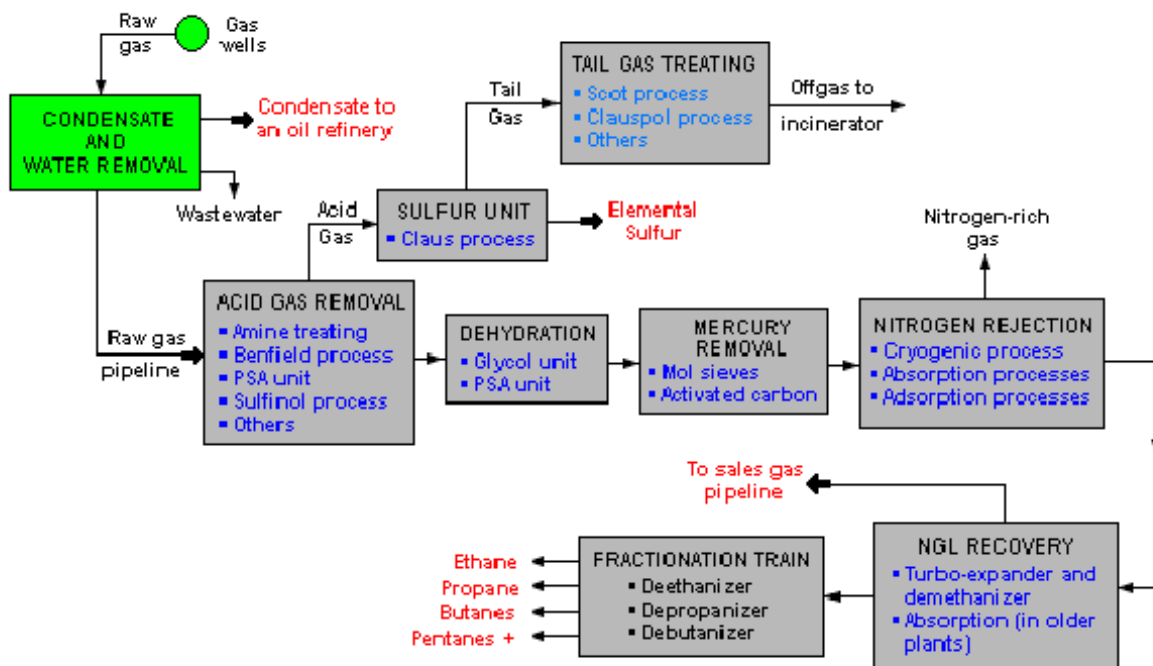


Figure 1. Process flow diagram for natural gas processing

gas will be sent through an amine treating process, having two products, first the acid gas, and second the now sweetened gas. Next the gas will be sent to a dehydrating unit. This step removes the water vapor from the gas, this could not be done with just normal separation techniques. Glycol dehydration is the most common method for the removal of water vapor. Fourth mercury is removed from the gas due

to its corrosive nature, and its large impact on process equipment made from aluminum. The gas is then sent to a unit to reject the nitrogen. Nitrogen can be rejected in various ways, however the cryogenic method is the most common for the removal of nitrogen. The next step in this process is the most important step, the demethanizer. This is the most important step because the methane that is being removed composes most of the natural gas. The last piece of the process is the fractionation train. This step is where ethane, propane, butane, and pentane + larger hydrocarbons are separated. Methane, ethane, propane, butane and pentane + larger hydrocarbon must all be separated purely for the greatest worth. these seven steps will be discussed in the next sections of this paper. Figure 3 above shows these steps in a process flow diagram.

Water, Oil, and Condensate Removal

The first part of gas processing involves removing the excess water, any oil that is with it, and removing any condensate from the gas. The removal of the free water can be done through a simple phase separation method. The removal of the water vapor, which requires a much more complex process, will be discussed in detail further in the report. Natural gas and oil will often come out of the same well together, so separating the gas from the oil must be done. When the oil and gas are in a reservoir underground, they are under extremely high pressure, causing a lot of the gas to be dissolved into the oil. However when the oil is brought out from the ground, the pressure can be reduced causing the gas to diffuse out of the liquid. Removing the condensate, requires a little more work than the previous two separation method. In the natural gas, there could be large hydrocarbons in the gaseous form that need to be removed and shipped to an oil refinery. Passing the gas stream through a cooling heat exchanger causes the heavier hydrocarbons to liquefy. This condensate can then be sent with the oil to a refinery, and the natural gas will be sent to the next step in processing.

Acid Gas Removal

The removal of hydrogen sulfide, carbon dioxide and mercaptans is necessary for the processing of natural gas. The most common method to remove these acid gases is by amine treating. Amine treating uses one of the following four amines to purify the sour gas stream: monoethanolamine, diethanolamine, diisopropylamine and methylethanolamine. Figure 4 below shows the process flow diagram for the amine treating process. Sour gas enters an absorber (flue gas in the picture), where it

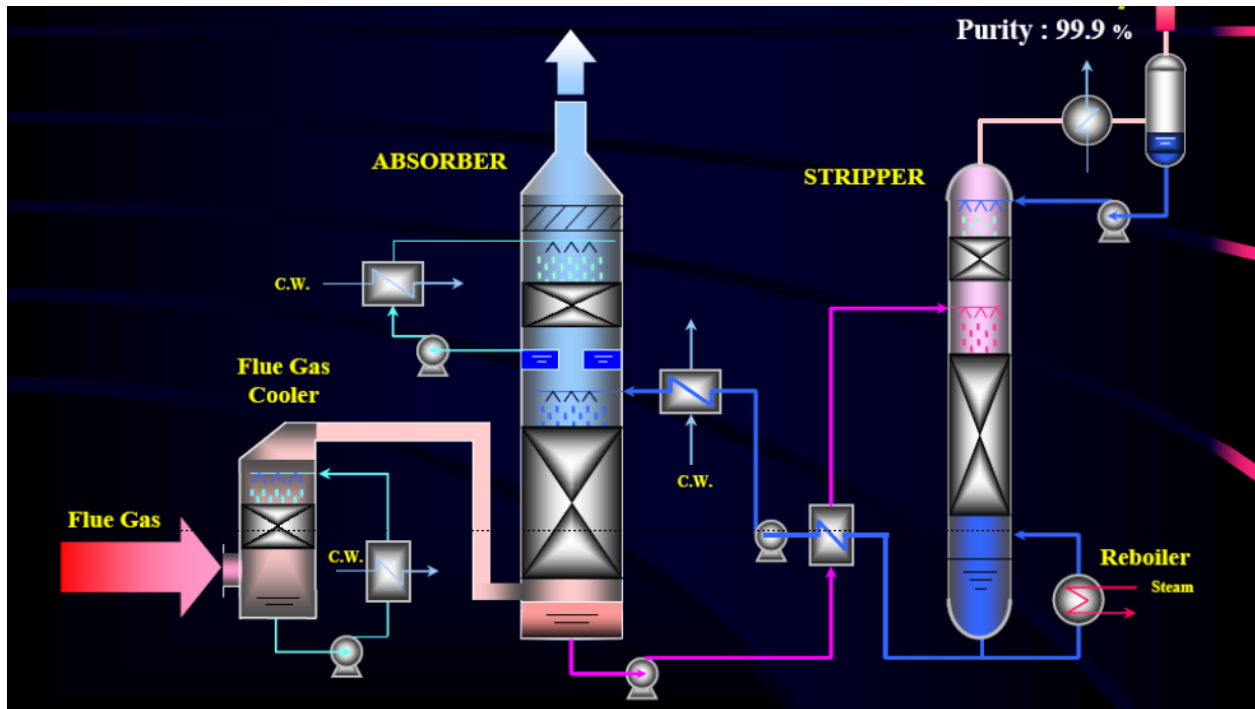


Figure 2. Amine treating process for removal of acid gases

comes into contact with an amine solution flowing down. The amine solutions have an affinity for the sour gases, causing it to absorb the gases out from the stream. The now sweetened gas exits the top of the absorber. The sour gas rich amine is then transported back to a regenerator. The regeneration process involves sending the amine to a stripper, where the amine is heated with steam and a reboiler, causing the sour gas to dissociate from the amine, and exit the top of the stripper. The amine is then cooled down and sent back to the top of the absorption column to repeat this process. Other processes exist such as the sulfinol process, and the Benfield process that are used to remove acid gases. The sulfinol process is basically the same as the amine treating process; however instead of just using an amine as the absorbent, sulfane is used. Using the combination of diisopropylamine and sulfane allows for the absorbent solution to have the added benefits of chemical absorption and physical absorption. Chemical absorption causes for the sour gas to be held tightly to the absorbent, while physical absorbent hold the gas loosely. This implies that chemical absorption is better at trapping the gas, however it requires more energy to break the bonds and dissociate the gas. Physical absorption is not as good at trapping the gas, however it does not require as much energy to trap the gas. The Benfield process is also similar to the sulfinol process, but is just patented by a different company.

There is another side step, the Claus process, that will not be discussed thoroughly, however it is shown above in the process flow diagram, so it will be briefly mentioned. The by product from the amine treating process, the sulfide, is sent to a Claus process to retrieve the elemental sulfur. This process produced more than 64,000,000 metric tons of sulfur during the year 2005. This process is used in all refineries and gas processing plants to recover sulfur.

Dehydration

The next step is the removal of water vapor. Water must be removed from the natural gas stream to prevent complications during transportation, such as corrosion or hydrate formation. The most common process for this task is known as glycol dehydration. Glycol dehydration is very similar to amine treating, in that it uses an absorption column, and absorbent to remove the water, and a regeneration column. The most commonly used absorbents are triethylene glycol, diethylene glycol, ethylene glycol and tetra ethylene glycol. These are chosen due to their chemical affinity for water. However they also have a small affinity for methane, so as the absorbent is flowing down the column, the water will be removed, but a little methane will also be taken out. The difference from the amine process is in the regeneration mode, where the methane can be recovered. Figure 5 displays this process, and it can be seen that the water rich glycol stream is heated up in a still. However this stream is only heated slightly, it is then sent to a flash tank where some of the methane can be recovered. The stream is then sent back to the still where the rest of the water vapor is evaporated out from the glycol. This process normally reduces water vapor down to 5 lb/MMscf of gas, but can be tweaked to be able to reduce the water vapor down to 1 lb/MMscf of gas. Another factor of this process is that by using the flash tank to remove the methane not only is it recovered, but green house gas emissions are reduced.

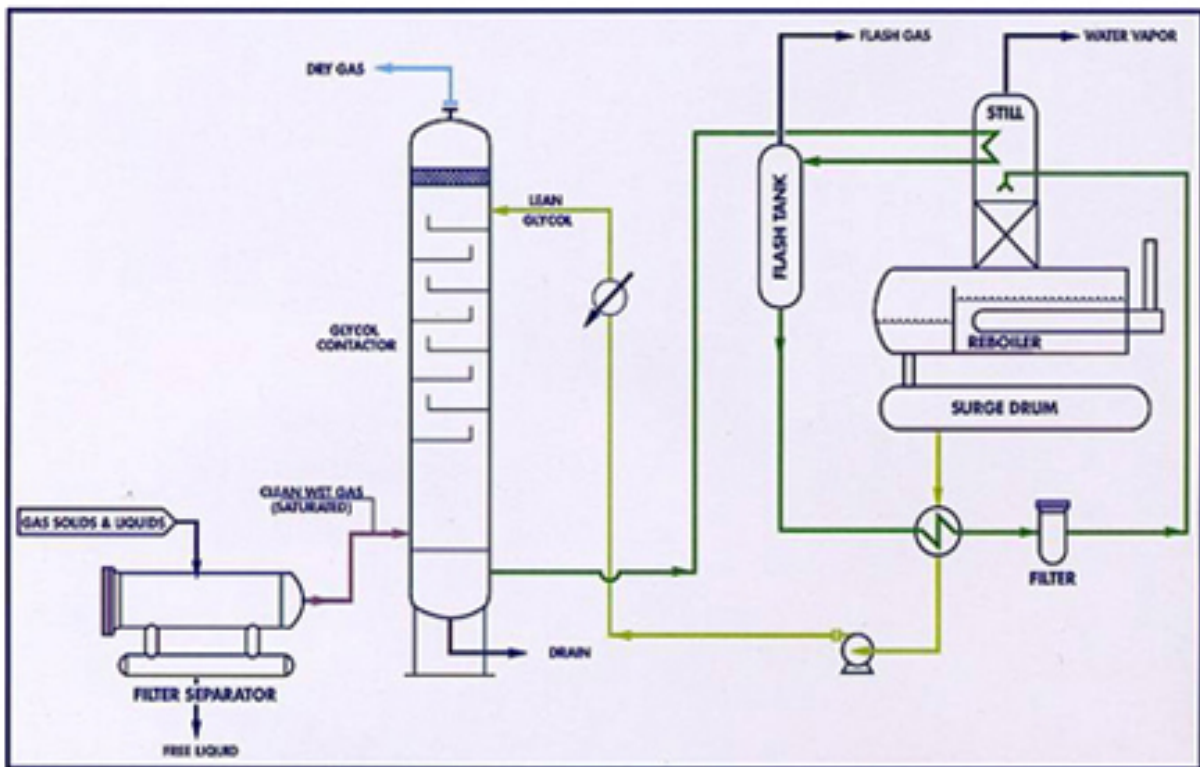


Figure 3. Glycol dehydration process for the removal of water vapor from the gas stream

Mercury Removal

Mercury must be removed from the natural gas streams due to its corrosive nature. If mercury is not removed before the demethanization process, or nitrogen rejection process, the aluminum heat exchangers used will quickly be destroyed. These two processes use aluminum heat exchangers because of the cryogenic processes. The aluminum aids in the extreme cooling due to its high heat transfer coefficient. Mercury can be easily removed using vanadium oxide supported with silicon. A less efficient but still applicable process would be to use activated carbon or a molecular sieve. Activated carbon works very well due to its extremely large surface area to volume ratio. A molecular sieve is similar to a membrane, and allows for the removal of mercury and some water molecules also. Molecular sieves are made from adsorbents such as activated carbon or zeolites.

Nitrogen Removal

Nitrogen must be removed from the gas stream since if left in, the heating value of the natural gas would be reduced. Many methods exist to remove nitrogen from natural gas, such as pressure swing adsorption, cryogenic methods, and membrane separation. The cryogenic process is the most commonly used, however the details of how a cryogenic process work will be discussed in a later section. The pressure swing adsorption method is also commonly used; however it has a disadvantage, unlike the cryogenic method, of not being useful for large scale production. This method removes nitrogen due to adsorption under extreme pressure. The nitrogen is passed through a column packed with adsorbent such as activated carbon under high pressure. The nitrogen begins to attach to the activated carbon, until all of the surface area is filled with nitrogen. Once all of the adsorbent is filled, the pressure in the vessel is reduced. Figure 4 part b shows how the nitrogen will adsorb or desorb based upon pressure. Once this pressure is reduced the nitrogen will desorb and exit the column, while the natural gas has already passed through the column nitrogen free. Figure 6 part a displays the column under high pressure, and then the column under low pressure. This process is semi-continuous, since there is a delay time for the regeneration mode of the adsorbent.

Nitrogen Rejection

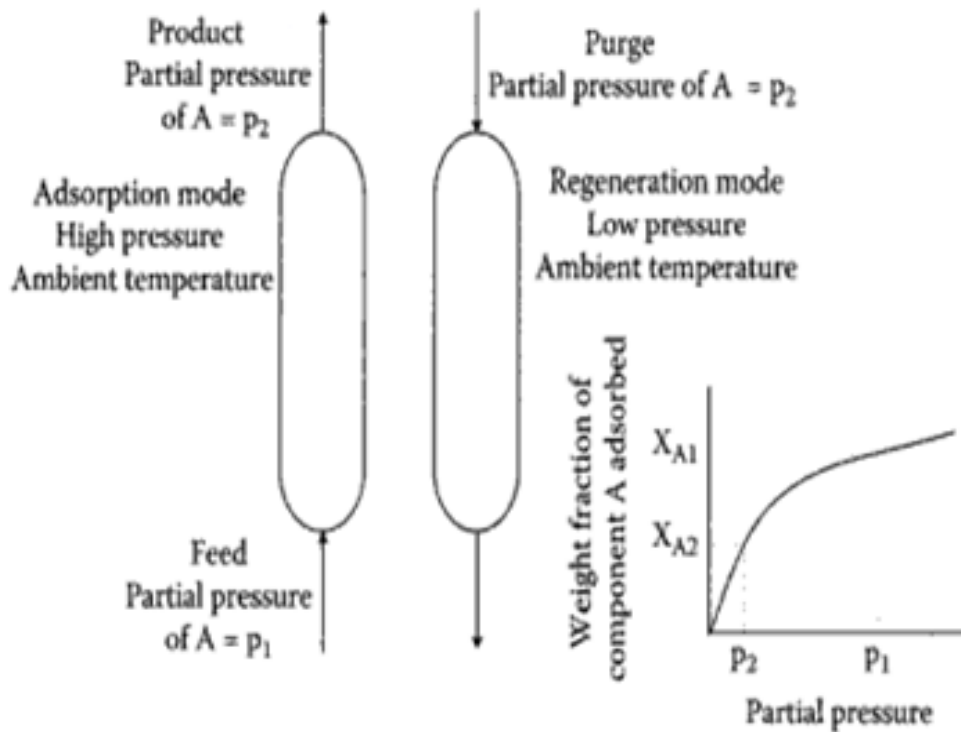


Figure 4. Flow diagram for pressure swing adsorption

Membrane separation can also be used to remove the nitrogen; however this has a lowered production rate than the pressure swing adsorption. Membranes operate on the atomic level, by having small pores where only compounds that are small enough may pass through. When molecules pass through the membrane it is known as permeation. The permeability of a membrane to a component is what determines the selectivity of a membrane. Glassy polymer membranes are found to have the best permeability to nitrogen, however the difference between the selectivity of nitrogen and methane is too small for just one membrane to accomplish the separation. A few membranes in series will remove all of the nitrogen from the natural gas stream, however this is not a very efficient separation.

The Demethanizer

As stated above this is the most important aspect of natural gas processing, and requires the largest fixed capital investment. This process separates the methane from all of the larger hydrocarbons. A cryogenic process using a turbo-expander is used to lower the temperature down far enough for the liquefaction of the gas stream. Figure 7 below is a process flow diagram of the demethanizer. The

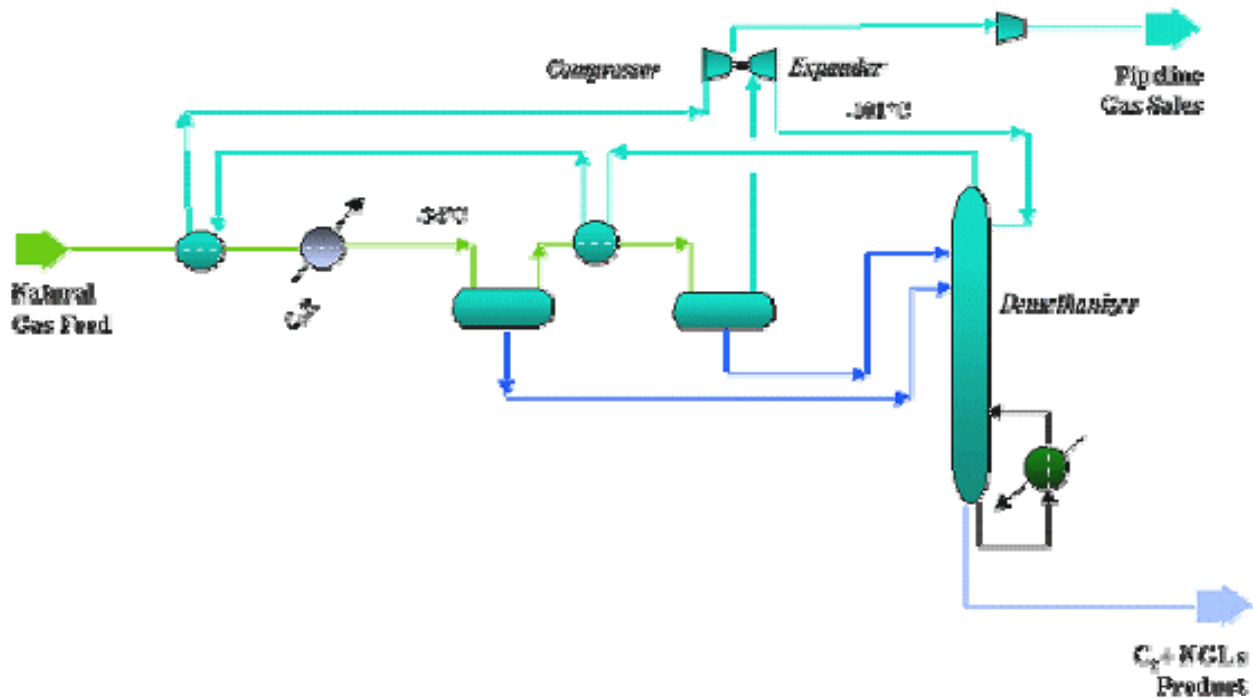


Figure 5. Process flow diagram for the demethanizer

natural gas comes from the nitrogen rejection process and is cooled through two heat exchangers. The first heat exchanger cools the natural gas by the methane product from the distillation column. Secondly the natural gas is then cooled down by a refrigeration cycle, most likely using R-12 or R-22 as the refrigerant. The stream is now fed to a flash tank, where the liquid exits the bottom, is passed through a valve and sent to the column (the picture does not show the valve, however this does happen to reduce the temperature). The gas passes through another heat exchanger and then sent to another flash tank. Again liquid exits the bottom, goes through a valve and then into the column. The gas is then sent to a turbo-expander which is used to drastically drop the temperature, thus liquefying the natural gas stream. This stream enters the column, to allow for the distillation of methane. The methane exits the top, still extremely cold and is used to cool the incoming natural gas stream. The methane is then compressed back to pipeline conditions where it is then sent to be sold. The heavier hydrocarbons such as ethane, propane, butane, and larger hydrocarbons exit the bottom of the demethanizer and are sent to the last step in natural gas processing.

The Fractionation Train

The last step is used to separate each of the LNG's into each component through three different processes. First the LNG's are sent to a deethanizer, which is distillation column used to boil the ethane out from the mixture, and have the propane and heaviers exit the bottom of the stream. Next the LNG's are sent to a depropanizer, where the same method use for the deethanizer applies here. The last step is when the stream is fed to a debutanizer, same concept as the previous two methods, causing the butane to exit the top of the tower and pentane + larger hydrocarbons to exit the bottom.

Novel Process

The novel process developed has many advantages over the current method used for natural gas processing. First it is much more cost effective than the current method by having extremely reduced operating costs. This process has the potential to have much less of an environmental impact by

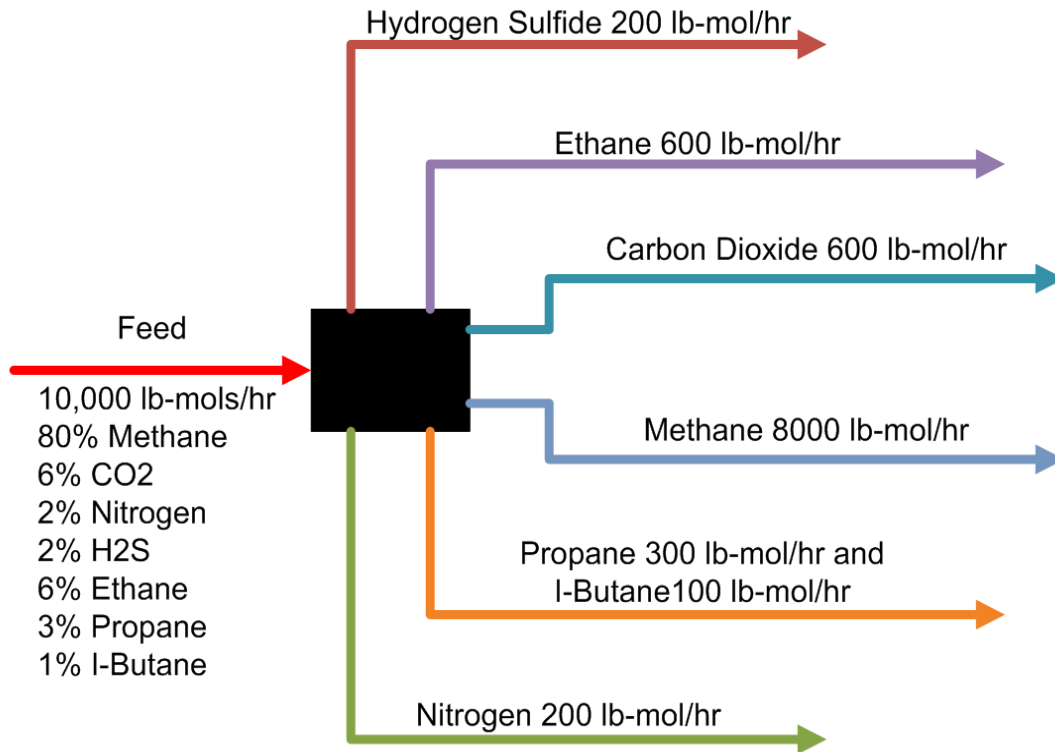


Figure 6. Representation of the novel method with the processes blacked out.

reducing greenhouse emissions. It can separate most of the contaminants in natural gas, and split each stream such as methane, and ethane into the separate components. The last benefit is that everything can be done using one process just with different stages. Figure 6 shows a process flow diagram of how this process works, however the methods cannot be described and are represented by a black box. Referring back to figure 6, this process only separates the components listed under the feed stream. Water and mercury are not listed in this stream. This is not because the process is unable to separate these components; this process had just not been tested for separating those components. If the process is unable, mercury could be removed before or after the novel method with no repercussions. There is uncertainty in certain parameters, so three cases were evaluated. The first case is the optimistic view that our parameters are within reasonably practical ranges and render the best economics. The second is the pessimistic view that the parameters are in feasible extremes and they render the worst economics. The last case is the average case, where parameters are between the two extremes. These parameters will be able to be determined from a few experiments that will be conducted at some point in the future. The benefit of this novel method is that all three of these cases result in a lower annualized cost than the current method used.

For a fair comparison of the current method and the novel method, the economics of only the processes shown in figure 7 will be used. Mercury removal, water removal, and dehydration will not be compared to the novel method.

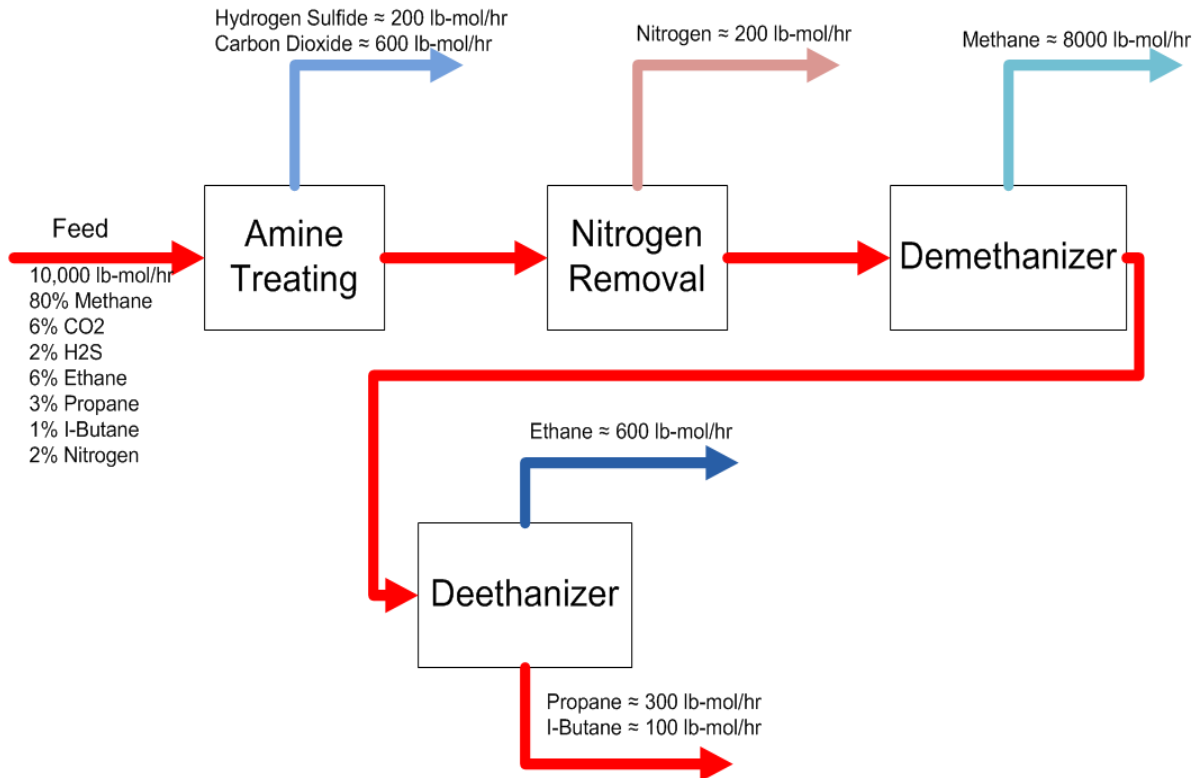


Figure 7. Current processes that will be used for the economic comparison.

Economics

The economics of the amine treating process, the demethanizer process, and the deethanizer process will be discussed below. The nitrogen rejection process is not compared in this report due to the time restrictions of this project. However the economics are still in the favor of this process, even without comparing it to each step of the process shown in Figure 11.

Amine Treating economics

Figure 12 below is the process flow diagram that was used to determine the economics of the amine treating process. Table 1 displays which each piece of equipment used from this simulation to determine the total equipment cost. Table 2 displays the total operating costs of the process. Figure 12 was taken from Proll's application library and adjusted to match the required flowrates. Figure 15-11 from "Plant Design and Economics for Chemical Engineers" authored by Peters, Timmerhaus and West, was used to analyze the economics of the two columns. The column dimensions used for the economic analysis are

listed in the description portion of Table 1. Dimensions were found by using the tray hydraulics function from Proll for sizing. Figure 14-20 from PT&W was used to determine the economics of both heat exchangers evaluated. The two heat exchangers with the red circles around them were the only heat exchangers used for equipment cost. The heat exchanger with a green circle is a representation of the heat exchanger with a red circle at the top. The heat exchanger with the green circle has no function. The temperature entering is the same as the temperature leaving this exchanger. Proll's calculator was used to determine the U*A of each heat exchanger. By assuming a U of 0.5kW/K the total area, which is listed in the description section of Table 1, was found and used to calculate cost. The pumps cost was found by using Figure 12-23 from PT&W using the parameters listed in Table 1. The operating costs are the major down fall of this process. The second column requires 139 million BTU's of heat in the reboiler. Using natural gas as a cheap source of heat being \$6 per million BTU's of heat, still causes most of the total operating costs to come from the reboiler. Water and electricity are also in the table, however they have no major effect on the operating costs.

Cost of Equipment		
Equipment	Description	Price (\$)
Column - 1	4.88 meters tall, 2.02 meters in diameter	\$23,000
Column - 2	6.71 meters tall, 3.60 meters in diameter	\$58,000
Heat exchanger - 1	530 square meters	\$59,000
Heat exchanger - 2	615 square meters	\$69,000
Pump	38,000 gallon flow, 235 psi rise	\$68,000
Total		\$277,000

Table 1. Equipment costs for amine treating process

Operating Costs		
Utilities		Price (\$/hr)
Cooling Water	19,800 gallons/hr (\$0.08/1000kg)	\$5.98
column reboiler	139 million BTU/hr (\$6 per million BTU)	\$834
Pump	97.53 Kw (\$0.06/Kw)	\$5.85
Total		\$845.83

Table 2. Operating costs for amine treating process

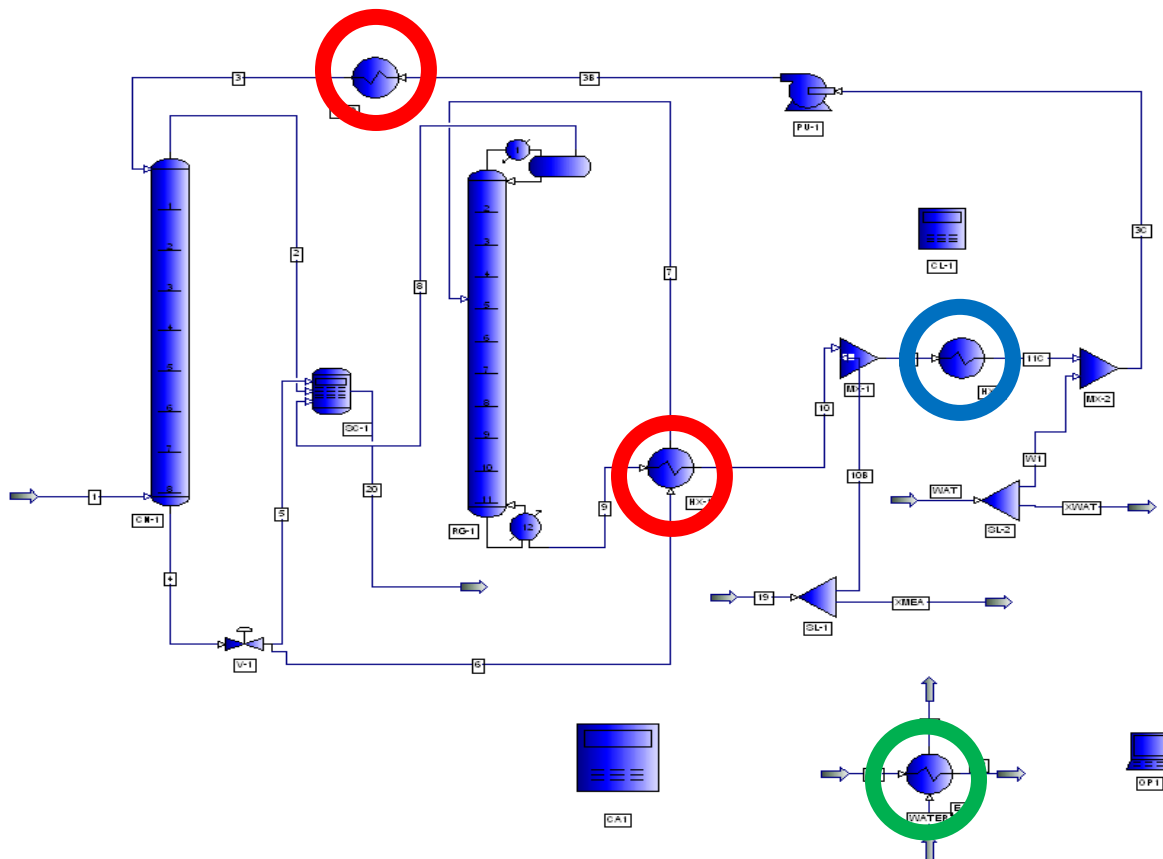


Figure 8. Simulation used for economic analysis of amine treating process.

Demethanizer

Figure 9 below is the process flow diagram used to determine the economics of the demethanizer. This process requires the largest fixed capital investment; however the operating costs are significantly lower than the amine treating process. This process flow sheet is an actual simulation of a demethanizer gas plant here in the United States. The flow rate was adjusted to match the flow rates used in the process. Table 3 is a list of each piece of equipment used in the economic evaluation. Table 4 is a breakdown of the operating costs for this process. The one column, and the seven heat exchangers shown below were calculated the exact same was as done for the amine process. Dimensions for the column and area for the exchangers were also found the same way as above. The heat exchanger with the blue circle is the only heat exchanger that was not calculated directly. One of the heat exchangers from the refrigeration cycle below was referenced to it and was used to calculate the area. The refrigerant, which accounts for a large portion of the fixed capital investment, was assumed to be good for the life of the process, 15 years. R-12 was used, and found to be \$22 per pound if buying more than 1200 lb's at a time. A calculator was used in this process that multiplied the refrigerant flow rate, in units of lb/hr, by \$22. The three compressors costs were calculated using Figure 12-28 from PT&W. The electricity required to power the compressors was used in determining the cost. The one expander was done the exact way as the compressors, since economic information could not be found for it.

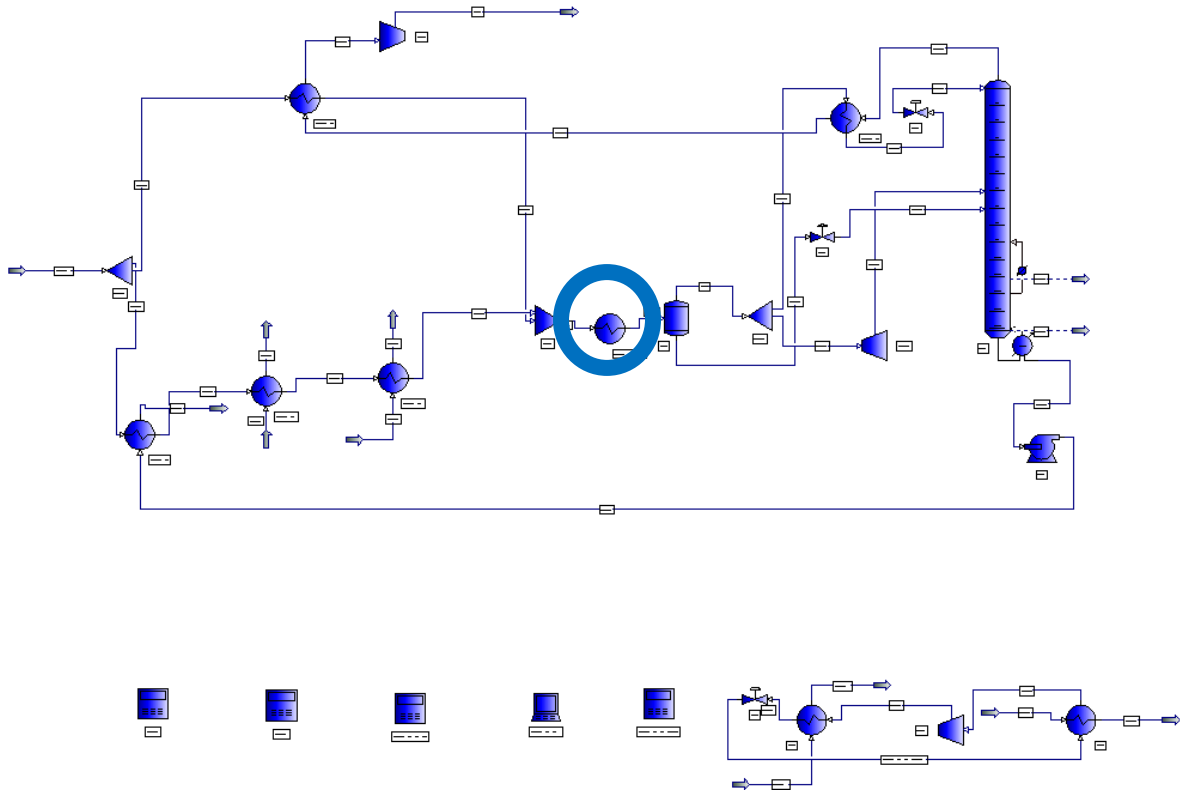


Figure 9. Process flow diagram of a demethanizer, this process is the simulation of a real plant here in the united states.

Cost of Equipment		
Equipment	Description	Price
Column	Diamter of 1.53 meters, Height of 8.54 meters	\$25,000
Heat exchanger 1	Area of 1055 square meters	\$118,287
Heat exchanger 2	Area of 15.6square meters	\$1,874
Heat exchanger 3	Area of 113.12 square meters	\$12,796
Heat exchanger 4	Area of 25.2 square meters	\$2,953
Heat exchanger 5	Area of 261.7 square meters	\$29,440
Heat exchanger 6	Area of 6.8 square meters	\$890
Heat exchanger 7	Area of 11.5 square meters	\$1,417
Refrigerant	For a 10 year period	\$880,000
Expander	1200 KW output	\$370,000
Compressor	Compreseing to pressure of inlet for deethanizati	\$50,000
Compressor 2		\$190,000
Compressor 3	Bringing methane back to pipeline pressure	\$640,000
Pump		\$3,000
Total		\$2,325,657

Table 3. Equipment cost of the demethanizer

Operating Costs		
Utility		Price (\$/hr)
Cooling water	using \$0.08 per 1000 kg of cooling water	\$1.17
Electricity	Two compressors and an expander	\$116.25
Total		\$117.42

Table 4. Operating costs for demethanizer

Compressor two which does not have a description in the box is the compressor used in the refrigeration cycle. The only two operating costs for this process are shown above. The cooling water is the cost of the water used in the refrigeration cycle at a cost listed in the description section of Table 4. The electricity of the process was used by using a calculator to compute the actual work of the three compressors minus the actual work produced by the expander. Electricity costs were assumed to be \$0.06 per kW. Adiabatic efficiencies of the compressors and expander were set to 80%

Deethanizer

Figure 10 below shows the process flow diagram for the deethanizer. This is the simplest process, involving only this column. No refrigeration cycle was needed, because the feed inlet was pressurized during the demethanizer process up to 660psig. This pressure allows for the condenser to operate

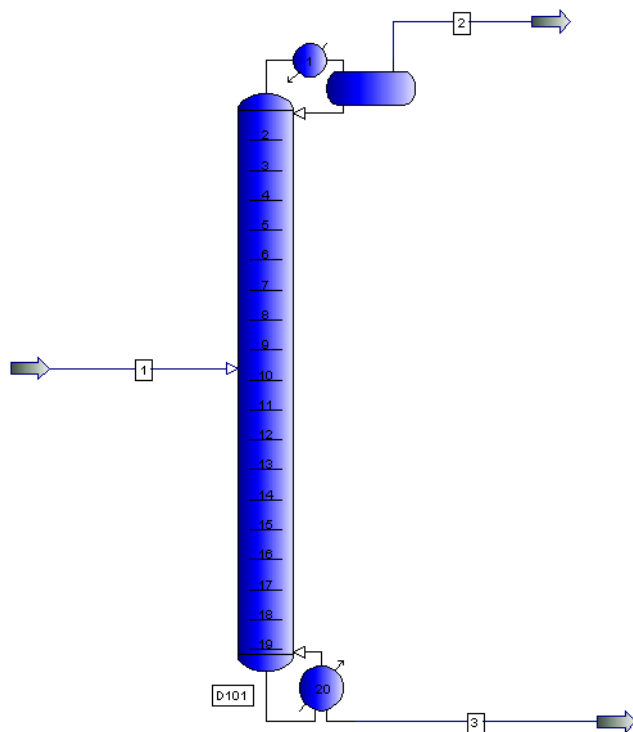


Figure 10. Process flow diagram for the deethanizer

above the cooling water temperature. Table 5 displays the equipment cost for this process, and Table 6 displays the operating cost for this process. The column was calculated the exact was as in the amine treating process. The dimensions were also found through the same method as above. The operating costs of the reboiler were calculated the exact way the operating costs of the reboiler for the amine process was calculated.

Cost of Equipment		
Equipment		Price
Column	8.7 meters tall, 1.86 meters in diameter	\$32,000

Table 5. Equipment cost of the deethanizer

Operating Costs		
Utility		Price
Reboiler	(8 million Btu's needed, 6 dollars/million BTU)	\$48

Table6. Operating cost for the deethanizer

Economic Comparison

The economics of the novel process are displayed below in Table 7 compared to the economics of the current process using only the amine treating, demethanizer and deethanizer processes. The current process row displays the fixed capital investment per 1000 feet of standard cubic gas, the operating costs and the annualized costs. The fixed capital investment was found using Figure 6-9 from PT&W for a fluid processing plant. These economics are not for a grassroots project, only for an addition to an already existing plant. The annualized cost is the fixed capital investment per day plus the operating

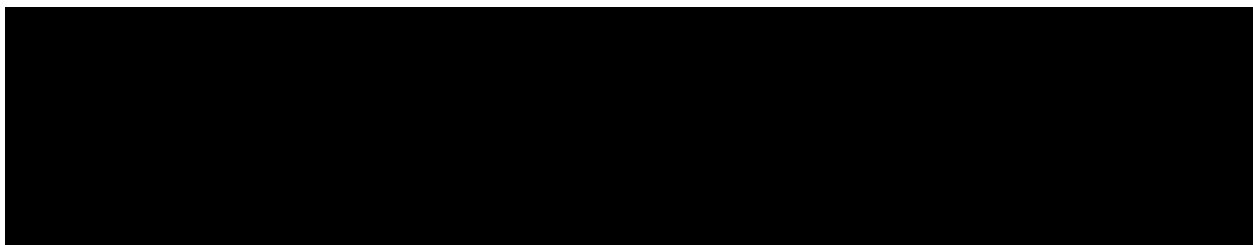


Table7. Economic comparison

costs per day. These economics display the extreme cost reductions of this novel process. The three cases are listed in the table, first if the undetermined parameters are not at any extreme. Second if the parameters are economically in our favor to one extreme. Third if the parameters are economically against us to one extreme. Even in the worst case scenario there is an annualized cost reduction by about 25%. In the best case scenario there is a cost reduction by 75%. The fixed capital investment for the novel process may be somewhat larger than the current, but due to the significant decreases in operating costs, this novel process is economically more efficient than the current method. If the

nitrogen rejection plants economics are determined, the novel process will even look better then. The economics were calculated using only a calculator in ProII. If the calculations need to be asses the ProII file may be looked into. Cost calculations included cooling water, electricity, heat exchangers, 2 compressors, 2 expanders, and 5 pumps.

Conclusion

The current method for natural gas processing is quite complex and requires many different processes for separation. A novel process has been developed that eliminated four of the major steps out of the seven, and combines them all into one step. The amine treating process, nitrogen rejection, the deethanizer and the demethanizers functions are all accomplished, with a cheaper annualized cost than the current method. The novel process has the ability to perform as a depropanizer also; however it was not done for this project. There are uncertain parameters, but even in the extreme case of these parameters causing our economics to be negatively affected, the novel process is still 25% cheaper than the current.

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