

Commercialization of Nitrogen-Rich Natural Gas

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Abstract

Currently, the natural gas supply in the United States does not support the nations demand. In subsequent years the United States will be faced with the decision to find alternative sources for natural gas or increase natural gas imports from foreign countries. A potential solution to ameliorate this issue is to utilize the nation's nitrogen rich natural gas reservoirs. The objective of this study is to identify and analyze potential uses for this low quality natural gas (LQNG). An economic analysis on the feasibility of production and commercialization of nitrogen rich natural gas was performed based on a mathematical model built to determine the best process combination based on maximizing net present value. The separation options include the purification of natural gas by cryogenic distillation, pressure swing adsorption, membranes, and molecular gate technology. The commercialization options include upgrading the natural gas to pipeline quality, conversion of methane to synthesis gas and its derivatives, and combustion of natural gas for power generation. The mathematical model found that urea was the most profitable process for natural gas field flow rates higher than 5 MMscf/day.

Table of Contents

Abstract	2
Introduction	5
Nitrogen Separation Technologies.....	10
Cryogenic Distillation	11
Pressure Swing Adsorption	11
Separation through membranes.....	12
Molecular Gate Pressure Swing Adsorption	13
Additional Processing.....	15
Dehydration	15
Desulfurization	15
Power Generation from Natural Gas	16
Steam Generation Units.....	16
Gas Turbines	17
NO _x emissions	17
Electricity Demand and Forecast	18
Synthesis Gas Product Selection	20
Hydrogen.....	21
Ammonia.....	21
Urea.....	22
Methanol.....	22
Formaldehyde	22
Acetic Acid.....	22
Dimethyl Ether	23
Synthetic Fuel.....	23

Mathematical Model	23
Results from the GAMS model.....	27
Conclusions and Recommendations	31
Resources	33

Introduction

Natural gas is one of the most vital sources of energy in the United States. It supplies approximately one half of all energy used in residential areas, and is one of the most promising fuel sources for industrial and commercial applications making up 18% of U.S. electricity generation by fuel sources¹. Natural gas is a fossil fuel primarily made up of methane along with traces of heavier hydrocarbons such as ethane, propane, and butane. The gas is colorless and odorless, but generates a great deal of energy when combusted. Natural gas is favored as a fuel source because unlike other energy sources, the combustion of natural gas is clean and does not emit harmful substances into the atmosphere.

The table below displays typical composition percentiles of natural gas.

Chemical	Formula	Composition Percentile
Methane	CH ₄	70-90%
Ethane	C ₂ H ₆	0-20%
Propane	C ₃ H ₈	
Butane	C ₄ H ₁₀	
Carbon Dioxide	CO ₂	0-8%
Oxygen	O ₂	0-0.2%
Nitrogen	N ₂	0-5%
Hydrogen sulfide	H ₂ S	0-5%
Rare gases	A, He, Ne, Xe	trace

Table 1: Natural gas composition percentiles²

Low Quality Natural Gas

Approximately 30% of all natural gas reserves in the United States contain low quality natural gas (LQNG). LQNG is gas from any reservoir containing excessive amounts of non-hydrocarbon components which place the gas outside of pipeline specifications. The most common contaminants of natural gas are carbon dioxide, nitrogen, and hydrogen sulfide. These non-combustible contaminants lower the

heating value of natural gas and must be removed prior to use. Changes in the heating value also impact the Wobbe index which is used to determine the interchangeability of fuel types. Aside from lowering the heating value, the contaminants are toxic, corrode pipe lines, and harm the environment¹. Water is also considered a contaminant due to risk associated with pipeline corrosion and freezing, however, all natural gas reservoirs contain quantities of water to some extent that must be removed by dehydration prior to processing. While there is no universal standard or government regulation for LQNG, the most commonly used specifications between gas purchasers and suppliers are:

- Natural gas containing greater than 2% carbon dioxide
- Natural gas containing greater than 4% nitrogen
- Natural gas containing greater than a 4% combination of carbon dioxide and nitrogen
- Natural gas containing greater than 4 ppm hydrogen sulfide

Minor contaminants of natural gas include helium, argon, hydrogen, and oxygen, however these chemicals typically act as inert gases and pose no major problems in processing LQNG.

LQNG contaminated by high concentrations of nitrogen account for 57% of all LQNG reserves, followed by carbon dioxide, and other contaminants as displayed in figure 1. In this study nitrogen was the primary contaminant targeted for removal to upgrade natural gas.

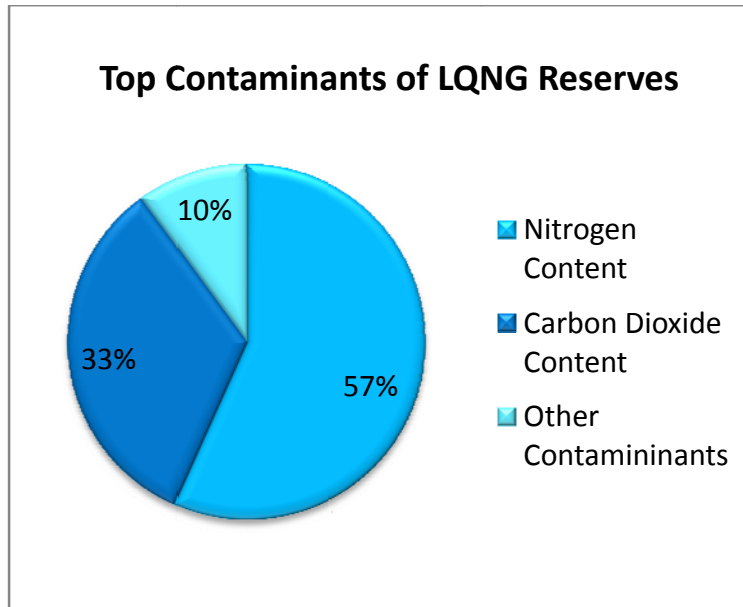


Figure 1: Major contaminates in natural gas

The mid-continent region has the largest area of LQNG reserves at 15.31 trillion cubic feet. Therefore, it would be advantageous to establish a process in this region to ensure a consistent supply of natural gas to process.

Region	High Nitrogen Natural Gas (TCF)
Mid-Continent	15.31
Rocky Mountain Foreland	3.61
Arkla-East Texas	1.67
Pernian Basin	0.94
West Coast Onshore	0.89
Williston Basin	0.4
Midwest	0.3
Appalachia	0.1

Table 2: High nitrogen natural gas by region in the United States

Statistics of high nitrogen content show that the majority of reserves contain 11-17% mole fraction of nitrogen.

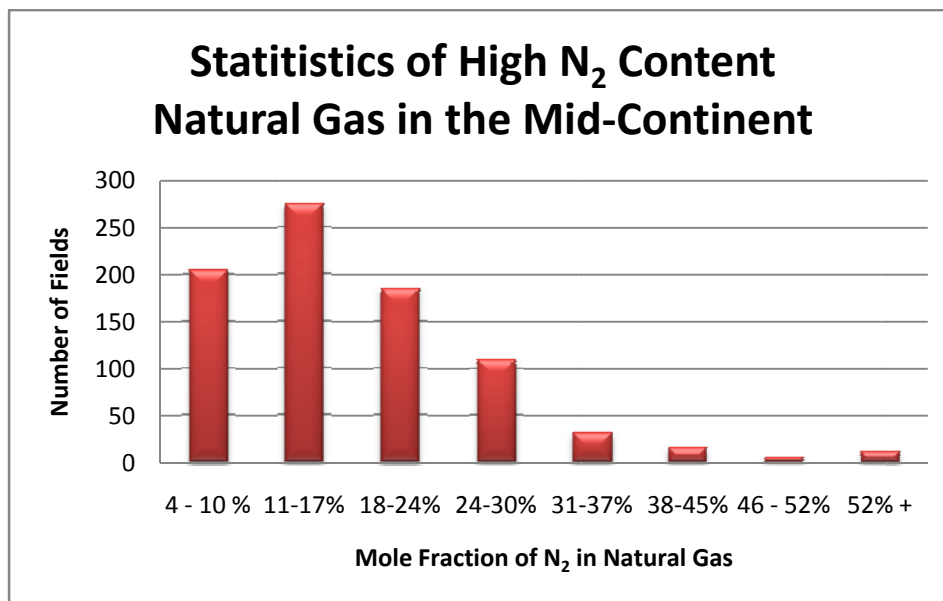


Figure 2: Statistics of high N₂ content natural gas in the mid-continent.

Superstructure of Processes

The twenty three processes examined as monetization options for LQNG are displayed in Figure 3. The chemical process is labeled in each box and the chemical produced is indicated by each process flow line. All intermediate products were taken into consideration for market sale. The three major pathways of process flow are as follows:

- The removal of nitrogen to obtain pipeline quality natural gas through separation processes.
- The combustion of natural gas as a fuel source to generate electricity for market and centralized utility.
- The conversion of natural gas to synthesis gas by methane steam reforming. Several chemicals and fuels can be developed from synthesis gases that have potentially promising markets.

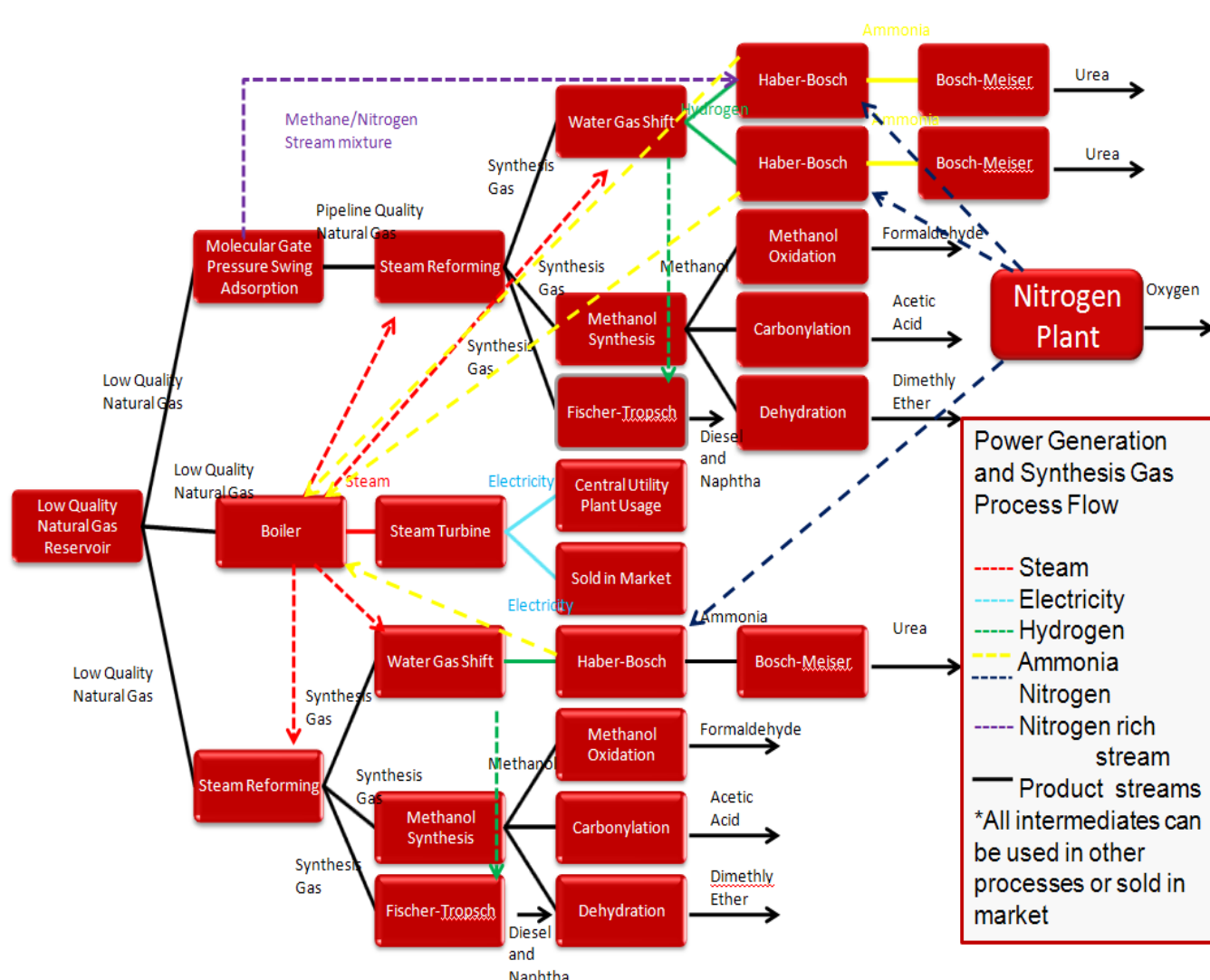


Figure 3: Superstructure diagram of monetization option model

The synthesis gas conversion was employed with and without the nitrogen contaminant to test the effects, if any, of reactor size by keeping nitrogen in the system as an inert. A nitrogen plant was also installed into the model to aid in ammonia and urea production. The process model took advantage of centralized utility with the flow of electricity, steam, and other chemicals from process to process as

necessary. The integration of centralized utility allows production to be independent of unfavorable market trends by eliminating the need to purchase outside goods. Each process will further be discussed in detail in the report.

Nitrogen Separation Technologies

Several options have been explored for the utilization of nitrogen rich natural gas reserves. Currently, the two main methods for removing nitrogen from natural gas are cryogenic distillation and pressure swing adsorption. The drawbacks to these applications are that they are both expensive and complex. Blending contaminated streams with high quality gas is another option, but sufficient flow volumes of high quality gas are needed to dilute the nitrogen present and the majority of LQNG reserves contain small quantities of gas. Separation through membranes and Molecular Gate adsorption are both promising applications that are currently in the development and early commercialization stage. Table 3 summarizes current nitrogen removal technologies.

Process	Method of Separation	Application	Total Capital Cost (\$/Mscfd)*	Operating Cost (\$/Mscf)*
Cryogenic Distillation	Distillation at cryogenic temperatures	High flow rates	\$1184	\$ 1.30
Pressure Swing Adsorption	Adsorption of methane	Small to Medium flow rates	\$1320	\$1.65
Membranes	Methane moves faster through barrier	Low flow rates	\$277	\$.30
Molecular Gate PSA	Adsorption of nitrogen	High Nitrogen Content	\$226	\$.16

Table 3: Nitrogen Separation Technologies⁴

Cryogenic Distillation

Cryogenic distillation is the most common method of removing nitrogen from natural gas. For nitrogen < 20% a single column can be used, otherwise a dual configuration is best. This technology is based on the use of cold temperatures (below -150 °C), therefore water vapor, carbon dioxide, C₃₊ hydrocarbons, and aromatics must all be removed in costly pretreatment operations⁴ to avoid damage to the equipment. Due to the complexity of cryogenic separation, it is not economically viable at rates lower than 50-100 MMscfd. However, most of the gas with high nitrogen content is located in smaller reserves where this technology would not be applicable⁴.

Pressure Swing Adsorption

After cryogenic distillation, pressure swing adsorption is the most widely used method for the separation of nitrogen from natural gas. Variations in the adsorbents polarity and size determine the degree of separation in this process. The main factors that determine the amount being adsorbed are the adsorbent being used, the component being adsorbed, temperature, and partial pressure of the adsorbate⁵.

Pressure swing adsorption involves two major steps: the introduction on LQNG feed at high pressures and regeneration of the adsorbent material at low pressures. Methane is adsorbed into the bed allowing nitrogen to be removed at feed pressure. Once nitrogen has been removed from the feed, regeneration is accomplished by dropping, or “swinging”, the column pressure allowing the gas to desorb, purging the adsorbent of methane. This requires costly recompression of the methane rich stream⁵ which makes this method unsatisfactory for the purposes being investigated.

Separation Through Membranes

Purifying nitrogen rich natural gas through the use of membranes poses many challenges, but it is currently being investigated with nitrogen-permeable glassy membranes or methane-permeable rubber membranes. Membranes are selective, semi-permeable barriers that allow different components to pass through at different rates. Permeability is defined as the rate at which gas moves through a membrane of standard thickness (1 cm) under a standard driving force (a pressure difference of 1 cmHg)⁵. This method has significant savings in energy cost compared to other methods of nitrogen removal due to the simplicity in operation.

At low temperatures, nitrogen is easily removed in rubber silicon membranes. Gas liquefies on the surface of the membrane, dissolves, diffuses, and then vaporizes on the other side. A high-pressure gas mixture feed passes along one side of the membrane allowing the molecules that permeate the membrane to be swept using a gas on the other side of the membrane in the so-called permeate stream. The non-permeating molecules that remain on the feed-stream side exit the membrane as the retentate stream⁵. An illustration of a spiral wound membrane, commonly used in natural gas purification due to its high packing density, is seen in figure 4.

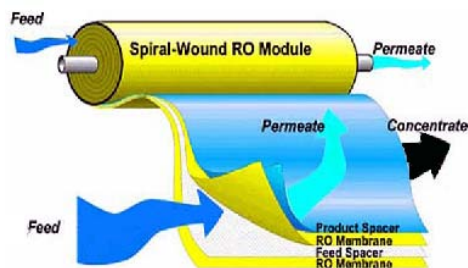


Figure 4: Spiral Wound membrane model

The process design used for a stand-alone membrane process is shown in Figure 5. Three consecutive heat exchangers are used to cool the feed gas in order to improve the degree of separation and condense valuable heavy hydrocarbons. The uncondensed portion of the feed gas is processed through the membrane to produce a methane rich permeate product and a high pressure nitrogen rich residue stream byproduct that is converted to a low pressure fuel stream after cooling the feed.

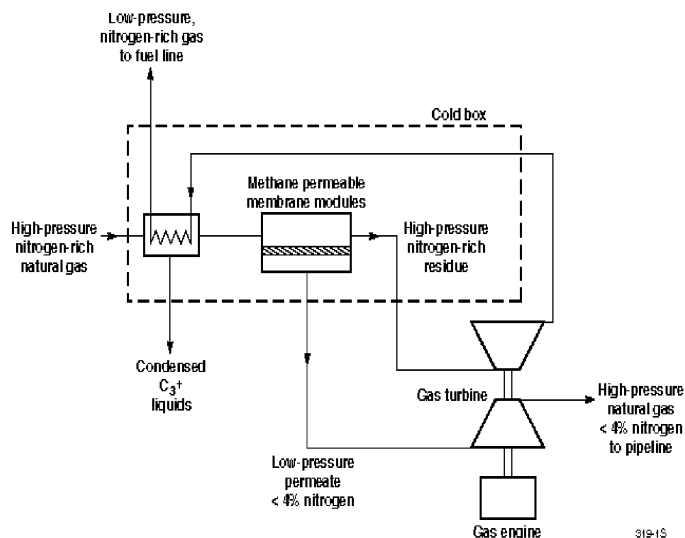


Figure 5: Membrane separation process flow diagram⁵

Molecular Gate Pressure Swing Adsorption

The molecular gate pressure swing adsorption process, originally developed by Engelhard Corporation, has proven to be more cost effective than the traditional process. This adsorption is unique from other adsorption processes, since the nitrogen is adsorbed instead of the methane. The simplicity and reliability of this new technology has made it a leading option for upgrading nitrogen contaminated streams since its commercialization in 2001⁶. The molecular gate nitrogen system is capable of handling flow rates as low as 0.5 MMscfd with the economics of scale increasing with flow rate.

The Molecular GateTM adsorbent material is titanium silicate (CTS-1) designed with size selective pore openings to remove nitrogen from methane. The molecular sieve with a pore size of 3.7Å is custom

designed to allow smaller nitrogen molecules (3.7 \AA) to adsorb into the bed, penetrating the crystalline structure while larger methane molecules (3.8 \AA) are excluded exiting the column at feed pressure⁶. Figure 6 illustrates separation by use of the Molecular Gate.

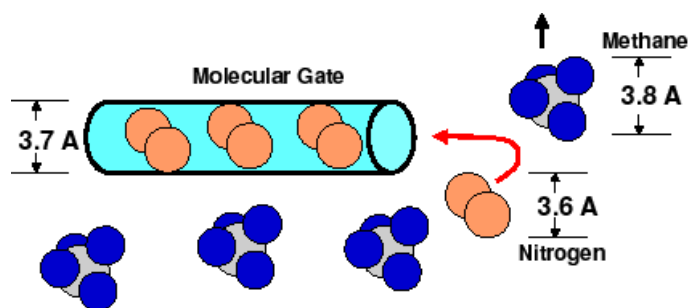


Figure 6: Molecular gate size selective separation mechanism⁷

The molecular gate operates at pressures ranging from 100 – 800 psia. A series of 3-9 absorbers are used in order to supply continuous operation. When the adsorbent is saturated with nitrogen, the vessel is replaced with a regenerated vessel. The methane rich stream is recycled to increase the methane recovery, and the spent vessel is depressurized to produce a low pressure nitrogen rich stream that can be used as a fuel source.

Additional Processing

Dehydration

All gas wells contain quantities of water that must be removed in order to avoid freezing, corrosion, and hydrate formation. Dehydrating natural gas usually involves one of two processes: absorption or adsorption. Absorption is the use of a drying agent, such as glycol, to remove water vapor while adsorption occurs when the water vapor is condensed and accumulated on a solid or liquid surface⁷.

In glycol dehydration, either diethylene glycol (DEG) or triethylene glycol (TEG)⁷ and liquid desiccant dehydrators serve to absorb water vapor from the gas stream in a liquid gas contactor. Glycol has a high affinity for water; therefore, it will serve to steal the water out of the gas stream. The heavy glycol particles will then sink to the bottom of the contactor where water is boiled out of the solution in order to reprocess the glycol. A recent addition to this technology is the introduction of a flash tank separator-condenser to improve methane recovery. This operation allows the capture of methane that was carried away with the glycol stream recovering up to 90 - 99% of methane what would have otherwise been flared into the atmosphere⁷.

Solid desiccation dehydration is a method that involves two or more adsorption towers filled with a solid desiccant, typically activated alumina, granular silica gel, and other materials with high water capture weight percents. Wet gas passes around the particles of desiccant material, and water is retained on the surface of these desiccant particles. A high temperature heater is used to vaporize saturated columns leaving dry desiccant allowing for further dehydration.

Desulfurization

Hydrogen sulfide is both poisonous and foul-smelling; therefore, a mandatory limit of 4 ppm is set for all transmission lines. The combustion products of hydrogen sulfide release sulfur dioxide into the

atmosphere which is a significant environmental concern. Amine solutions are used to remove the hydrogen sulfide through the amine or Girdler process which works similarly to glycol absorption. Contaminated gas is run through a tower containing an amine solution that has a high affinity for sulfur. Monoethanolamine (MEA) and diethanolamine (DEA) are the most common solutions used. Like glycol dehydration, the amine solution can be processed and regenerated for continuous removal of hydrogen sulfide⁷.

Each step in the process model called from dehydration and desulfurization processing prior to operation, therefore it was not taken into cost considerations.

Power Generation from Natural Gas

One consideration for the commercialization of LQNG is electrical power generation. Since the 1970's, natural gas has become the fuel source of choice due to economic, environmental, and technological advantages. New power plants commonly use natural gas as an alternative to coal and nuclear sources which release high levels of pollutants into the air. The high nitrogen content in the gas stream gives it a medium heating value (200 to 800 BTU/scf)⁸. Combustion of fuel for electrical power generation is normally conducted using steam unit, gas turbines, or a combined-cycle turbine.

Steam Generation Units

Steam units are the most basic combustion form of power generation. The process involves the burning of fossil fuels in a boiler to heat water and produce steam that powers a turbine and generates electricity. While the simplicity of this operation is advantageous the process performs poorly in terms of energy efficiency converting only 30-35% of the thermal energy produced into steam. Steam units are commonly used for the combustion of large coal and nuclear generation plants⁸.

Gas Turbines

Gas turbines operate by using the heated gases of fossil fuels to power the turbine and generate electricity. Turbines are made up of three major components, a compressor, combustor, and power turbine. The compressor draws in ambient air and compresses it up to 30 times ambient pressure. In the combustor, fuel is introduced, ignited, and burned. Hot gases from combustion are diluted with air from the compressor and directed to the power turbine section at temperatures up to 2600 °F. Here, energy is expanded into the power turbine and recovered in the form of shaft horsepower⁴. This process is illustrated in figure 8.

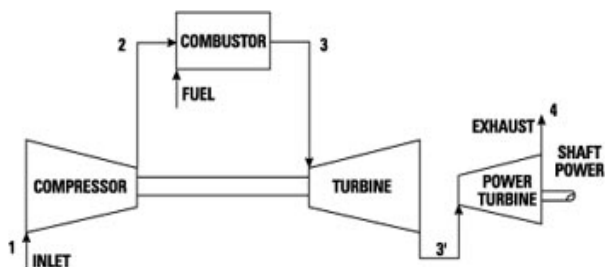


Figure 8: Gas turbine process flow diagram⁸

It was determined that the combination of a steam boiler and gas turbine were necessary for process operation in the process flow model created.

Nitrogen Oxide Emissions

When combusting natural gas with nitrogen, one of the byproducts formed is nitrogen oxide (NO_x), which is any binary combination of nitrogen and oxygen. NO_x emissions are very harmful to the environment and can be fatal to humans at high concentrations. NO_x reduction can be accomplished using post-combustion control techniques. Post-combustion technologies chemically reduce NO_x to molecular nitrogen (N₂) and water with or without the use of a catalyst.

Specific NO_x control technologies were identified from the United States EPA control technology database search, technical literature, control equipment vendor information, and personal process knowledge and engineering experience. Potentially applicable control options for NO_x identified as a result of the above research are summarized in the Table 4 below. The table also provides a typical control range for each option.

Control Technology	Typical Emission Levels
SCONO _x TM	2-5 ppm
XONON flameless combustion	3-5 ppm
Selective catalytic reduction (SCR)	5-9 ppm
Selective non-catalytic reduction (SNCR)	9-25 ppm
Non-selective catalytic reduction (NSCR)	9-25 ppm
Dry low NO _x combustor	9-25 ppm
Water or steam injection	25-40 ppm

Table 4: Applicable NO_x Control Options⁴

The control technology being used in this process is selective catalytic reduction due to the cost effectiveness and pollutant control of this method. The technology has been applied to many industrial combustion turbines and has been provide reliable. This technology works by mixing ammonia with the NO_x emissions and running the mixture over a zeolite based catalyst, this breaks down the mixture into nitrogen and water.

Electricity Demand and Forecast

Figure 10 represents the growing demand for electricity in the United States. Industrial, commercial, and residential usages are factored into this forecast.

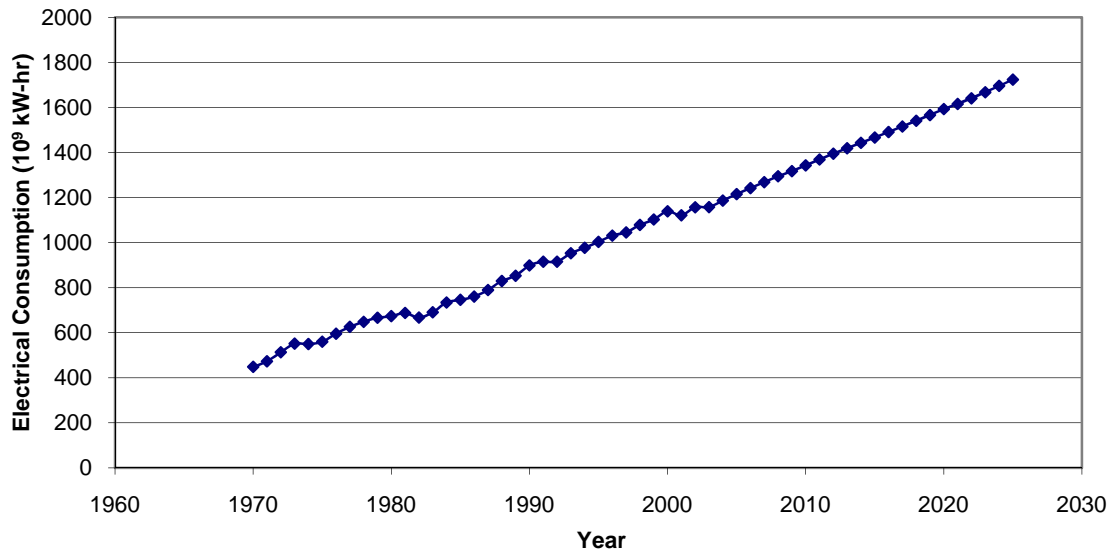


Figure 10: Growing demand for electricity in the United States⁴

Figure 11 shows the stability of the electrify market. This is due to a decrease in the distribution component (making up 24% of the market) along with a gradual increase in generation component (64% of market). Uncertainties affecting the electricity market in the United States include price fluctuations due to climates, regional markets, demand, and raw fuel cost⁴.

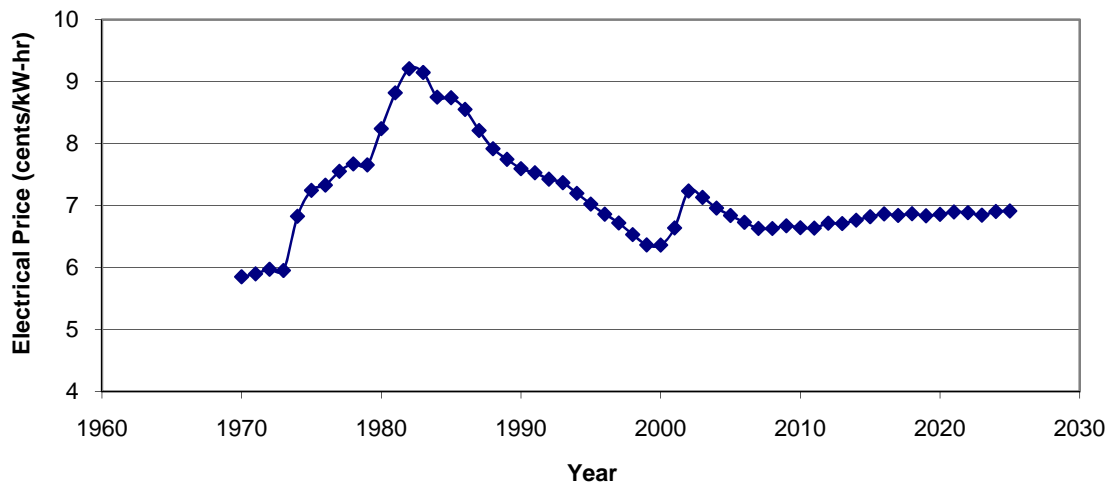
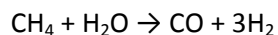


Figure 11: Projected market for electricity in the United States⁴

Synthesis Gas Product Selection

Synthesis gas is a gaseous mixture made up of varying concentrations of carbon monoxide and hydrogen. Syngas is produced from the gasification of carbon containing fuel by the follow equation.



Synthesis can also be used as an intermediate to produce several different products and fuels. For this evaluation eight different products were considered and compared to find the most valuable operation for the commercialization of low quality natural gas. These products were analyzed on the basis of demand, raw material and market price, operating cost, and capital investment. As illustrated in figure 3, each process was evaluated with and without nitrogen as a reactant or inert.

Hydrogen

Hydrogen is a colorless, odorless gas that is synthesized by the steam reforming of methane. Steam reforming is the most common method of producing commercial bulk hydrogen. At temperatures of 700-1100°C in the presence of a metal-based catalyst, such as nickel, steam reacts with methane to form hydrogen and carbon monoxide by the following reaction.



Additional hydrogen can be recovered at low temperatures along with carbon dioxide in the water shift reaction.



Hydrogen is most commonly used for the processing of fossil fuels and the production of ammonia or methanol³.

Ammonia

Ammonia is a colorless alkaline gas with a penetrating odor. It is synthesized by the Haber - Bosch process, with the use of an iron substrate (in which aluminum oxide and potassium oxide are used as promoters) to react hydrogen and nitrogen to form ammonia.



The reaction is carried out under operating conditions of 150-250 atm and 450 - 500°C. Ammonia is one of the most largely produced inorganic chemicals as a key component in the fertilizer industry. Other uses include the production of urea (also substantial in fertilizers), nitric acid, and ammonium nitrate³.

Urea

Urea is produced as a solid typically in the form of prills or granules. It is most commonly used in fertilizers, plastics, and as protein supplement in animal feed. Urea is created by reacting ammonia with carbon dioxide³.



Methanol

Methanol, the simplest alcohol, is a light, volatile, colorless, and flammable chemical whose uses include antifreeze, solvents, fuels, and as an intermediate in the production of other products. Methanol is formed from synthesis gas in steam-methane reforming or partial oxidation at low temperature and high pressures³.



Formaldehyde

From the catalytic oxidation and dehydrogenation of methanol, formaldehyde is created. Silver metal or iron oxide with molybdenum and vanadium are the most common catalysts used.



The chemical is most commonly used to produce polymers and a wide variety of specialty chemicals.

Acetic Acid

Acetic acid, also known as ethanoic acid, is a weak carboxylic acid used in the production of vinyl acetate monomer and acetic anhydride. The chemical is corrosive and its vapor causes irritation of the eyes, nose, and throat, however it is best recognized as the chemical that contributes to the pungent taste and smell of vinegar. A rhodium-based catalyst is used to produce acetic acid from methanol by methanol carbonylation³.



Dimethyl Ether

Dimethyl ether is colorless, gaseous ether commonly used as aerosol spray propellant or as a refrigerant. It is also commonly used in conjunction with propane to decrease temperatures as low as negative 60°F. This feature is significant in cryogenic distillation. Dimethyl ether is produced in the dehydration of methanol by the following equation:



Synthetic Fuel

Synthetic fuel, or synfuel, is a liquid fuel source obtained from natural gas. The Fischer-Tropsch process involves the reaction of synthesis gas over an iron or cobalt catalyst to produce liquid hydrocarbons. Typical catalysts used for this reaction are iron and cobalt. The reaction is displayed in equation x, where n is a positive integer.



Diesel and naphtha are the most common products produced from synthetic fuel. Diesel can be used as a direct fuel source for diesel powered engines, and naphtha is used as a feed source to create higher octane rated gasoline³.

Mathematical Model

In order to determine the most profitable commercialization options for LQNG, a mathematical model was coded and run in the Generic Algebraic Modeling System (GAMS). The model uses Mixed Integer Linear Programming (MILP) methodology where continuous; integer and binary variables are combined

in a set of linear constraints that determine the feasible region for the solution of the problem. A total investment of \$100,000,000 was set to maximized is the Net Present Value (NPV) of the project.

The following assumptions were made in this model:

- 1.) The minimum accepted rate of investment was set to 11%, this is based on the investment being entered into an established market. (Design pg. 322)
- 2.) The maximum investment available is \$100,000,000.
- 3.) The project life is assumed to be twenty years.
- 4.) There is a standard inflation rate applied to all final product costs and raw material costs, the reason for this, is because it is very difficult to predict the future prices of many of the chemicals.
- 5.) Natural gas was previously taken from the ground and delivered; therefore there was no cost in obtaining the natural gas. This assumption leads to very high net present worth values, since the natural gas is “free” and all cost associated extracting the gas from the reservoir site were negligible.

The model sets were defined as follows, the variable i is set to represent the 23 possible processes displayed in figure 1, j corresponds to the chemicals used within the operation, and t is a time span of 20 years during which operating conditions remain constant. The following table defines variables used in the model.

Variable	Definition
$\text{capacity}(i,t)$	capacity of each process
z	net present worth
$Y(i,t)$	binary variable
$\text{FCI}(i,t)$	fixed capital

revenue(j,t)	revenue
sales(i,j,t)	total sold
input(i,j,t)	total input into process
output(i,j,t)	total output from process
flow(i,k,j,t)	flow from one process to another
raw(i,j,t)	raw materials needed for processes
materialcost	total raw materials cost
operatingcost(i,t)	operating cost
expansion(i,t)	expansion
initialcapacity(i,t)	initial capacity

Table 4: GAMS variables defined

The capacity of each process is set by a minimum and maximum value. Capacity ranges were varied in order to generate data relating NPV to capacity for profitable processes. Capacity restrictions were set as follows.

$$initialcapacity(i,t) - Y(i,t) * \min capacity(i) \geq 0 \quad (10)$$

$$initialcapacity(i,t) - Y(i,t) * \max capacity(i) \leq 0 \quad (11)$$

Similarly, the expansion of processes increasing capacity over time was governed by the following equations.

$$expansion(i,t) - X(i,t) * \min expansion(i) \geq 0 \quad (12)$$

$$expansion(i,t) - X(i,t) * \min expansion(i) \leq 0 \quad (13)$$

The chemical flow is defined by the input and output of each process. Inputs include raw materials and chemicals that flow from one process to the next.

$$input(i, j, t) = raw(i, j, t) + \sum_{k \neq i} flow(k, i, j, t) \quad (14)$$

The stoichiometry of each reaction was accounted for by the following:

$$input(i, j, t) = f(i, j) * \sum_j input(i, j, t) \quad (15)$$

To further define the flow of the system, mass balances and constraints on output values were defined.

This standard mass balance states that everything that comes into the system must come out. The variable gamma was used to represent flow from one process to the next.

$$\sum_j input(i, j, t) = \sum_j output(i, j, t) \quad (16)$$

$$output(i, j, t) = sales(i, j, t) + \sum_{k \neq j}^{k \neq j} flow(i, j, k, t) \quad (17)$$

$$flow(i, k, j, t) \leq gamma(i, j, k) * output(i, j, k) \quad (18)$$

To ensure that the market is not oversaturated with products, constraints were set on sales and demand trends.

$$\sum_i sales(i, j, t) \leq demand(j, t) \quad (19)$$

Revenue generated from each process is the raw profit made prior to any deductions, such as operating costs. To account for costs associated with maintenance, labor, and utilities, operating cost must be calculated for each process.

$$revenue(j, t) = price(j, t) \sum_i sales(i, j, t) \quad (20)$$

$$operating\ cost(i, t) = delta(i) \sum_t^{t \leq t} Y(i, t) + expansion(i) \sum_j output(i, j, t) \quad (21)$$

Fixed capital investment, is the amount of money invested to start up the process. As stated, a \$100,000,000 investment was allocated for the construction and operation of the commercialization processes.

$$FC(i,t) = Y(i,t) * \alpha(i) + \beta(i) * initialcapacity(i,t) \quad (22)$$

$$\sum_{i,t} \frac{FC(i,t) + material\ cost(t) * (\frac{0.1}{10})}{int\ erest^{year(t)}} \leq investment \quad (23)$$

Finally, the objective function of the mathematical model is to maximize the net present worth of the project based on the following equation.

$$NPV(z) = \sum_t (\sum_j revenue(j,t) - \sum_i operating\ cost(i,t) - \sum_i FC(i,t) - \frac{material\ cost(t)}{int\ erest^{year(t)}}) \quad (24)$$

Using GAMS to construct the superstructure of processes illustrated by Figure 3 was essential in determining the best options for nitrogen rich natural gas commercialization. In using this program detailed spreadsheets were created specifying the input stoichiometry, output stoichiometry, demand, cost of raw materials, and flow from each process over a twenty year period for all twenty three processes. With the compilation of economic equations, process costs, and chemical flow and reaction data, GAMS was able to successfully generate results for the 176,640,000 combinations defined in a matter of seconds. This is also beneficial because different factors such as capacity and nitrogen content could easily be altered to generate new results based on varying specifications.

Results

The mathematical model evaluated the 23 processes and reported operating cost, revenue, capital cost, and raw material cost. The net present value (NPV) of each process was also calculated based on the specified criterion in equation 24. NPV is a profitability calculation that determines if a process is advantageous based on the difference of all cash inflows and outflows associated with a given process. A profitable process is defined by a positive NPV while an unprofitable process will have a negative value. This numerical factor was imperative in deciding which process should and should not be built.

Two different capacities and three different nitrogen contents were tested in the model to determine the type of process that would be most profitable. For a reserve size smaller than 5MMSCF/D with a nitrogen content less than 30%, the most profitable option was to upgrade the natural gas using the molecular gate technology and sell the pipeline quality gas. The reasoning behind the simple solution is that more complex operations would not generate enough revenue to make up for their high capital costs.

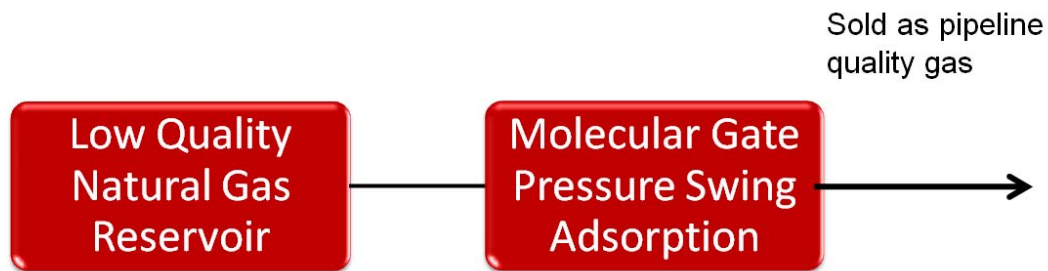


Figure 12: Results for $Q < 5\text{MMSCF/D}$ and Nitrogen Composition 4 - 30%

If the reserve capacity is set greater than 5 MMSCF/D and the nitrogen content is between 15-30%, then the best option is to upgrade the natural gas using the molecular gate technology and then converting it to urea using the synthesis gas conversion route. The nitrogen plant is capable of supplying extra nitrogen needed and provides a market for oxygen. Steam and electricity generated from the contaminated natural gas will work as centralized utility to fuel the other processes.

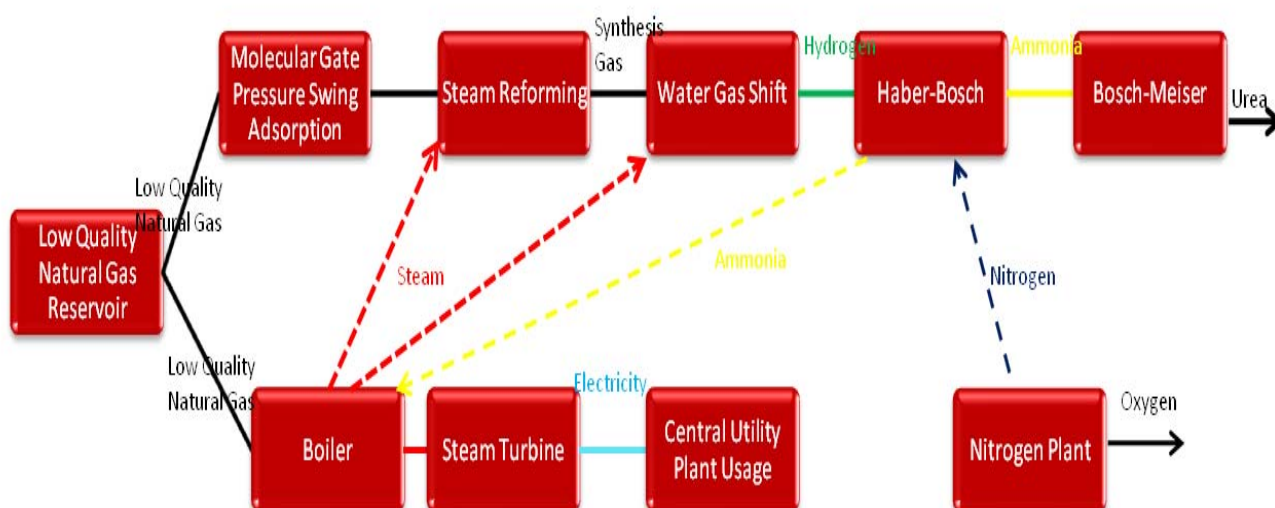


Figure 13: Results for $Q > 5\text{MMSCF/D}$ and Nitrogen Composition 15- 30%

The last option considered a reserve size greater than 5 MMSCF/D and a nitrogen content less than 15%. The production of urea was also favored for this option; however, the subsequent purification was not necessary due to the low concentration of nitrogen. The reduction in nitrogen allowed for smaller reactor sizes in the process allowing the nitrogen to remain the process as an inert without impacting costs. Centralized utility for steam, electricity, and nitrogen were also factors of this operation as well.

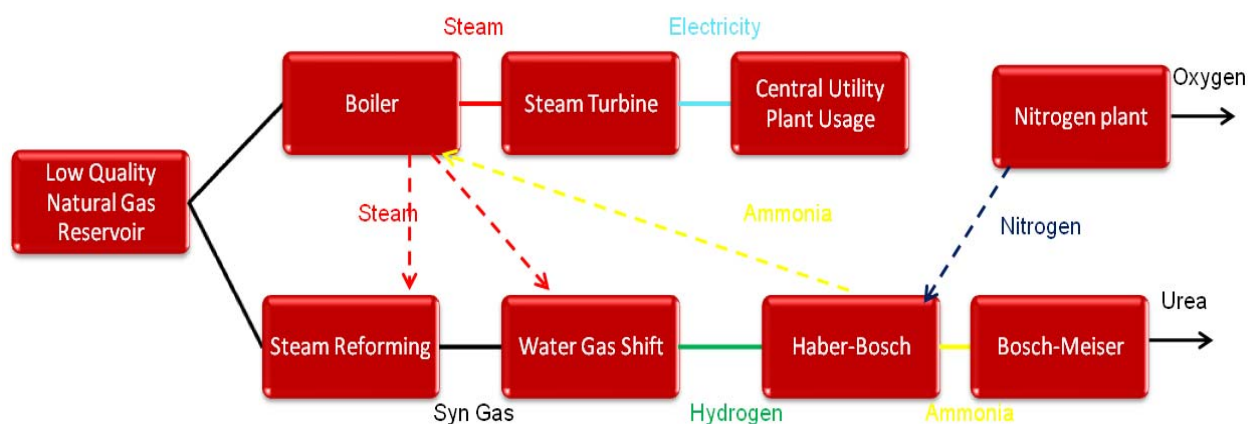


Figure 15: Results for $Q > 5\text{MMSCF/D}$ and Nitrogen Composition 4- 15%

Table 5 below shows the investment costs and NPV for all three options considered.

Option #	Reserve Size	% N ₂ Content	Initial Investment	NPV
1	3 MMSCF/D	15%	\$475,000	\$ 20,425,000
2	10 MMSCF/D	25%	\$9,250,000	\$ 138,600,000
3	10 MMSCF/D	10%	\$6,200,000	\$169,350,000

Table 5: Summary of GAMS Results

Since urea was the most economical choice of the mathematical model market of urea was explored. Approximately 90% of urea is used in producing fertilizer; while the other 10% is used in various commodities such as cigarettes, toothpaste, pretzels, etc.. Since these markets have been established for long periods of time and are fairly constant the demand for urea has been constant for the past seven years as shown in Figure 16.

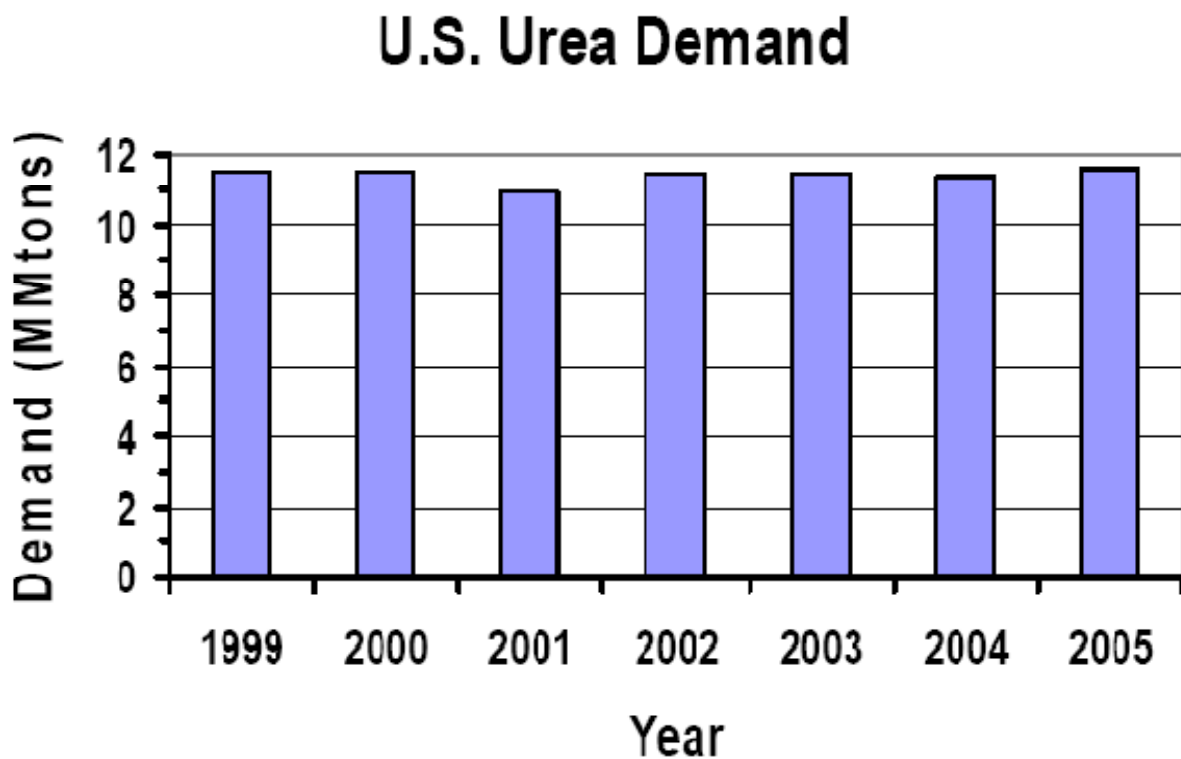


Figure 16: Urea demand forecast³

The price of urea over the past has been volatile and is dependent on the market price of nitrogen and natural gas. Since both nitrogen and natural gas are being produced in the plant, the price should be stable.

Conclusions

With the forecast of the natural gas demand in the United States continuing to exceed the supply of natural gas, low quality natural gas is a great alternative. The evaluation of low quality natural gas leads to two major conclusions. The first is that the most economical way of separating the nitrogen from natural gas is using pressure swing adsorption with molecular gate technology. The second is that the most economical product produced from nitrogen rich natural gas varies by reserve capacity and nitrogen content. If reserve capacity is low the natural gas is most profitable by removing the nitrogen using the PSA process and selling the natural gas via pipeline. If reserve capacity is high the most profitable product produced is urea and is most economically produced by separating the nitrogen out of the natural gas before processing at high nitrogen contents and keeping the nitrogen in when processing at low nitrogen contents.

Resources

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