PROCESS DESIGN AND SIMULATION OF NATURAL GAS DEHYDRATION USING TRIETHYLENE GLYCOL

A Thesis

by

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ABSTRACT

Natural gas is a major source of energy and a source of feedstocks used for a large number of petrochemical products, therefore its production is vital for the world economy. Every year the world uses close to 100 trillion standard cubic feet of natural gas. All of this gas requires treatment before it enters the pipeline, making natural gas processing by far the largest market for industrial gas separation processes and equipment. Natural gas needs to be dehydrated in order to avoid corrosion following water condensation, especially in the presence of acid gases and plugging that may occur if the natural gas temperature reaches the hydrate formation temperature.

Among the many available options for natural gas dehydration, absorption by means of triethyleneglycol (TEG) has been used for many years and it is now a widely industry established process. Absorber-stripper units represent a proven, well-accepted technology in the gas processing industry mainly due to TEG's low volatility, high hygroscopicity and high thermal stability. Also, because of perfect performance of TEG application in the natural gas dehydration field, numerous research focus on the TEG dehydration process to improve the dehydrating parameters.

In this research thesis, a brief review of the current methods used by the industry for natural gas dehydration is presented, and the engineering fundamentals of each process are discussed. Approximately 40,000 absorber-stripper units are in operation in the United States and many more around the world. The water content of high pressure, water-saturated gas is usually 1000 ppm and the objective of glycol absorption gas dryers is to bring this concentration to 100 ppm.

The main goal of this research work is to perform a systematic analysis on the use of TEG for the dehydration of natural gas by developing a process simulation model with cost estimation. Different system designs and the effects of operating parameters on the performance of TEG dehydration will be investigated. Furthermore, this work will discuss the limitation of natural gas dehydration using TEG and propose future alternative methods of natural gas dehydration using membranes.

Key Words: Natural gas, dehydration, triethyleneglycol, process simulation, modeling

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I. INTRODUCTION

I.a. Natural gas as the fuel for energy transition.

Energy is here to stay. The pandemic will no doubt lead to a new normal for how the world works and how businesses operate, but it is also revealing the fundamental unsustainability of a collapse in economic activity and development. It may be hard to imagine the recovery when energy demand has fallen off a cliff and natural gas prices are testing generational lows. However, when the COVID-19 crisis and the economic shock waves it has unleashed subside, the planet's thirst for energy will remain. For starters, a billion people around the world don't have electricity, and close to 3 billion don't have access to clean fuel for cooking. Providing more energy to people while reducing its impact on the planet is one of the 21st century's greatest challenges.

Natural gas can help to meet that challenge by reducing emissions and improving air quality when it replaces coal and diesel. Natural gas is also a reliable partner for renewable energy sources; providing critical support for wind, solar and hydroelectricity by helping to match supply and demand requirements. Natural gas is also vital in parts of the economy that are more difficult to electrify, including industrial processes and freight transport.

Natural gas has been a major enabler of change to a cleaner energy mix, especially in the power sector. Gas has steadily displaced coal for baseload generation and has been integral to enabling the dramatic growth of intermittent renewable electricity sources, such as solar and wind. With carbon emissions half that of coal, natural gas has received relatively little credit for lowering emissions. In the United States, for example, gas has been responsible for 50 percent of the carbon emissions reductions since 2007 (see figure 1). Advances in upstream gas production technologies and costs as well as midstream infrastructure development mean that we now take an abundant, stable, low-cost gas supply for granted in North America and many other parts of the world. Innovations in liquefied natural gas (LNG) financing and development are transforming the way we think about connecting that plentiful supply to far-flung sources of demand. Gas-to-power projects hold the promise of filling electricity supply gaps around the world, and every forecast shows natural gas to be a growing part of the energy mix.



Figure 1: Use of natural gas has helped reduced carbon emissions. [1]

The key issues that support the idea that natural gas would play a big role in the future energy mix are summarized below [5]:

- There are abundant supplies of natural gas in the world, and many of these supplies can be developed and produced at relatively low cost. In the U.S., despite their relative maturity, natural gas resources continue to grow, and the development of low-cost and abundant unconventional natural gas resources, particularly shale gas, has a material impact on future availability and price.
- Unlike other fossil fuels, natural gas plays a major role in most sectors of the modern economy — power generation, industrial, commercial, and residential. It is clean and flexible. The role of natural gas in the world is likely to continue to expand under almost all circumstances, as a result of its availability, its utility, and its comparatively low cost.
- 3. In a carbon-constrained economy, the relative importance of natural gas is likely to increase even further, as it is one of the most cost-effective means by which to maintain energy supplies while reducing CO₂ emissions. This is particularly true in the electric power sector, where, in the U.S., natural gas sets the cost benchmark against which other clean power sources must compete to remove the marginal ton of CO₂.
- 4. In the U.S., a combination of demand reduction and displacement of coal-fired power by gas-fired generation is the lowestcost way to reduce CO₂ emissions by up to 50%. For more stringent CO₂ emissions reductions, further de-

carbonization of the energy sector will be required; but natural gas provides a cost-effective bridge to such a low-carbon future.

- 5. Increased utilization of existing natural gas combined cycle (NGCC) power plants provides a relatively, low-cost short-term opportunity to reduce U.S. CO₂ emissions by up to 20% in the electric power sector, or 8% overall, with minimal additional capital investment in generation and no new technology requirements.
- 6. Natural gas-fired power capacity will play an increasingly important role in providing backup to growing supplies of intermittent renewable energy, in the absence of a breakthrough that provides affordable utility-scale storage. But in most cases, increases in renewable power generation will be at the expense of natural gas-fired power generation in the U.S.
- 7. The current supply outlook for natural gas will contribute to greater competitiveness of U.S. manufacturing, while the use of more efficient technologies could offset increases in demand and provide costeffective compliance with emerging environmental requirements.
- Transformation of the current approach to appliance standards to one based on full fuel cycle analysis will enable better comparison of different energy supply options in commercial and residential applications.
- 9. Natural gas use in the transportation sector is likely to increase, with the primary benefit being reduced oil dependence. Compressed natural gas (CNG) will play a role, particularly for high-mileage fleets, but the advantages of liquid fuel in transportation suggest that the chemical conversion of gas into some form of liquid fuel may be the best pathway to significant market penetration.

Every year, the world produces close to 132 bcm (Billion cubic meters) of natural gas. According to International Energy Agency in 2019 global production of natural gas hit a new high, breaking the 4 Tcm (trillion cubic feet) threshold for the first time with 4.088 Bcm (billion cubic feet) produced, +3.3% compared to 2018. [2] This trend is expected to continue as natural gas is considered to be the transitional fuel towards a more sustainable future where there will be limited use of fossil fuels in order to mitigate the effects of global warming and climate change.

The COVID-19 pandemic had a critical impact on the global natural gas market in 2020. Both supply and demand contracted along with economic activity as governments across the world imposed restrictive measures to mitigate the virus' impact. Global natural gas production in 2020 fell by 2.5%, down to 4014 Bcm, its first decline since the financial crisis. Since that previous drop in 2009, global natural gas production had expanded by almost 1 Tcm (trillion cubic feet), with an annually compounded growth rate of 2.5%. At the OECD level, both OECD Americas and OECD Europe contributed to the 26.1 Bcm (billion cubic feet) cut in natural gas production in 2020, driven respectively by the USA (-1.4% y-o-y, -13.5 Bcm) and the Netherlands (-27.9% y-o-y, -9.3 Bcm), following the continuous enforcement of production caps on the Groningen field. Year-over-year (y-o-y) is a method of evaluating two or more measured events to compare the results at one period with those of a comparable period on an annualized basis OECD Asia and Oceania partially balanced this trend, with a 11.5 Bcm increase (+7.6% y-o-y) in natural gas production in 2020, just over half of the previous year's growth. [3]



Figure 2 :World natural gas production by region, 1973-2020. [3]

In 2020, global demand for natural gas shrank by 1.2%, falling to 3 970 Bcm, below the 4 Tcm floor reached in 2019.

At the OECD level, natural gas demand in 2020 contracted by 27.4 Bcm, or by - 1.5%. Here again, OECD Americas and OECD Europe were the main two contributors to the decline, driven by the United States (-21.2 Bcm, -2.4% y-o-y) and the United Kingdom (-6.5 Bcm, -8.2% y-o-y) coupled with Spain (-3.5 Bcm, -9.9% y-o-y) and France (-3.3 Bcm, -7.7% y-o-y).

Non-OECD countries experienced a comparable decrease in 2020, with a contraction of 22.6 Bcm (-1.0% y-o-y), led by Non-OECD Europe and Eurasia with preliminary information for the Russian Federation pointing to a fall in demand of 21.9 Bcm (-4.3% y-o-y).



Figure 3:World natural gas demand by region, 1973-2020. [3]

Despite its vital importance to the national economy as seen from the graphs above, natural gas has often been overlooked, or at best taken for granted, in the debate about the future of energy in the U.S. Over the past two or three years this has started to change, and natural gas is finding its place at the heart of the energy discussion. There are a number of reasons for this shift. The recent emergence of substantial new supplies of natural gas in the U.S., primarily as a result of the remarkable speed and scale of shale

gas development, has heightened awareness of natural gas as a key component of indigenous energy supply and lowered prices well below recent expectations. Instead of the anticipated growth of natural gas imports, the scale of domestic production has led producers to seek new markets for natural gas, such as an expanded role in transportation.

I.b. A Brief History of Natural Gas in the U.S. [5]

The somewhat erratic history of natural gas in the U.S. over the last three decades or so provides eloquent testimony to the difficulties of forecasting energy futures, particularly for natural gas. It also serves as a reminder of the need for caution in the current period of supply exuberance. The development of the U.S. natural gas market was facilitated by the emergence of an interstate natural gas pipeline system, supplying local distribution systems. This market structure was initially viewed as a natural monopoly and was subjected to cost-of-service regulation by both the Federal government and the states. Natural gas production and use grew considerably under this framework in the 1950s, 1960s, and into the 1970s.

Then came a perception of supply scarcity. After the first oil embargo, energy consumers sought to switch to natural gas. However, the combination of price controls and tightly regulated natural gas markets dampened incentives for domestic gas development, contributing to a perception that U.S. natural gas resources were limited. In 1978, convinced that the U.S. was running out of natural gas, Congress passed the Power Plant and Industrial Fuel Use Act (FUA) that essentially outlawed the building of new gas-fired power plants. Between 1978 and 1987 (the year the FUA was repealed), the U.S. added 172 Gigawatts (GW) of net power generation capacity. Of this, almost 81 GW was new coal capacity, around 26% of today's entire coal fleet. About half of the remainder was nuclear power.

By the mid-1990s, wholesale electricity markets and wellhead natural gas prices had been deregulated; new, highly efficient and relatively inexpensive combined cycle gas turbines had been deployed; and new upstream technologies had enabled the development of offshore natural gas resources. This contributed to the perception that domestic natural gas supplies were sufficient to increase the size of the U.S. natural gas market from around 20 Tcf/year to much higher levels. New gas-fired power capacity was added at a rapid pace.

Between 1989 after the repeal of the FUA and 2009, the U.S. added 306 GW of generation capacity, 88% of which was gas fired and 4% was coal fired.2 Today, the nameplate capacity of this gas-fired generation is significantly under-utilized, and the anticipated large increase in natural gas use has not materialized.

By the turn of the 21st century, a new set of concerns arose about the adequacy of domestic natural gas supplies. Conventional supplies were in decline, unconventional natural gas resources remained expensive and difficult to develop, and overall confidence in gas plummeted. Natural gas prices started to rise, becoming more closely linked to the oil price, which itself was rising. Periods of significant natural gas price volatility were experienced.

This rapid buildup in natural gas price, and perception of long-term shortage, created economic incentives for the accelerated development of an LNG import infrastructure. Since 2000, North America's rated LNG capacity has expanded from approximately 2.3 billion cubic feet (Bcf)/day to 22.7 Bcf/day, around 35% of the nation's average daily requirement. This expansion of LNG capacity coincided with an overall rise in the natural gas price and the market diffusion of technologies to develop affordable unconventional gas. The game changing potential of these technologies, combined with the large unconventional resource base, has become more obvious over the last few years, radically altering the U.S. supply picture.

Referred to as the Shale Revolution, the sudden boom in natural gas production, thanks largely to economical extraction from shale-abundant areas such as the Permian Basin, transformed the U.S. energy industry. The country quickly became the world's largest producer of natural gas and a key exporter to Mexico and Canada via pipeline. Advancements in the liquefied natural gas (LNG) industry enabled the U.S. to start exporting further afield, particularly to South Korea and Japan. According to a McKinsey report titled The Future of Natural Gas in North America, the U.S. is expected to "head the list of the world's top LNG exporting regions" by 2023. [4]

Industry experts agree that the displacement of coal by natural gas in the energy mix has been a source of positive change for the country. The larger supplies and lower prices of natural gas have reduced the country's reliance on imported petroleum, causing total fuel exports to outweigh imports and thus leading to a level of energy independence the U.S. has never seen before. LNG exports are booming.



U.S. LNG imports and exports, 1985-2019

Source: U.S. Energy Information Administration, Natural Gas Monthly, June 2020

Figure 4: U.S. LNG imports and exports, 1985-2019.

The U.S. Energy Information Administration's (EIA) Annual Energy Outlook 2021 Reference case projects that growth in natural gas consumption in the United States between 2020 and 2050 will be driven by exports and industrial use: consumption growth from the other sectors will increase slowly or stay flat. In the Reference case projection, U.S. natural gas production will increase to 43.0 trillion cubic feet Tcf (trillion cubic feet) in 2050 as consumption increases to 35.7 Tcf. EIA expects natural gas prices will remain low compared with historical levels, and that low price drives the Annual Energy Outlook 2021 Reference case's projection of increased production. Energy Information Administration expects that exports will rise as production outpaces consumption throughout the projection period.

With economic growth driving U.S. industrial output, natural gas consumption by the industrial sector will increase by 3.6 Tcf, or 35%, from 2020 to 2050 and account for more than 75% of the 4.6 Tcf growth in U.S. natural gas consumption from all sectors during that period. Relatively low natural gas prices drive a growing U.S. chemicals

industry, the largest domestic natural gas-consuming industry because it uses natural gas as a raw material (feedstock) as well as for heat and power. According to the Annual Energy Outlook2021 Reference case, the bulk chemical industry will account for 45% of the industrial sector's increased natural gas consumption, or 1.6 Tcf, through 2050.

Natural gas consumption in the U.S. power sector will reach 12.1 Tcf in 2050, up 0.4 Tcf (4%) from 2020. In 2020, natural gas consumption in the power sector increased by 4% from 2019 to 11.7 Tcf because of relatively low natural gas prices and COVID-19-related disruptions in the power sector's coal supplies. Amid higher natural gas prices in 2021, EIA projects that consumption of natural gas by the power sector will decrease by 16% to 9.9 Tcf. Natural gas consumption will then increase slowly until 2027 because of projected growth in natural gas-fired generation and because of new, more energy-efficient combined-cycle turbine systems. These systems limit growth in power consumption because they use less fuel to produce each kilowatt-hour of electricity than older combined-cycle units or other fossil-fueled generators. Beyond 2036, EIA projects that consumption of natural gas in the U.S. power sector will continue to steadily increase.



Annual U.S. natural gas consumption by sector and net exports (2000–2050) trillion cubic feet

Figure 5: Annual U.S. natural gas consumption by sector and net exports according to Energy Information Administration Annual Energy Outlook 2021.

The Annual Energy Outlook 2021 projects growth in natural gas consumption by other end-use sectors as well. Beyond 2040, natural gas consumption in the U.S. transportation sector increases as natural gas becomes a more predominant fuel for heavy-duty vehicles and freight rail. The residential sector's natural gas consumption remains nearly flat, and commercial buildings show low-to-moderate growth because of energy efficiency improvements (particularly commercial energy management controls and sensors) in space heating.

I.c. Natural gas treatment and supply chain.

Natural gas possesses remarkable qualities. Among the fossil fuels, it has the lowest carbon intensity, emitting less CO_2 per unit of energy generated than other fossil fuels. It burns cleanly and efficiently, with very few non-carbon emissions. Unlike oil, natural gas generally requires limited processing to prepare it for end use as we will see in the upcoming paragraphs. These favorable characteristics have enabled natural gas to penetrate many markets, including domestic and commercial heating, multiple industrial processes, and electrical power.

Natural gas also has favorable characteristics with respect to its development and production. The high compressibility and low viscosity of natural gas allows high recoveries from conventional reservoirs at relatively low cost, and also enables natural gas to be economically recovered from even the most unfavorable subsurface environments, as recent developments in shale formations have demonstrated. These physical characteristics underpin the current expansion of the unconventional resource base in North America, and the potential for natural gas to displace more carbon-intensive fossil fuels in a carbon constrained world.

On the other hand, because of its gaseous form and low energy density, natural gas is uniquely disadvantaged in terms of transportation and storage. As a liquid, oil can be readily transported over any distance by a variety of means, and oil transportation costs are generally a small fraction of the overall cost of developing oil fields and delivering oil products to market. This has facilitated the development of a truly global market in oil over the past 40 years or more.

By contrast, the vast majority of natural gas supplies are delivered to market by pipeline, and delivery costs typically represent a relatively large fraction of the total cost in the supply chain. These characteristics have contributed to the evolution of regional markets rather than a truly global market in natural gas. Outside North America, this somewhat inflexible pipeline infrastructure gives strong political and economic power to those countries that control the pipelines. To some degree, the evolution of the spot market in Liquefied Natural Gas (LNG) is beginning to introduce more flexibility into global gas markets and stimulate real global trade.

Natural gas has different supply chains depending or whether it will be transported by pipeline or by LNG.



NATURAL GAS SUPPLY CHAIN

Figure 6: Natural gas supply chain.

Gas field:

When a prospect has been identified and evaluated and passes an oil company's selection criteria, an exploration well is drilled in an attempt to conclusively determine the presence or absence of oil or natural gas. Hydrocarbon exploration is a high-risk investment and risk assessment is paramount for successful exploration portfolio management. Exploration risk is a difficult concept and is usually defined by assigning confidence to the presence of imperative geological factors. Although there is some variability in the details of well construction because of varying geologic, environmental, and operational settings, the basic practices in constructing a reliable well are similar.



Source: U.S. Energy Information Administration

Figure 7: Schematic geology of natural gas resources.

The ultimate goal of the well design is to ensure the environmentally sound, safe production of hydrocarbons by containing them inside the well, protecting groundwater resources, isolating the productive formations from other formations, and by proper execution of hydraulic fractures and other stimulation operations. Oil and gas production include drilling, extraction, and recovery of oil from underground, either onshore or subsea. Every oil and gas production facility is different. The size, shape and features match the climate and characteristics of the location, as well as the type of reservoir and the specific hydrocarbons within it.

Component	Canada	Kansas	Texas
C1	77.1	73.0	65.8
C2	6.6	6.3	3.8
C3	3.1	3.7	1.7
C4s	2.0	1.4	0.8
C5s+	3.0	0.6	0.5
H ₂ S	3.3	0.0	0.0
CO,	1.7	0.0	0.0
N ₂	3.2	14.7	25.6
He	0.0	0.5	1.8

Figure 8:Composition of Natural Gas in Different Locations [8]

Processing:

Processing plants clean raw natural gas by separating impurities and the various hydrocarbons and fluids from pure natural gas, producing what is known as 'pipeline quality' dry natural gas, also known as methane. A fully operational processing plant delivers pipeline quality dry natural gas that can be used as fuel by residential, commercial, and industrial consumers. Natural gas transported on the mainline natural gas transportation (pipeline) system in the United States must meet specific quality measures so that the pipeline network (or grid) can provide uniform quality natural gas. Wellhead natural gas may contain contaminants and hydrocarbon gas liquids (HGLs) that must be removed before the natural gas can be safely delivered to the high-pressure, long-distance pipelines that transport natural gas to consumers. Natural gas typically moves from natural gas and oil wells through a gathering system of pipelines to natural gas processing plants for treatment. Natural gas processing can be complex and usually involves several processes, or stages, to remove oil, water, HGLs, and other impurities such as sulfur, helium, nitrogen, hydrogen sulfide, and carbon dioxide. The composition of the wellhead natural gas determines the number of stages and the processes required to produce pipeline-quality dry natural gas. These stages and processes may be integrated into one unit or operation, be performed in a different order or at alternative locations (lease/plant), or not be required at all.

Raw natural gas typically consists primarily of methane (CH₄) and ethane (C₂H₆), the shortest and lightest hydrocarbon molecules. It often also contains varying amounts of:

Heavier gaseous hydrocarbons: propane (C_3H_8), normal butane (n- C_4H_{10}), isobutane (i- C_4H_{10}) and pentanes. All of these are collectively referred to as Natural Gas Liquids or NGL and can be processed into finished by-products. Liquid hydrocarbons (also referred to as casinghead gasoline or natural gasoline) and/or crude oil.

- Acid gases: carbon dioxide (CO₂), hydrogen sulfide (H₂S) and mercaptans such as methanethiol (CH₃SH) and ethanethiol (C₂H₅SH).
- > Other gases: nitrogen (N_2) and helium (He).
- Water: water vapor and liquid water. Also dissolved salts and dissolved gases (acids).
- Mercury: very small amounts of mercury primarily in elemental form, but chlorides and other species are possibly present.

Naturally occurring radioactive material (NORM): natural gas may contain radon, and the produced water may contain dissolved traces of radium, which can accumulate within piping and processing equipment. This can render piping and equipment radioactive over time.

The raw natural gas must be purified to meet the quality standards specified by the major pipeline transmission and distribution companies. Those quality standards vary from pipeline to pipeline and are usually a function of a pipeline system's design and the markets that it serves. In general, the standards specify that the natural gas:

Table 1			
USA national natural gas pipeline composition specifications ^[3]			
Component	Specification		
CO ₂	< 2 mol%		
H ₂ O	<120 ppm		
H ₂ S	<4 ppm		
Hydrocarbons (C3+)	950-1050 Btu/scf		
Inert gases	Inert gases <4 mol%		

Figure 9: U.S. national average natural gas pipeline composition specifications.

The natural gas should:

- Be free of particulate solids and liquid water to prevent erosion, corrosion or other damage to the pipeline.
- Be dehydrated of water vapor sufficiently to prevent the formation of methane hydrates within the gas processing plant or subsequently within the sales gas transmission pipeline. A typical water content specification in the U.S. is that gas must contain no more than seven pounds of water per million standard cubic feet of gas.
- Contain no more than trace amounts of components such as hydrogen sulfide, carbon dioxide, mercaptans, and nitrogen. The most common specification for hydrogen sulfide content is 0.25 grain H₂S per 100 cubic feet of gas, or approximately 4 ppm. Specifications for CO₂ typically limit the content to no more than two or three percent.
- Maintain mercury at less than detectable limits (approximately 0.001 ppb by volume) primarily to avoid damaging equipment in the gas processing plant or

the pipeline transmission system from mercury amalgamation and embrittlement of aluminum and other metals.



Basic stages of natural gas processing/treatment [9], [10], [11].

Figure 10: Scheme diagram for natural gas treatment processes.

<u>Gas-oil-water separators</u>: Pressure relief in a single-stage separator causes a natural separation of the liquids from the gases in the natural gas. In some cases, a multi-stage separation process is required to separate the different fluid streams.

<u>Condensate separator</u>: Condensates are most often removed from the natural gas stream at the wellhead with separators much like gas-oil-water separators. The natural gas flow into the separator comes directly from the wellhead. Extracted condensate is sent to storage tanks. The condensate is usually then transported to an oil refinery and the water is treated and disposed of as wastewater.

<u>Acid gas removal:</u> There are several processes available for that purpose as shown in the flow diagram, but amine treating is the process that was historically used. However, due to a range of performance and environmental constraints of the amine process, a newer

technology based on the use of polymeric membranes to separate the carbon dioxide and hydrogen sulfide from the natural gas stream has gained increasing acceptance. Membranes are attractive since no reagents are consumed. The acid gases, if present, are removed by membrane or amine treating and can then be routed into a sulfur recovery unit which converts the hydrogen sulfide in the acid gas into either elemental sulfur or sulfuric acid. Of the processes available for these conversions, the Claus process is by far the most well-known for recovering elemental sulfur, whereas the conventional Contact process and the WSA (Wet sulfuric acid process) are the most used technologies for recovering sulfuric acid. Smaller quantities of acid gas may be disposed of by flaring. The residual gas from the Claus process is commonly called tail gas and that gas is then processed in a tail gas treating unit (TGTU) to recover and recycle residual sulfurcontaining compounds back into the Claus unit. Again, as shown in the flow diagram, there are a number of processes available for treating the Claus unit tail gas and for that purpose a WSA process is also very suitable since it can work auto thermally on tail gases.

<u>Dehydration</u>: A dehydration process removes water that may cause the formation of undesirable hydrates and water condensation in pipelines. The next step in the gas processing plant is to remove water vapor from the gas using either the regenerable absorption in liquid triethylene glycol (TEG), commonly referred to as glycol dehydration, deliquescent chloride desiccants, and or a Pressure Swing Adsorption (PSA) unit which is regenerable adsorption using a solid adsorbent. Other newer processes like membranes may also be considered.

<u>Contaminant removal</u>: Nonhydrocarbon gases such as hydrogen sulfide, carbon dioxide, water vapor, helium, nitrogen, and oxygen must also be removed from the natural gas stream. The most common removal technique is to direct the natural gas though a vessel containing an amine solution. Amines absorb hydrogen sulfide and carbon dioxide from natural gas and can be recycled and regenerated for repeated use.

<u>Nitrogen extraction</u>: Once the hydrogen sulfide and carbon dioxide are reduced to acceptable levels, the natural gas stream is routed to a Nitrogen Rejection Unit (NRU)-cryogenic distillation process, where it is further dehydrated using molecular sieve beds.

Natural Gas Liquids Fractionation (NGLs Recovery) [12],[13]:

The NGL fractionation process treats the gas exiting from the separators at an oil terminal or the overhead fraction from a crude distillation column in a refinery. Fractionation aims to produce useful products including natural gas suitable for piping to industrial and domestic consumers; liquefied petroleum gases (Propane and Butane) for sale; and gasoline feedstock for liquid fuel blending. The recovered NGL stream is processed through a fractionation train consisting of up to five distillation towers in series: a demethanizer, a deethanizer, a depropanizer, a debutanizer and a butane splitter. It uses another cryogenic low temperature distillation process involving expansion of the gas through a turbo-expander followed by distillation in a demethanizing fractionating column. The gaseous feed to the NGL fractionation plant is typically compressed to about 60 barg and 37 °C. The feed is cooled to -22 °C, by exchange with the demethanizer overhead product and by a refrigeration system and is split into three streams: condensed liquid passes through a Joule-Thomson valve reducing the pressure to 20 bar and enters the demethanizzer as the lower feed at -44.7 °C. Some of the vapor is routed through a turbo-expander and enters the demethanizer as the upper feed at -64 °C. The remaining vapor is chilled by the demethanizer overhead product and Joule-Thomson cooling (through a valve) and enters the column as reflux at -96 °C. The overhead product is mainly methane at 20 bar and -98 °C. This is heated and compressed to yield a sales gas at 20 bar and 40 °C. The bottom product is NGL at 20 barg which is fed to the deethanizer. The overhead product from the deethanizer is ethane and the bottoms are fed to the depropanizer. The overhead product from the depropanizer is propane and the bottoms are fed to the debutanizer. The overhead product from the debutanizer is a mixture of normal and iso-butane, and the bottoms product is a C5+ gasoline mixture.

<u>Sweetening process</u>: The recovered streams of propane, butanes and C5+ may be "sweetened" in a Merox process unit to convert undesirable mercaptans into disulfides and, along with the recovered ethane, are the final NGL by-products from the gas processing plant. Currently, most cryogenic plants do not include fractionation for economic reasons, and the NGL stream is instead transported as a mixed product to standalone fractionation complexes located near refineries or chemical plants that use the components for feedstock. In case laying pipeline is not possible for geographical

reason, or the distance between source and consumer exceed 3000 km, natural gas is then transported by ship as LNG (liquefied natural gas) and again converted into its gaseous state in the vicinity of the consumer.

Transportation and Transmission:

Natural gas transmission pipelines are wide-diameter pipelines and are often the longdistance portion of natural gas pipeline systems that connect gathering systems in producing areas, natural gas processing plants, other receipt points, and the main consumer service areas. When natural gas arrives at the locations where it will be used (usually through large pipelines), it flows into smaller diameter pipelines called mains and then into smaller service lines that go directly to homes or buildings.

Natural gas, which is converted to liquid form to facilitate its storage and transport, is called liquefied gas. Its characteristics are the lack of odor, color, toxicity and corrosion. The gas is liquefied at a pressure close to atmospheric pressure and cooled to about -161 °C. Liquefied natural gas (LNG) shipping provides a low-cost, safe, and environmentally responsible method to move large volumes of product long distances. LNG is transported in specially-built tanks on double-hulled ships. LNG carriers are among the safest in the shipping industry, having made more than 100,000 voyages without major incident. Before liquefaction of natural gas, it is necessary to remove water, nitrogen, carbon dioxide, hydrogen sulfide and other sulfur compounds as we discussed previously. By removing these impurities, solids cannot be formed by cooling the gas. After the process, the liquefied natural gas is reduced almost 600 times compared to its initial state. As a result, it becomes more economical to transport it by sea through special liquefied natural gas LNG vessels.



Figure 11:Liquified natural gas ship for the transportation of natural gas.

Due to the fact that liquefied natural gas is a very cold liquid, its storage is not carried out under pressure. Therefore, the fact that liquefied natural gas is a compressed gas does not apply. Also, the density of water is about 467 grams per liter higher than the density of liquefied natural gas. This causes the liquefied natural gas to float and evaporate in case it spills into the water, as it is lighter than that.



Figure 12: LNG supply chain.

The processes that make up the LNG supply chain are the following:

- ➢ Extraction
- Transport to liquefaction plants via pipelines
- > Liquidation
- Storage in cryogenic tanks
- Loading on liquefied natural gas tankers
- Transportation by sea
- Unloading at storage facilities
- Regasification

Network power supply

There are three ways in which refrigeration is produced on an industrial scale and these are through free expansion (Joule-Thomson method of expansion), through expansion by offering mechanical work (Claude method) and finally, through successive condensation-evaporation cycles (Pictet cycle). However, in practice for the liquefaction of natural gas, only the latter method is used. The liquefaction of natural gas on the basis of large loading is carried out with emphasis on the efficiency of the process. The scale of operations means that production with the lowest installed capacity and the lowest fuel consumption is economically advantageous. Because the heat that must be removed from the gas to cool it to -160 ° C is eventually discharged into air or water, several complex systems have been developed. The first gas liquefaction processes used arrays of single refrigeration units in series. ach refrigerant is used in a separate closed loop that provides cooling in specific temperature ranges. Typically, propane, ethylene and methane are used to provide a wide, balanced cooling range. After compression, three temperature levels for each of the three refrigerants form a nine-step sequence. Each of these temperature levels corresponds to a predetermined pressure drop (in the separation vessels) for the refrigerant to evaporate in heat exchange with the gas supply and a separate refrigerant stream that requires cooling. In this way, heat is removed from the gas at successively lower temperatures.



Figure 13: LNG liquification process [15].

The cost of liquefied natural gas depends on its production, liquefaction, maritime transport, gasification and storage. The following figure shows the cost chain of liquefied natural gas for a specific case of transport, which shows the share of each process in the total cost.

LNG value chain	
Exploration and production	Liquefaction
$4.74 \times 10^{-4} - 9.48 \times 10^{-4} \text{ MJ}^{-1}$	$7.58 \times 10^{-4} - 1.14 \times 10^{-3} \text{ MJ}^{-1}$
Shipping	Re-gasification and storage
3.79×10^{-4} - $9.48 \times 10^{-4} \text{ MJ}^{-1}$	2.84×10^{-4} - 4.74×10^{-4} MJ ⁻¹

Figure 14: LNG cost value chain.

In conjunction, the value chain of liquefied natural gas can be divided into four categories, which are exploration-production (25%), liquefaction (40%), transportation (20%) and gasification-storage (15%). The transport of liquefied natural gas is the only way of transporting natural gas from distant fields of production to the respective countries of consumption. Any cost comparison between liquefied natural gas transportation and pipeline transportation must be linked to the project requirements. Generally, a liquefied natural gas installation is the only solution in case pipeline transportation is not possible for technical or other reasons or if the distance is long enough. The cost of liquefied natural gas transportation is lower than that of submarine pipelines even for distances of hundreds of kilometers, while land pipeline transportation is almost always cheaper than liquefied natural gas transportation, unless the distance is extremely long.



Source: Institute of Gas Technology.

Figure 15:Transportation cost of natural gas.

Distribution

Distribution is the final step in delivering natural gas to customers. While some large industrial, commercial, and electric generation customers receive natural gas directly from high-capacity interstate and intrastate pipelines (usually contracted through natural gas marketing companies), most other users receive natural gas from their local gas utility, also called a local distribution company (LDC). LDCs are regulated utilities

involved in the delivery of natural gas to consumers within a specific geographic area. There are two basic types of natural gas utilities: those owned by investors, and public gas systems owned by local governments [16].

Local distribution companies typically transport natural gas from delivery points located on interstate and intrastate pipelines to households and businesses through thousands of miles of small-diameter distribution pipe. The delivery point where the natural gas is transferred from a transmission pipeline to the local gas utility is often termed the 'citygate' and is an important market center for the pricing of natural gas in large urban areas. Typically, Utilities take ownership of the natural gas at the citygate and deliver it to each individual customer's meter. This requires an extensive network of smalldiameter distribution pipe. The U.S. Department of Transportation's Pipeline and Hazardous Materials Safety Administration reports that there are just over 2 million miles of distribution pipe in the U.S., including city mains and service pipelines that connect each meter to the main.

Because of the transportation infrastructure required to move natural gas to many diverse customers across a reasonably wide geographic area, distribution costs typically make up about half of natural gas costs for households and small volume customers. While large pipelines can reduce unit costs by transmitting large volumes of natural gas, distribution companies must deliver relatively small volumes to many more different locations. According to the Energy Information Administration (EIA), transmission and distribution costs represented about half of a typical residential natural gas customer's monthly gas utility bill in 2009, with costs of the physical natural gas commodity itself representing the other half.

The United States has a vast natural gas pipeline system, which can quickly and economically distribute natural gas to and from almost any location in the lower 48 states. Gas is distributed using 305,000 miles of transmission pipelines (see map below), while an additional 2.2 million miles of distribution pipes transport gas within utility service areas. The distribution system also includes thousands of delivery, receipt, and interconnection points; hundreds of storage facilities and approximately 50 points for exporting and importing natural gas. It is straight forwards from the very begging that according to the map below Texas has the largest natural gas pipeline network established in the United States.



Figure 16: U.S. natural gas pipeline system.

Durability, Resiliency and Redundancy of Natural Gas Supply [17]

The natural gas market and available supply are vast. According to The World Bank, about 141 billion cubic meters (bcm) of natural gas was flared worldwide in 2017, which is a slight reduction from the 148 bcm flared in 2016. Russia continues to be the world's largest gas flaring country. In the United States, natural gas vented and flared increased by 12.5% in 2017 totaling 235,570 million cubic feet. To put this in perspective; in 2017 alone, the United States had over 33.35 trillion cubic feet (Tcf) in natural gas gross withdrawals, 27.29 Tcf in dry gas production, 27.11 Tcf in natural gas consumption and over 125 billion cubic feet in net exports. With such a high rate of consumption, one would logically question how long we can sustain this consumption based on known supply? As of January 1, 2016, there were about 2,462 Tcf of technically recoverable resources of dry natural gas in the United States. Of note, technically recoverable reserves include both proved reserves and unproved resources. Nonetheless, the US Energy Information Administration estimates that if consumption remained at the 2016 rate of about 27.5 Tcf per year, (which was higher than the 2017 rate of 27.11 Tcf), the United States has enough natural gas to last about 90 years. In comparison, proven coal

and oil reserves are equivalent to around 150 and 53 years at current production levels. The largest "end uses" of natural gas in the United States are Electric Power Generation, Industrial and Residential, which account for 34%, 29% and 16% of consumption respectively. Acknowledging that there is ample supply, we must now look at the sequence of processes involved in the production and distribution of natural gas and evaluate its durability, resiliency, and redundancy in providing uninterrupted supply to both vital national infrastructure throughout the United States. Threats to the natural gas supply chain can be a natural or man-made occurrence; it can be an individual, entity, or action that has or indicates the potential to harm life, information, operations, the environment, and/or property. If an adversary (or nature) could somehow disrupt the United States supply of natural gas, thus impeding the ability to generate electricity, provide heating and cook meals; not only would this severely impact our quality of life, but this could potentially render vital infrastructure exposed and provide a temporary competitive advantage to the adversary. As such, the ability of the natural gas supply chain to withstand wear, pressure, or damage is critical. It is the industry's position that incidents, whether anthropogenic or natural, should be managed by local and state governments, under the construct of the National Response Framework (NRF).

Resiliency in the natural gas supply chain speaks to its ability to resist, absorb, recover from, or successfully adapt to adversity or a change in conditions. A resilient system is one that can recover quickly from difficulties and limit impact to operations. One-way resiliency is built into operations is to identify critical components and choke points and incorporate redundancy. Redundancy, in the engineering sense, is the inclusion of extra components that are not strictly necessary to functioning but are intended to increase the reliability of the system; typically, as a backup or fail-safe. Redundancy within the US natural gas supply chain enables critical components to continue to operate in case of disruptions to the system. Recognizing the critical components, and their placement within the system, provides the context to understand the consequences, both upstream and downstream, of an impacted component in the natural gas supply chain. For example, processing plants, pipelines, market hubs and storage facilities are all critical components in the production and distribution of natural gas. The US natural gas supply chain has over 500 natural gas processing plants, over 305,000 miles of natural gas pipeline, over 30 major market hubs and over 400 storage facilities. The cross-connect

capabilities of these critical components enable uninterrupted supply in the event a facility or region is disrupted. In addition to redundancy, resiliency is also achieved by the methodology, policy and procedures employed to make the system tolerant to stressors. In this regard, resiliency is deeply embedded in the design of the US natural gas supply chain which incorporates rapid response capabilities with automatic response triggers. Altogether, the redundancy of components and the resiliency of the system design prevent traditional chokepoints in the natural gas supply chain.

II. NATURAL GAS DEHYDRATION PROCESSES

The removal of water from natural gas is a common operation and is usually performed close to the wellhead to avoid hydrate formation and corrosion in the gas gathering system. Water is a problem in the gas phase, both in gas processing and in pipeline transport. Natural gas from wells invariably contains humidity. Gas also becomes wet in the sweetening unit of a gas processing facility when it comes into contact with the aqueous solution of a solvent, such as methyl diethanolamine (MDEA), used to remove the acid gases contained in the raw gas.

Component	Wellhead Gas, <u>Mole%</u>	Pipeline Gas, <u>Mole%</u>
Methane (CH ₄)	70 - 98	95 - 98
Ethane (C2H6)	1 - 10	2 - 5
Propane (C3H8)	Trace - 5	0.5 - 1.5
Butanes (C ₄ H ₁₀)	Trace - 2	0.2 - 0.5
Pentanes (C_5H_{12})	Trace – 1	Trace
Hexanes (C_6H_{14})	Trace - 0.5	Trace
Heptanes & heavier $(C_7H_{16}^+)$	Trace	Trace
Carbon Dioxide (CO2)	Trace - 3*	0.5 - 2.0
Nitrogen (N2)	Trace – 15*	0.5 - 1.5
Hydrogen Sulfide (H ₂ S)	Trace - 2*	<0.000004
Water (H ₂ O)	Trace - 5	<0.0001

Figure 17:Natural gas composition in wellhead and Pipeline.

The existence of water vapor in natural gas can cause serious problems in gas transportation and processing. For example, water vapor in crude gas dissolves carbon dioxide and hydrogen sulfide to form acid, which causes corrosion of pipes and equipment. Another severe problem is the hydrate formation or freezing, which may block process equipment and instruments reducing the pipeline transmission capacity, resulting in too much power consumption. Hence, the dehydration of natural gas is indispensable to the transmission and consumption of natural gas. The main problems with water in gas are:

Corrosion of pipelines in the presence of CO₂

CO₂ dissolves in condensed water, forming carbonic acid (H₂CO₃), which dissociates in bicarbonate (HCO₃–), carbonate (CO₃²-) and hydrogen (H+) ions. The latter is reduced at the steel surface to form H₂ (2H+ + 2e- \rightarrow H₂). The two

electrons needed for reducing H+ are donated by iron (Fe), which dissolves into the aqueous solution (Fe \rightarrow Fe²⁺ + 2e–). For pipeline transportation, the allowed residual humidity generally ranges from 1 lb/MMsft³–7 lb/MMsft³, depending on the environmental conditions.

Slugs formation

In two-phase flow, liquid waves can reach the top of the pipework encroaching the gas cross-section. When this happens, liquid slugs travel in the same direction as the stream, with relatively high velocity, albeit lower than that of the gas. This results in vibrations and mechanical shocks to the piping fittings (e.g., bends and valves). The fittings superimpose a change to the direction of the velocity vectors. The change of the flow direction generates the thrusts on the piping walls according to the macroscopic momentum balance. Since the slugs are randomly formed, their impingement on the piping/equipment wall may result in dangerous vibrations and mechanical stress on the materials of construction.

➢ Hydrate formation

In natural gas processing, hydrates are hard crystalline structures wherein water molecules encompass molecules of CH₄, C₂H₆, CO₂ or H₂S, which are trapped in molecular "cages." The water molecules of the reticular structure are tied to each other by H₂ bonds, and they are tied to the guest molecules through Van der Waals interactions. These solid structures are a source of erosion and plugging. This latter is particularly troublesome, as decomposition of hydrates during removal can generate large volumes of gas with explosion hazards.



Figure 18: Hydrate formation in natural gas pipeline.
Water, as the most common impurity in natural gas, often reaches saturation. Therefore, the water content in natural gas is usually expressed by water dew point temperature in industry. The water content of natural gas at saturation is dependent on temperature and pressure. With increasing pressure of the gas, the water content decreases, and with increasing temperature the water content in the gas increases. This is well presented in Figure No. 20, Chapter 20, in the GPSA Data Book, 12th Edition. The water content of the gas can be calculated using the following equation:

$$W_{water} = 593,335 * exp^{(0.05486*T_g)} * P_g^{-0.81462}$$

Where w_{water} is in kilograms of water per 106 m_s^3 of natural gas, T_g is temperature of natural gas in °C, and P_g is pressure of natural gas in MPa.

In addition to the above challenges, water vapor increases natural gas volume while decreasing heating value. It can also cause plugging in cryogenic plants, which call for a water dewpoint specification of less than -100° C. These issues can be effectively addressed by removing the humidity contained in natural gas by means of gas dehydration processes. These processes can be grouped into two categories: absorption on glycol and adsorption on solid sorbent.

By far, the most widely used technology is absorption of water with diethylene or triethylene glycol. Just in the United States, there are approximately 40.000 absorber-stripper units are in operation at gas wellheads. The water content of high pressure, water-saturated gas is usually \sim 1000 ppm, and the objective of the glycol absorption gas dryers is to bring this concentration to \sim 100 ppm, which would be sufficient to prevent condensation, hydrate formation, and corrosion in the pipeline. Because the mass of water removed by the dryer is small, glycol absorbers are much smaller than carbon dioxide amine absorbers. A typical system that is designed to dry 10 million scfd (standard cubic feet per day) of gas can be purchased for \$100.000 and is fully automated for unattended operation, using pneumatic controls and valves and pumps. The operating costs are only a few cents per 1000 scf of gas treated.

The opportunity for membranes lies in processing raw gas to meet these specifications. Of this huge market, membranes have less than a 5% share, but this is changing: membrane-based removal of natural gas contaminants is growing faster than any other segment of the membrane gas separation business. The membrane dehydration process offers many advantages when compared with the conventional processes such as chemical absorption, physical adsorption and cryogenic cooling, etc. Also, their high selectivity and low operating cost make them an ideal candidate for natural gas treatment applications.

Industry-established Methods for Natural Gas Dehydration:

If the temperature of pipeline walls or storage tanks decreases below the dew point temperature of the water vapors present in the gas, the water starts to condense on those cold surfaces, and the following problems can appear.

- Natural gas in combination with liquid water can form methane hydrate. Methane hydrate is a solid in which a large amount of methane is trapped within the crystal structure of water, forming a solid similar to ice. The methane hydrate production from a unit amount of water is higher than the ice formation. The methane hydrates formed by cooling may plug the valves, the fittings or even pipelines.
- Natural gas dissolved in condensed water is corrosive, especially when it contains CO₂ or H₂S.
- Condensed water in the pipeline causes slug flow and erosion.
- Water vapor increases the volume and decreases the heating value of the gas.
- Natural gas with the presence of water vapor cannot be operated on cryogenic plants.

There are several technologies for the purpose of gas dehydration available on today's market. Four of them are widely recognized and applied since many years, each of them relying on a different principle. They are briefly described in the following subsections.

Absorption on glycol

The most widely-used method for industrial dehydration of NG is absorption. Absorption is usually performed using triethyleneglycol sorbent (TEG). The most-used glycols are diethylene glycol (DEG) and triethylene glycol (TEG). In the glycol molecules, hydroxyl groups (–OH) and ether functional groups (–CH₂-O-CH₂–) are present. These groups give rise to H₂ bonds, which explains their remarkable hygroscopicity and their desiccant properties. Absorption proceeds at low temperatures

and the absorbed water is boiled out from TEG during regeneration in a reboiler at high temperatures. Since their molecular weight is greater than water, the glycol molecules boil at a comparatively higher temperature. Glycols can be easily regenerated by distillation. It should be observed that both DEG and TEG are subject to thermal degradation; therefore, the distillation temperatures must be kept below the initial decomposition temperatures i.e., 328°F (164°C) and 404°F (207°C), respectivelywhich are lower than their normal boiling points. The industrial absorption dehydration process proceeds in a glycol contactor (a tray column or packet bed). In a contactor, a countercurrent flow of wet NG and TEG is arranged. During the contact, the TEG is enriched by water and flows out of the bottom part of the contactor. The enriched TEG then continues into the internal heat exchanger, which is incorporated at the top of the still column in the regeneration section of the absorption unit. It then flows into the flash drum, where the flash gases are released and separated from the stream. The TEG then runs to the cold side of the TEG/TEG heat exchanger. Just afterwards, the warmed TEG is filtered and then runs into the regeneration section, where is it sprayed in the still column. From there, the TEG runs into the reboiler. In the reboiler, water is boiled out of the TEG. The regeneration energy is around 282 kJ per liter of TEG. Regenerated (lean) TEG is then pumped back through the hot side of the TEG/TEG and NG/TEG heat exchanger into the top of the contactor. The entire method is depicted in the following scheme.



Figure 19: TEG Absorption Dehydration Scheme.

Generally, DEG is preferred in hydrates inhibition service where the concentration of the lean glycol (i.e., the glycol coming from the regeneration unit) is required to be in the 85%–95% range and can be regenerated at relatively low temperature. TEG is preferred in gas dehydration service. The contacting internals may be trays, random packing or structured packing. The latter is preferred for its specific gas capacity and low glycol entrainment, which require a comparatively smaller contactor diameter. Free water and condensate possibly entrained in the raw gas are knocked out in a separator upstream of the contactor. As the regeneration step is carried out at near-atmospheric pressure, the high-pressure rich glycol withdrawn from the contactor bottom is let down through a level control valve. The resultant two-phase flow is then routed to the glycol flash drum, where the absorbed hydrocarbons and part of the inert gas are separated from the rich glycol.

After filtration and pre-heating, the rich glycol is sent to the still column for water-glycol separation.

The cost-effective design of a gas dehydration unit is the result of the optimum combination of the glycol circulation rate, the lean glycol concentration, the contactor temperature, the stripping gas flowrate and the number of contactor trays or the number of height equivalent to a theoretical plate (HETP) for structured packing. Figure 20

shows that by increasing the glycol flowrate, the dewpoint depression (i.e., the difference in dewpoint temperature between the gas entering and leaving the contactor) increases for a given lean glycol concentration [18].



Figure 20: Effect of glycol rate and glycol purity on dewpoint depression.

For a given flowrate, the dewpoint depression increases with glycol purity. Since the rich glycol must be pressurized up to the operating pressure of the contactor and since the duty of the reboiler is correlated to the glycol flowrate, the lower the glycol flowrate, the lower the energy consumption of the gas dehydration process. Therefore, a sound design practice aims to achieve the highest possible glycol purity.

The glycol purity can be increased beyond the purity attainable with a distillation operation by sequencing the still column with a small stripping unit (also known as a Stahl column), where water is further removed by means of a stripping gas (typically fuel gas). The wet stripping from the Stahl column is sent to the still column and ends up as offgas for disposal at a pressure close to atmospheric. Typically, the offgas is flared because the pressure is too low to be used as fuel. Figure 21 shows how the glycol purity rises with increased stripping gas. However, the curve tends to flatten out. Beyond 30 sm³/m³ of TEG, the gain of glycol purity becomes marginal. Therefore, continuing to increase the stripping gas flowrate does not make economic sense, as valuable fuel gas would be wasted.



Figure 21:Effect of stripping gas on glycol purity.

Advanced technologies have been developed to attain a glycol purity greater than 99% without using an external stripping gas. One process (Coldfinger process) makes use of a water exhauster where part of the vapor in equilibrium with the lean glycol is locally condensed. As water is removed from the vapor phase, further drying of the lean glycol flowing through the water exhauster is obtained. This technology achieves lean glycol purity of greater than 99.9%.

Another process, (DRIZO process) based on azeotropic distillation, has a third component to remove water. In this process, the water and the hydrocarbon contained in the still overhead vapor are condensed and separated from the non-condensable gas. The hydrocarbon stream is then kicked back in the regeneration section of the dehydration unit after being heated to 150°C.

A third process (DRIGAS process) uses the non-condensable gas exiting the still overhead separator as stripping gas. In this case, the gas from the separator is directed to the stripping gas heating coil of the reboiler. In this arrangement, it is possible to use any flow of stripping gas without having to import fuel gas.

Both the second and third processes are able to produce a lean glycol with a purity greater than 99.98%, and ultimately achieve a dewpoint depression of 100°C against the 45°C of a standard gas dehydration unit when the contact temperature is approximately 25°C. However, it must be said that these advanced processes entail additional equipment relative to standard glycol units.

Adsorption on solid sorbent:

This family of technologies is based on the van der Waals interactions between water and the surface of a solid desiccant, typically accommodated in fixed-bed columns. Due to these interactions, it is possible to dry natural gas to less than 0.01 ppm. The van der Waals bonding is not as strong as chemical bonding. Upon heating, the increased kinetic energy of the adsorbed molecules loosens these bonds, enabling the separation of water from the sorbent. This phenomenon is used to regenerate the sorbent when it has become exhausted. As the top layer of fresh desiccant comes into contact with the wet natural gas, it soon becomes water-saturated, and a mass transfer zone (saturation front) forms. Above the mass transfer zone, the bed is saturated-i.e., the "wet" sorbent is in equilibrium with the wet inlet gas, and the water concentration in the gas flowing through the upper side of the mass transfer zone remains unchanged. No further adsorption takes place in this zone. Below the mass transfer zone, the desiccant is in contact with dry gas, and so it remains fresh. Within the mass transfer zone, the water content is reduced from the inlet concentration, C_{in}, to the equilibrium value of the fresh adsorbent, as represented by the green line in figure 22. It is highlighted that the mass transfer zone can be seen as the length of the bed involved in the absorber process at time τ.[18]



Figure 22: Adsorption process principles.

As time passes, the mass transfer zone moves downward through the bed until it reaches the bottom of the column. At this point the entire bed has become water-saturated, and the adsorption process comes to an end. In time, the water dewpoint at the tower outlet draws an "S" curve, known as the breakthrough curve, represented by the blue line in figure 22. When the water concentration at the bed outlet touches the (Cb, τ b) point (the water dewpoint corresponding to the gas specification) on the breakthrough curve, the fixed bed is considered exhausted. It is then excluded from the production cycle and regenerated. In industrial practice, the end of the production cycle is not set by the analytical measurement of water dewpoint in the treated gas; rather, it is set by a predetermined time τ (estimated to be close to τ b).[18]

Temperature swing adsorption (TSA) is one of the widely used processes in gas plants to remove water from the feedstock, and hence decreasing the dew point of natural gas. Adsorption involves the use of a solid desiccant contained in a column to capture the water vapor from the wet gas stream on its surface. Physical adsorbents having the ability to be regenerated in the process such as molecular sieve and silica gel are most common. As such, the dehydration process consists of cyclic batch operation, being adsorption until the bed is loaded with water and subsequent regeneration. In order to guarantee continuous operation, the batch stages need to be alternated between multiple columns, each operating at a different stage. This means regeneration of a column needs to be finalized before another column becomes fully loaded during adsorption. Regeneration includes heating of the bed such to release the captured components, followed by a cooling stage to prepare the column for adsorption again. Both are usually performed by diverting a portion of the dry gas stream and circulating it through the regeneration loop. Typically, a compressor is used as driving force, in order to reinsert the gas used for regeneration back into the wet gas production stream. For the heating stage the regeneration gas is heated to high temperature. When the full column reaches the desired end temperature, the heating stage is terminated by switching off the heater. The column is then cooled by the cold regeneration gas, such to make it ready for the next adsorption cycle. This method is known as temperature swing adsorption (TSA) and it is shown in figure 23. Regeneration can also be performed by change of pressure - pressure swing adsorption (PSA). A combination of those two methods (PSA and TSA) seems to be a promising future option for adsorption dehydration of NG. This idea is still in the research process.



Figure 23: Scheme of the temperature swing adsorption (TSA) dehydration

Activated alumina, silica gel and molecular sieves are the most-used sorbents for drying natural gas. Activated alumina is the least-expensive sorbent material for drying natural gas to -70° C. The major disadvantages of activated alumina are the co-adsorption of hydrocarbons, which results in a reduced water load and loss of production, and the rehydration by contact with wet gas at high temperature during the regeneration stage. Silica gel features a high-water adsorption capacity and can also adsorb Cs+ components, making it available for the simultaneous removal of water and gasoline from natural gas. The water dewpoint attainable with silica gel is around -55° C to -60° C. Molecular sieves are synthetic zeolites (i.e., metal aluminosilicates) with three-dimensional crystalline structures containing interconnecting cavities of uniform size, separated by equally uniform, narrower openings. Molecular sieves can dry natural gas to a dewpoint lower than -100° C. For this reason, these materials are eligible for drying the raw gas intended for cryogenic hydrocarbon recovery applications.

Adsorption is a dynamic process involving batch-wise operations; the continuity of the entire system is ensured by the synchronicity of the columns. When one tower is in adsorption mode, the other is in regeneration mode. When the adsorption tower becomes exhausted, the previously regenerated tower can promptly enter the production cycle.

The adsorption process is favored by low temperature. After a bed has been heated, typically at 170°C–260°C, it is cooled to 30°C–40°C to make it fresh again. Therefore, a regeneration cycle includes both heating and cooling stages.

In the process arrangement shown in figure 23, a slipstream (typically 10%–20% of the raw gas) is used as regeneration gas. To create the driving force needed to circulate the gas through the regeneration loop, the regeneration gas is taken upstream of the control valve and reinjected into the adsorption circuit downstream of the control valve. The overall driving force for the regeneration gas circulation is provided by this control valve.

The major disadvantage of this process arrangement is the relatively high pressure drop between the raw gas and the dry gas, which requires an increasing energy consumption when the dry gas must be compressed. In such cases, the pressure drop can be minimized by inserting a recycle compressor in the regeneration loop, as illustrated in figure 24.



Figure 24: A low-pressure-drop adsorption process.

In the process configuration shown in FIG. 6, the recycle compressor is fed with a slipstream of dry gas. In other configurations it recirculates the wet gas exiting the three-phase separator. Dry gas is more effective in removing water and does not partially rehydrate the bed during the cooling cycle.

In both figure 23 and 24, the regeneration gas is fed to the bottom of the tower during heating and cooling. During the cooling cycle, the bottom part of the regenerated bed picks up a small quantity of water when wet gas is used as regeneration gas, as shown in figure 23. This water pickup does not take place when dry gas is used for the upflow regeneration pattern. In this case, the bottom of the bed is always contacted by dry gas, and the result is a more efficient regeneration step. A similar effect can be attained with the downward regeneration pattern, in which the regeneration gas flows from the top to the bottom of the tower.

Both process setups have filter systems. At the gas dehydration unit inlet, a filter is necessary to remove solid materials (piping scales and rust), along with the free water possibly entrained by the gas. The solid materials must be removed because they foul the sorbent bed, causing a higher pressure drop along the bed and even clogging. Free water must be removed by means of coalescer filters because it causes breaking and powdering of the sorbent.

Since each tower is subject to cyclic temperature swing, over time some sorbent beads crash, producing fines and powder. These solid materials can cause operational troubles in downstream processes and to the gas cooler of the regeneration loop. Therefore, mechanical filters must also be installed on the outlet sides of the gas dehydration unit and upstream of the gas cooler.

Finally, it is worth noting that the cycle length of an adsorption process is established on the basis of an operating labor schedule, resulting in usual 8-hr, 12-hr, 16-hr and 24-hr cycles. Shorter cycle lengths are more economical in terms of equipment sizing and desiccant charge; however, operating costs may be higher due to more frequent operation of valves and shorter desiccant life, which entails more frequent replacement.

Condensation

The third conventional dehydration method employs gas cooling to turn water molecules into the liquid phase and then removes them from the stream. Natural gas liquids and condensed higher hydrocarbons can also be recovered from NG by cooling. The condensation method is therefore usually applied for simultaneous dehydration and recovery of natural gas liquids. Natural Gas can be advantageously cooled using the Joule-Thompson effect (JT effect). The JT effect describes how the temperature of a gas changes with pressure adjustment. For Natural gas, thanks to expansion, the average distance between its molecules increases, leading to an increase in their potential energy (Van der Waals forces). During expansion, there is no heat exchange with the environment, and no work creation. Therefore, due to the conservation law, the increase in potential energy leads to a decrease in kinetic energy and thus a temperature decreases of natural gas. However, there is another phenomenon connected with the cooling of wet natural gas. Attention should be paid to the formation of methane hydrate. Hydrates formed by cooling may plug the flow. This is usually prevented by injecting methanol or monoethylenglycol (MEG) hydrate inhibitors before each cooling. Figure 25 depicts an industrial application of dehydration method utilizing the JT effect and MEG hydrate inhibition.

The wet NG is throttled in two steps inside the flash tanks. The lower temperature (due to the JT effect) of the gas stream in the flash tanks leads to partial condensation of the water vapors. The droplets that are created are removed from the gas stream by a demister inside the flashes. In cases where cooling by the JT effect is insufficient (the usable pressure difference between the inlet and outlet of the gas is insufficient), the air pre-cooler and the external cooler are turned on. Since dehydration is normally applied to large volumes of NG, the external coolers need to have high performance, so this type of cooling is very energy expensive. For dehydration of low pressures NG the external coolers consumes up to 80% of total energy of dehydration unit. However, if the usable pressure difference is high, the JT effect inside the flashes is so strong that internal heating of the flashes is required to defreeze any methane hydrate or ice that may form. A condensation method is applied when suitable conditions for the JT effect are available.



Figure 25: Dehydration method utilizing the JT effect and hydrate inhibition

Supersonic separation

The principle of this method lies in the use of the Laval Nozzle, in which the potential energy (pressure and temperature) transforms into kinetic energy (velocity) of the gas. The velocity of the gas reaches supersonic values. Thanks to gas acceleration, sufficient temperature drops are obtained. Dew temperature of water vapor in NG is reached, and nucleation of the droplets proceeds. Figure 8 depicts the basic design of a supersonic nozzle.



Figure 26: Design of a supersonic nozzle for NG dehydration

At the inlet to the nozzle there are static blades which induce a swirling flow of the gas. The water droplets that form, are separated by the centrifugal force on the walls. The centrifugal force in the supersonic part of the nozzle can reach values up to 500.000 g. The thin water film on the walls moves in the direction of flow into the separation channel. The separation channel leads into the heated degas separator. From here, the slip gas is returned back to the main stream and the water condensate is removed. After separation of the water, it is important to recover the pressure of the gas from its kinetic energy. A shock wave is used to achieve this. Generally, shock waves form when the speed of a gas changes by more than the speed of sound. In supersonic nozzles, the shock wave is created by rapid enlargement of the nozzle diameter. This part of the nozzle is called the diffuser. Thanks to the diffuser 65 - 80% of the inlet pressure is recovered. The scheme of a supersonic dehydration line working on the principle introduced here is depicted in Figure 27.



Figure 27: Scheme of a supersonic dehydration line

General Comparison

Each of the methods presented here has its advantages and disadvantages.

Absorption by TEG is nowadays the most widely used method. Outlet dew temperature around -10°C is usually reached and this water concentration is sufficient for pipeline distribution of natural gas. Indeed, with improved reboiler design (Vacuum Stripping, Drizo, Coldfinger), the outlet dew temperature is even 2 - 3 times lower. However, TEG has a problem with sulfur, and with gas contaminated with higher hydrocarbons. The TEG in the reboiler foams, and with time it degrades into a "black mud". BTEX emissions (the acronym stands for benzene, toluene, ethylbenzene and xylenes) in the flash gases and in the reboiler vent are a further disadvantage.

Adsorption dehydration can achieve very low outlet water concentration $T_{dew} < -50^{\circ}$ C, and contaminated gases are not a problem. Even corrosion of the equipment proceeds at a slower rate. However, adsorption requires high capital investment and has high space requirements. The adsorption process runs with at least two columns (some lines use three, four, or as many as six). Industrial experience indicates that the capital cost for an adsorption line is 2 - 3 times higher than when absorption is used. In addition, the operating costs are higher for adsorption than for absorption.

Temperature, pressure and gas composition heavily effect the amount of water to which can be dissolved in the gas phase. The combination of these parameters defines the amount to be removed from the gas stream, while having a certain dry gas water content specification. As such, the solution for an attractive dehydration unit not always lays in the unit itself. Nevertheless, when selecting a technology for dehydrating the gas, the level of required dehydration is the primary parameter in defining the technology. Solid desiccant technology can go down to the ppm level, and is therefore the technology for e.g. LNG facilities. Molecular sieve material is superior to activated alumina and silicagel; respectively dry gas water contents of around 0.1, 5 and 10 ppm can be realized. The general overview of areas suitable for application of target dehydration method is depicted on the following Figure 28. [19],[20]. Figure 29 represents the comparison table with the advantages and disadvantages of the main natural gas dehydration processes.



Figure 28: Overview of areas suitable for application of target dehydration.

Advantages:	Use of triethylene glycol <100ppm	LNG applications <0.01 ppm	Simple process
	Mature process, widely utilized	Less influenced by feed gas conditions	Could meet dry gas transportation requirements
	Low Capex and Opex	Dew point of dry gas -50°C	
Disadvantages:	solvent foaming when heavy hydrocarbon content in the feed gas is high	High Capex and OpexHigh energy consumptionin solid desiccantregeneration.	Formation of hydrates (need for hydrate inhibitors) High energy consumption

Figure 29: Main advantages and disadvantages of the dehydration processes.

III. SIMULATION OF NATURAL GAS DEHYDRATION USING TEG

Among different kinds of liquid desiccants, TEG is the most widely used solvent for absorption, owing to its low volatility, high hygroscopicity, and high thermal stability. The process initially involves an absorption column, which aims to remove water from the gas stream. The stream of water-enriched glycol then undergoes a regeneration process, which initially involves separation in an expansion vessel from the hydrocarbon mixture contained therein. After heating the stream of water-rich glycol (rich TEG) using alternators, it enters a distillation column where the glycol is separated from the water by means of a stripping gas (methane). Finally, the pure glycol returns to the absorption column in order to repeat the whole process.

The fluid package selected for simulation by Aspen HYSYS is the Glycol package, which is specially used for glycol dehydration. This thermodynamic package uses the Two-Sim-Tassone (TST) EoS combined with a NRTL activity coefficient model through advanced mixing rules. It represents the compressibility more accurately than other methods like the Redlich–Kwong equation of states, including the Soave modified version, and the Peng and Robinson equation of state. Moreover, the glycol package has the essential pure and binary interaction parameters for components usually used in the dehydration process. Salman et al.38 conducted the comparison between glycol package and GPSA-recommended model for TEG dehydration in predicting the water content. The results evinced the validity of the TST– NRTL model used in the glycol package, which demonstrated that the glycol package could predict accurate results and could be used for developing a TEG dehydration model.

Design assumptions:

The following assumptions were made to develop the design model:

i) The mass transfer process take place on each tray

ii) The regenerator is well lagged; hence, the heat losses are negligible.

iii) The associated gases in liquid phase attached to the rich TEG are considered.

iv)The component in feed to the regenerator are two components ((water+ gases) and TEG).

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Figure 30: Natural Gas dehydration process using Triethylene Glycol as solvent simulation process scheme (Aspen Hysys V8.8).

v) The effect of change in total molar flow rate is ignored, an average value is assumed

vi)Vapour-liquid equilibrium relationship is described using Raoult's law.

Components in feed stream:

Components of feed stream	Mass fraction
Methane	0.80
Ethane	0.09
Propane	0.05
i-Butane	0.005
n-Butane	0.01
i-Pentane	0.0025
n-Hexane	0.0025
Nitrogen	0.005
CO2	0.025
H ₂ O	0.0007

Table 1: Components in the feed stream of the simulation.

The operation conditions of the main equipment of the process are the following:

- \blacktriangleright Feed = 1120 m³/h of wet gas
- > Contractor column (P=52 bar, $T=54^{\circ}C$, Trays=3)
- Flash drum-Hydrocarbon remover
- Distillation column(P=1.27 bar, T=100°C-204°C,Trays=3)
- ➢ Glycol purity 98%
- ➢ Water concentration on dry gas 30 ppm.
- > <u>Design parameters 1: Stripping gas flow</u>

2: Distillation column pressure

Simulation results with stripping gas flow as design variable.

The following tables is obtained by keeping the operating pressure of the regenerator constant and changing the supply of the stripping gas. In this case the design variable is the supply of stripping gas.

Striping gas flow (kmol/h)	% wt. Lean TEG purity	ppm(mole) water in dry gas	Lean TEG (kmol/h)	% TEG Loss	Reflux (kmol/h)
0	91.58	50.39	37.95	0.003	2,38E-02
10	92.79	41.8	37.46	0.012	2,11E-02
20	95.17	27.54	36.52	0.023	3,05E-02
30	96.4	20.46	36.06	0.032	3,93E-02

Table 2:Simulation results with striping gas flow as design variable.

Table 3: Loads in kW for simulation using striping gas flow as design variable.

Load in (kW)							
Striping gas flow	HE-1	HE-2	Reboiler	Condenser	TEG cooler	1 st	2 nd
(kmol/h)						pump	pump
0	214.5	250.36	355.5	3,37	203.45	0.556	8.588
10	212.47	249.36	358.7	5	204.97	0.556	8.586
20	209.42	247.83	362.7	7,469	206.08	0.553	8.548
30	206.89	247.11	367	9,77	207.58	0.551	8.525

Increasing the supply of stripping gas increases the purity of TEG. This is because the pressure in the distillation column is kept constant, so the system removes a quantity of water to maintain that pressure. This fact is also verified by the following equation.

$$P \sim \sum_{i} y_{i} P = (y_{H20} * P) + (y_{CH4} * P) (1)$$

Water concentration in dry gas:

TEG enters the suction column with greater purity, resulting in more water being trapped and thus reducing its concentration in the dry gas.

TEG flow:

The higher the stripping gas supply to the distillation column, the more TEG is carried to the peak product, resulting in increased losses while reducing the flow of TEG entering the suction column. Also, the amount of TEG lost is replenished and therefore theoretically the flow of the TEG lean should remain constant.

Reflux:

As the amount of stripping gas enters the distillation column increases, the amount of reflux increases, which is justified by the mass balance, as a larger amount of mixture will liquefy, and a larger amount will enter as a reflux.

HE-1 Duty:

For the first heat exchanger, given the Q_{reflux} load and heat load for the second heat exchanger, the temperatures of streams s2, s3 and s9 are known. This results in the charge of the HE-1 heat exchanger, through which the current temperature s10 is obtained. Increasing the flow of the stripping gas leads to a reduction of the load due to reduced flow.

HE-2 Duty:

Given the temperatures of streams s4 and s5, the load of the alternator depends on the amount that enters. Increasing the temperature reduces the amount of pure TEG and therefore the amount of "rich TEG" coming out of the absorption column. Thus, the load of the second heat exchanger (HE-2) is necessarily reduced.

Boiler:

The boiler load increases as a result of the larger amount entering the column and must be heated.

Condenser:

Similar to the boiler, the larger the amount to be liquefied and the required load will be greater.

Glycol Cooler:

In chains, the condenser follows the line of the two alternators, so with known current temperatures of s10 and s11, and depending on the molar flow, its load decreases.

1st Pump:

The required power depends on the pressure difference and the mass-molar flow passing through it. As with other processing machines, the power is reduced.

2nd Pump:

The power is kept constant because the pressure difference is constant and the molar flow does not change significantly.

It is observed that for stripping gas supply 20 kmol / h, greater TEG purity is achieved than that of the specification. For reasons of energy economy, values close to 20 kmol / h are tested, in order to provide the minimum possible quantity, while meeting the specification. By repeated test procedure, this amount is obtained at 19 kmol / h and the water content of the gas after the absorption column is 29.34 ppm.



Figure 31: Temperature profile in the contractor column.

At the bottom of the column the temperature is lower, as expected, due to the absorption effect. The temperatures (as indicated by the program) starting from the top and going

down to the bottom are 31.52 °C for the first tray, 27.48 °C for the second tray and 26.42 °C for the third tray. Therefore, all disks are considered necessary for this separation.



Figure 32: Temperature profile in distillation column.

It is observed that between steps 1 and 3, the temperature remains constant. This means that the 5 steps are not necessary for the separation (including the two steps, the boiler and the condenser, that is). The separation process could be carried out efficiently, in the presence of two or even one step. Most likely, the surface provided by the two additional disks helps in the better steam-liquid contact or in the processing of more quantity.

In the absorption column the highest concentration is of TEG and the lowest of water. As we move from the top to the bottom the TEG molar fraction decreases and the water equivalent increases. This makes sense as TEG absorbs water from the supply gas stream. The concentration of TEG is constantly increasing, as expected, as we move from the top to the bottom, because TEG is the heaviest component.

Unlike water, its concentration is constantly decreasing because it is the lightest component in the column. In addition, the vapor pressure of triethylene glycol remains practically constant as it depends on the temperature and the second, remains constant in the column disks. The vapor pressure may change along the regenerator, but this does not affect the results



Graph 1: Variation of lean TEG composition with change in stripping gas flow.

The two quantities are proportional, and this is also verified by equation (1) where a linear relationship between the fraction of the stripping gas and the fraction of water is valid. In addition, since the less water there is in the mixture, the purer the TEG, which means that this linearity applies to both of these quantities (purity TEG-stripping gas flow).



Graph 2: Variation of water composition in dry gas with change in stripping gas flow.

Similar to the previous diagram, the linearity is valid, but here the amounts are inversely proportional because more gas means cleaner TEG and this in turn implies cleaner natural gas, ie a lower concentration of water in the dry gas.



Graph 3: Variation of TEG losses with change in stripping gas flow.

In terms of TEG losses, it is clear from the diagram that higher stripping gas flow also means greater losses. Examining the flows where a quantity of TEG is lost from the system, it is observed that the largest losses occur in the "vapor" flow. This is justified because the incoming gas somehow sweeps away a small amount of TEG.



Graph 4: Variation of distillation condenser duty (kW) with change in stripping gas flow.

The heat load required for cooling increases in proportion to the amount of stripping gas that enters because more mixture means more energy required.



Graph 5: Variation of distillation reboiler duty (kW) with change in stripping gas flow.

By analogy with the case of the condenser, a proportional relationship also applies here since a larger number of components requires more energy in order to evaporate.

Simulation results with regenerator pressure as design variable.

The following tables is obtained by keeping the supply of stripping gas constant and changing the operating pressure of the regenerator. In this case the design variable is regenerator pressure of the distillation column. The following values were obtained for a stripping gas flow equal to 19 kg moles/h. This flow was found to be the minimum possible to meet the 30 ppm water limit in the dry gas mixture.

Pressure (bar) in reboiler	% wt. Lean TEG purity	ppm(mol) Water in dry gas	Lean TEG (kmol/h)	% TEG Loss
0.25	99	5.85	35.11	0.14
10	96.02	22.72	36.2	0.028
1.27	94.87	29.34	36.64	0.022
1.5	94.13	33.45	36.92	0.019

Table 4: Simulation results with reboiler pressure as design variable.

Load in (kW)							
Pressure	HE-1	HE-2	Reboiler	Condenser	TEG	1 st	2 nd
(bar) in reboiler					cooler	pump	pump
0.25	207.92	253.86	354.4	10.11	195.61	0.75	8.47
10	209.67	248.39	360.9	7.41	204.14	0.60	8.53
1.27	209.75	248	362.6	7.21	205.97	0.55	8.55
1.5	209.78	247.81	363.4	7.11	207.44	0.63	8.56

Table 5: Loads in kW f	for simulation using	regenerator pressure	as design	variable
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Graph 6: Variation of lean TEG composition with change in regenerator column pressure.

A linear, inversely proportional, relationship is observed between the operating pressure of the regenerator and the purity of the TEG lean. This is justified by equation (1). Under lower pressure conditions the volatility and therefore the purity of the component





Graph 7: Variation of water concentration in dry gas with change in regenerator column pressure.

Due to the reduction of pressure the boiling point of water is smaller therefore in a way both the vapor pressure and its relative volatility and for this reason at lower pressures its concentration is lower.



Graph 8: Variation of TEG losses with change in regenerator column pressure.

As the components become more volatile with decreasing pressure, more TEG is removed through the vapor flow, increasing the losses.



Graph 9: Variation of regenerator reboiler duty (kW) with change in regenerator column pressure.

In this case, due to the higher boiling points, the energy requirement of the boiler is higher at higher pressures. Conversely the condenser has lower energy requirements with increasing pressure since less steam is evaporated for the same reason as shown in the diagram below.



Graph 10:Variation of regenerator condenser duty (kW) with change in regenerator column pressure.

The last three diagrams are directly related to the operating pressure of the distillation column, which is not a linear function of the boiling point of each component in the mixture.

Energy Savings

Due to the perfect performance of TEG application in the natural gas dehydration field numerous research focuses on the TEG dehydration process to improve the dehydrating performances, such as predicting water removal efficiency, estimating TEG purity in tandem with stripping gas flow, equipment sizing and selection along side studies on the influence of solvent purity, stripping gas injection and even the thermodynamic equilibrium model.

Here are some points that need to be improved for the traditional TEG dehydration process.

- Because off-gas from the top of the regenerator is often vented to the atmosphere after combustion, it will lead to serious environment pollution and also energy waste.
- The traditional process is complicated with many various equipment; thus, it is unsuitable for a highly integrated requirement of the mobile modularized unit in the shale gas dehydration station.
- For waste TEG generated during maintenance, it is always collected by gravity and thus the TEG collection drum needs to be located underground, which adversely affects modularization and relocation.
- The complicated process and high energy consumption will definitely result in negative impacts on the economic performance, which is undesirable in shale gas exploration.

To make up the shortages of the traditional TEG dehydration process for natural gas processing an improved TEG dehydration approach is proposed based on heat integration and improved energy efficiency of the overall process. The performance of this proposed improved design was elaborated from aspects of energy efficiency, energy saving rate, economic, environment influence and so forth. The goal of the improved design is to reduces the energy requirements of the overall process by a number close to 70%. In the following graphs the actual and the target energy requirements of the process are depicted.



Graph 11: Total utilities used in the design and target value after energy savings.



Graph 12: Actual cooling utilities and target value of zero cold requirements.



Graph 13: Carbon emissions of the actual and the improved process design.



Graph 14: Actual and target heating utilities after energy savings.

In order to achieve the target goals of minimizing the energy requirements of the traditional design the heat cascade diagram of the overall process was made.



Figure 33: Heat cascade diagram of traditional natural gas TEG dehydration process.

Heat recovery between hot and cold streams is restricted by the shape of the Composite Curves and the fact that heat can only be transferred from higher to lower temperature. The minimum allowed temperature difference (ΔT_{min}) is an economic parameter that indicates a near optimal trade-off between investment cost (heat exchangers) and operating cost (energy). The point of smallest vertical distance (equal to ΔT_{min}) between the Composite Curves represents a bottleneck for heat recovery and is referred to as the Heat Recovery Pinch.

An alternative representation of the overall heating and cooling demands in a process is the Heat Cascade. From the heat cascade diagram, it is clearly visible that the addition of two heat exchangers will reduce the energy and requirements of the process and will minimize the cold utilities of the system. The blue arrow represents the streams of the process that need to be connected in the first added heat exchanger and the red arrow represents the location and the streams that need to be connected in order to minimize the heating utilities of the overall process.

After the heat cascade we can achieve the optimum conditions for the traditional natural gas dehydration using TEG process with the addition of two heat exchangers. The following values represent the optimum design parameters in our system:

Design Parameters	Value
Energy savings	Up to 70%
Cold utilities	Zero
Hot utilities	Minimized
Pressure in regenerator	1.27 bar
Stripping gas flow	20 kmol/hr
TEG purity	95.17
Water concentration in dry gas	30 ppm

Table 6: Optimum Conditions of the simulation of natural gas dehydration scheme.

IV. NOVEL PROCESSES FOR NATURAL GAS DEHYDRATION

Limitations and environmental concerns in TEG dehydration

One of the biggest challenges in operating a glycol gas dehydration system is addressing glycol loss. Most dehydration units are designed with a margin of 0.1 gallons of glycol per million feet of natural gas treated. If the system loses more than this, it affects processes.

One of the most common ways glycol is lost is through foaming. Glycol foaming happens most often when entrained hydrocarbons from production enter the glycol fluid. As the entrained glycol processes through the contactor tower (or "absorber") it will carry over the top of the tower with the sales gas when stable foam builds up on the trays. Foaming also causes poor contact between the gas and the glycol, significantly reducing the drying of the gas[24].

Causes of glycol foaming:

Temperature. Excessive temperatures can lead to a loss of glycol in the glycol reboilers. Temperatures above 400 F cause the vaporization and/or thermal decomposition of glycol. In particular, excessive top temperatures in the still column of the reboiler can allow vaporized glycol to escape to the atmosphere with the water vapor. High temperature differentials between the gas and glycol in the contactor can also cause foaming and glycol loss.

The dry glycol inlet temperature should be no more than 20 degrees F greater than the temperature of the gas. A drastic temperature differential tends to emulsify the glycol with any contamination it may contain. This causes excessive glycol foaming, and high gas velocities through the tower can carry the glycol foam downstream.

Adequate heat exchange will lower the temperature of the hot glycol coming from the reboiler so that it does not cause foaming in the contactor. Over time, heat exchangers can become plugged with build up from contaminates in the glycol causing them to not operate efficiently. Good filtration will help mitigate these issues.

<u>Turbulence</u>. Excessive turbulence and high liquid-to-vapor contacting velocities can also cause the glycol to foam. This condition may point to underlying mechanical or

chemical issues. Lowering the velocity of the gas through the contactor and removing chemical contaminates through good filtration can help prevent glycol foaming.

<u>Contaminants.</u> Other causes of foam that may be present in the process fluid include field corrosion inhibitors, salt, or finely-divided suspended solids. Contaminants like these present in the gas flow stream that were introduced upstream of the dehydration system need to be removed using different kinds of filtration.

Carbon filters can be used to remove hydrocarbon liquids from glycol to help prevent glycol foaming. These are typically installed downstream of the flash separator. Carbon or charcoal filters remove liquid hydrocarbons, compressor oils, degradation compounds and other carbon impurities from the glycol flow stream by catching these molecules in the charcoal's pores. Field corrosion inhibitors, salt and finely divided suspended solids need to be filtered through solid particle filters such as sock or horsehair filters. These will remove these small particles from the glycol flow stream and are found throughout the dehydration system.

<u>High pH Levels in Glycol.</u> High pH levels in glycol cause foaming, which leads to glycol being swept out by the high velocity of the gas. pH is a measurement of alkalinity or acidity of a fluid on a scale from 1-14. A pH rating from 0-7 means the fluid is considered acidic or corrosive, ratings of 7-14 indicate the fluid is alkaline. A rating of 7 is considered a neutral pH.

Often, a glycol analysis can be performed and will reveal high pH levels. Glycol with a pH level above 8.5 will tend to saponify hydrocarbons and cause foaming. Saponify is to turn fat or oil into soap, by reaction with an alkali. Alkaline neutralizers can be added to the glycol to help control high pH levels. Optimum operating pH levels of glycol should remain between 7 - 7.5 to keep the glycol from foaming, emulsifying, or becoming corrosive.

To dehydrate natural gas properly, the system needs clean glycol that is free from hydrocarbons and any other impurities. If foaming is encountered, the first step is to lower pressure and use an anti-foaming agent. This temporarily reduces the foam and continue processing gas. However, this is a temporary fix. To address the underlying issue, the best solution is to examine the filtration system and consider adding a carbon filter. Carbon filters are designed to remove dissolved impurities from the glycol
solution. In our system and simulation, a flash drum is also added to the natural gas dehydration process to remove all the heavy hydrocarbons in the feed stream.

Volatile organic compounds

Volatile organic compounds are compounds that have a high vapor pressure and low water solubility. Many VOCs are human-made chemicals that are used and produced in the manufacture of paints, pharmaceuticals, and refrigerants. VOCs typically are industrial solvents, such as trichloroethylene; fuel oxygenates, such as methyl tert-butyl ether (MTBE); or by-products produced by chlorination in water treatment, such as chloroform. VOCs are often components of petroleum fuels, hydraulic fluids, paint thinners, and dry-cleaning agents. VOCs are common ground-water contaminants.

Volatile organic compounds (VOCs) are emitted as gases from certain solids or liquids. VOCs include a variety of chemicals, some of which may have short- and long-term adverse health effects. Concentrations of many VOCs are consistently higher indoors (up to ten times higher) than outdoors. VOCs are emitted by a wide array of products numbering in the thousands. Examples include paints and lacquers, paint strippers, cleaning supplies, pesticides, building materials and furnishings, office equipment such as copiers and printers, correction fluids and carbonless copy paper, graphics and craft materials including glues and adhesives, permanent markers, and photographic solutions[25].

Although glycol (e.g., triethylene glycol (TEG) or mono- ethylene glycol (MEG)) absorption is the state-of-the-art technology for natural gas dehydration, it faces increasing environmental restrictions since the separation units can emit hazardous volatile organic compounds (VOCs), especially BTEX (benzene, toluene, ethylbenzene, and xylene), due to the decomposition of glycol from regeneration reboiler. Approximately, 40 tons per year are emitted in the atmosphere from a typical natural gas dehydration facility according to literature[26].

Another disadvantage of the TEG dehydration process is that in several cases the offgases are vented to atmosphere after combustion. Due to the open flame in the desorption column and the associated safety concerns, glycol dehydrators are ill-suited for use on offshore platforms. Moreover, glycol system operation is also complex and requires solvent storage, replacement, and disposal, which increases operating cost due to the factors such as large heating requirements and the need for continuously attention and maintenance. Also, waste TEG need to be collected on site which adversely affects modularization and relocation. Membrane contactor has advantages of high interface between gas and liquid phases and no flooding or foaming, which was reported to be feasible for natural gas dehydration. However, solvent regeneration/recycling is an energy-intensive process.

Rotating Packed Bed with Ionic Liquids

There has recently been an increase in exploitation of unconventional reserves such as shale gas, tight oil and tar sand by the production sector of the oil and gas industry. These unconventional reserves require complicated processing and therefore will be expensive to produce using conventional methods. The offshore oil and gas production and processing sectors are faced with a host of challenges coupled with volatile global energy demand. Some of these challenges have been identified as remote locations, harsh environments, extreme climates, and weight and size constraints. The recent fall in oil prices has further heightened the need for solutions which are safe, effective, cost-efficient; robust enough to ensure reliability and availability of equipment in hostile environments and have minimal impact are therefore required to overcome all these challenges. Process intensification can help address some of these issues by using systems which are energy efficient and use of minimal space [23].

Room temperature ionic liquids (ILs) have received great attention and have made great strides in both academia and industry over the past few years. Compared to traditional organic solvents, ionic liquids have a series of outstanding advantages. The negligible vapor pressure of ILs avoids evaporation losses during the regeneration process. Ionic liquids have high thermal and chemical stability which makes ionic liquids recyclable. Moreover, their properties can be tailored by changing the combination of anions and cations. These advantages make them widely used in electrochemistry, organic synthesis and catalysis, extraction and separation processes, and so forth. It is reported that ionic liquid 1-butyl-3-methylimidazolium acetate ([Bmim]- [Ac]) has high CH4/H₂O selectivity, high water sorption capacity, and fast sorption rate. Moreover, [Bmim][Ac] has a moderate viscosity and is noncorrosive.

A rotating packed bed (RPB) has the characteristics of high mass transfer efficiency, excellent micromixing efficiency, and low pressure drop, which has been extensively used in absorption, distillation, polymer devolatilization, reaction, nanoparticles, and preparation. In the rotating packed bed, the liquid passing through the packed mesh can be torn into fine droplets, threads, and thin films by the centrifugal force, and the interface between gas/liquid or liquid/liquid is renewed violently, which significantly intensifies the mass transfer and micromixing. Because of the high mass transfer efficiency, a much smaller absorption unit is required and thus the capital cost can be reduced. Moreover, RPB can be applied to high viscosity fluid systems, such as polymerization of butyl rubber and polymer devolatilization, due to the significant intensification of micromixing.



Figure 34: Schematic diagram of dehydration in RPB.

Membrane Separation

In the last decades, selective membranes have been used more widely in gas processing particularly for acid gas removal from natural gas and natural gas dehydration in order to reduce maintenance costs, lower energy consumption, and enable major savings in the weight and size of the installations. They offer great potential flexibility for handling feed streams of varying compositions or flow rates. As a result, membrane-based separation technology seems to be a promising alternative to absorption and adsorption processes, especially for offshore applications due to the modularity and ease of scale-up. Membrane gas or vapor separation systems are often compact with a small footprint,

and without moving parts and the need of on-site attention when operated in remote/subsea locations which enables a higher potential application in subsea natural gas processing comparing to absorption technology. The design of a membrane module requires a model that can accurately predict the flow behavior and the effect of operating parameters on the membrane separation performance. During the last decades, different flow models have been proposed to meet this purpose. Although the mathematical basis of all the models are the same (i.e., solving transport equation across membrane with material balance, pressure drop, and energy balance coupled with appropriate boundary conditions), they involve different solutions. One of the major problems associated with membrane separation systems for natural gas dehydration is the loss of methane with water vapor in the permeate streams [26],[27]. Different types of membranes tested for H2O/CH4 separation in natural gas dehydration were reviewed in the literature [30,31], and very high H2O/CH4 selectivity (several thousands) for some membranes such as polyimide (Kapton) cellulose acetate, and Nafion® 117 were reported. It should be noted that the reported performances (both H2O permeability and H2O/CH4 selectivity) were mostly obtained at a low membrane operating pressure. Among them, the commercial polymeric mem branes of PEEK-SEPTM (Air Liquide) used for natural gas dehydration has low BTEX emission and less required pre-treatment. Moreover, the Pebax® thin film composite membranes developed by MTR Inc. presented good performance for H₂O/CH₄ separation at a low feed pressure of 2 bar but a reasonable water permeance of 0.055 m³ (STP)/ (m²·h·bar) and a low H₂O/CH₄ selectivity of 47 at 30-60 bar was reported from their field testing [30,31]. Thus, membrane performance (especially H₂O/CH₄ selectivity) will be significantly influenced in the real operating natural gas processes compared to lab-scale synthetic gas permeation testing. Although many polymeric and inorganic membranes were developed for H₂O/CH₄ separation, the process feasibility of such membrane systems has not been conducted to document the potential for natural gas dehydration at large-scale, especially to achieve the specific low water content (e.g., dew point of -40 °C) in natural gas.

Membrane systems dehydrate the gas by passing a high-pressure feed over a selective gas permeable membrane with the permeate side of the membrane maintained at a lower pressure as compared to the feed side. As gas flows over the membrane, the highly permeable gas components, typically contaminants to be removed, permeate selectively to the low-pressure side and are concentrated in the permeate gas stream. Water vapor is one of the most permeable gas components. The high permeability of the water vapor as compared to other feed gas components allows membrane units to permeate the water vapor selectively and thus reduce the water content of the resulting high pressure product gas to low levels required by pipeline specifications.



Figure 35: Conventional cross-flow design with the permeate stream at atmospheric pressure (15% CH4 loss) .[31]



Figure 36: Countercurrent design using a dry gas stream as sweep gas (0.78% CH4 loss).[31]

The driving force of the membrane separation is

Permeability
$$PA \equiv \frac{Na*\lambda}{Am*(p2-p1)}$$

where, N_A is the steady state flux of gas through the film, λ is the film thickness, A_m is the film surface area and p_2 and p_1 are the upstream (high) and downstream (low) partial pressure of gas A, respectively.

Diffusivity and Solubility

$$\alpha 1,2 = \frac{D1 * S1}{D2 * S2}$$

where, D is the average effective diffusivity and S is the apparent sorption coefficient.



Figure 37:Schematic illustration of an industrial thin film composite membrane used for natural gas dehydration. Profiles of water and methane permeances in the different membrane layers is depicted [30].



Figure 38: Exploded view of a conventional spiral-wound membrane module in cross flow mode for natural gas separation.[32]

The modular nature of membrane systems, their light weight, large turndown ratio, and low maintenance make them competitive with glycol units in some situations. Based on commercial experience of field units installed and several studies, membranes are most economically attractive for dehydration of gas when flow rates are small, for example less than 10 MMscfd. Membrane units are also competitive with TEG dehydrators on offshore platforms at larger flow rates due to the low weight and footprint, leading to considerable platform capex savings as a result. Certainly, the reliability and simplicity of membranes make them attractive for offshore and remote site applications, provided the low pressure permeate gas is used effectively. The added benefit, compared to TEG units, is the absence of BTEX emissions with membrane systems.

The low cost and wide industry acceptance of glycol dehydration systems has proved to be a stiff barrier to membrane competition. However, a few membrane dehydration systems have been built. Producing competitive membrane dehydration systems for natural gas treatment is not a membrane material performance problem[26].



Figure 39: Effect of permeate pressure on the efficiency of a membrane natural gas dehydration system.[13]

The problem is a loss of methane, with the water vapor permeating the membrane. Membrane units used to dry air also lose a fraction of the high-pressure air to the permeate. In air dehydration, this loss of air to the permeate is inconsequential; with natural gas, a loss of even 1% of the feed gas makes the process noncompetitive. Water has much higher diffusivity than methane. Both solubility and diffusivity favor permeation of water over methane.

The reason these very high selectivity membranes lose methane to the permeate gas is due to pressure ratio limits on membrane performance. One way to reduce the methane loss to an acceptable level is to use a small vacuum pump to reduce the pressure of the permeate gas to 1-2 psia. The membrane system then becomes small, and the methane loss decreases to <1%. The cost of such a membrane-vacuum system could be

competitive with glycol dehydration, and in offshore applications, the small footprint and low weight would be attractive. A membrane system would have approximately one-fifth the weight and footprint of a glycol absorption plant. However, the potential hazard posed by air leaks contaminating the permeate gas has to date made operators reluctant to send the gas to the plant fuel line, so the gas must be vented or flared, and even a methane loss of <1% normally is not economically acceptable. Thin composite copolymers membranes (good separation H2O/CH4 in the thin layer, good mechanical strength, transport resistance from supporting microporous and paper layers).

Another solution to this problem (a), is to operate the membrane system at a permeate pressure close to atmospheric pressure and then recompress the permeate gas. Compressing the gas would cause almost all of the water vapor to condense and the remaining gas could be sent back to the high-pressure feed. The problem with this system is cost of the permeate compressor. This cost is larger than the cost of the membrane system, so this approach is not appealing.



Figure 40: Membrane system designs for dehydration of natural gas (a) dehydration using a recycle compressor and (b) dehydration using a permeate sweep gas.

Yet another process design (b), which was developed by Air Products and used in a few systems is shown in Figure 31. In this process, a sweep gas of dry methane is passed across the permeate side of the membrane. The sweep gas increases the effective pressure ratio for water transport and reduces methane loss to ~1%. The wet sweep gas-permeate mixture leaving the membrane unit is sent to a small secondary methane drying

loop, which produces clean dry methane to be recirculated. The complexity of the system and the need for a small compressor has limited use to a few offshore applications.

Key design limitations:

□ CH4 loss across the membrane area.

While methane permeates from the high-pressure feed to the permeate due to the methane partial pressure difference across the membrane, the helium sweep gas permeates to the feed side due to the helium partial pressure difference across the membrane.

- □ Area needed for separation to reach 100 ppm specification. Capital cost of a membrane system often scales linearly with the membrane are requirement.
- □ Higher sweep gas flow for higher water permeance.
- Use of dry gas sweep gas decreases both the required area and the methane loss. If the dry inert gas need to be generated for dehydration only the cost of dry gas production can be prohibited.

A proposed membrane dehydration design could be the following:



Membrane Gas Dehydration

Figure 41: Membrane gas dehydration scheme.

Membrane systems dehydrate the gas by passing a high-pressure feed over a selective gas permeable membrane with the permeate side of the membrane maintained at a lower pressure. As gas flows across the membrane, the highly permeable gas components are removed selectively to the low-pressure side. Water vapor is one of the most permeable gases. The high permeability of water allows membrane units to reduce water content of the feed gas to low levels required by pipeline specifications. The membrane system will generate high pressure product gas to the targeted water dew point. The water vapor is removed as the low pressure permeate/tail gas. The tail gas is recycled to front end of the compressor and combined with the feed gas stream. The compressed gas is cooled and the condensed water separated as liquid. Again, the closed loop system eliminates fugitive air emissions and maximizes hydrocarbon recovery. An alternate design is to use a moderate vacuum on the permeate side and a condenser prior to the membrane unit to increase the separation efficiency and to lower hydrocarbon losses to the tail gas stream. This design is most economical wherein the rejected water rich stream can be used as fuel or flared.

V. <u>FUTURE WORK-CONCLUSION</u>

Natural gas is usually accompanied by large amount of water vapor from the reservoir. Removing this water is a major task for the process engineers. Therefore, natural gas plants are designed different offshore and onshore processes to handle water removal from the gas stream is handled to meet pipeline specifications of water content in the processed gas stream. The modeling of the natural gas dehydration and TEG regeneration was successfully completed by HYSYS. The key parameters that influence the TEG dehydration process were TEG flow rate, the temperature of the reboiler, reflux ratio, column pressure and the stripping gas flow rate. To obtain the desired level of the parameters a series of plots were displayed. The plots that are presented are based on the calculations carried out from the case study section in HYSYS.

Although extensive literature studies are available on the process simulation and parameter optimization of the natural gas dehydration process, none of the research is focused on the process optimization as a whole minimizing the total energy consumption, the capital and operational cost of the equipment, the carbon emissions and other environmental parameters while having as constrains the lean solvent concertation (TEG purity), water removal efficiency (specifications) along side stripping gas flow and TEG loses and consumption. A more holistic approach is needed to further optimize and integrate the traditional natural gas dehydration process using triethylene glycol as a solvent.

To enhance the performance of the system and maximize potential benefits of the improved dehydration process the intrinsic correlation of the dehydration performance with key parameters such as the lean solvent concentration, stripping gas consumption and TEG circulation rate needed to be investigated thought further simulation. Furthermore, in order to further improve the energy savings of the process apart from heat integration, power integration needs to be researched because in the simulation there is a high-pressure area (52 bar) and a low-pressure area (1.27 bar) and in order to reduce the pressure a Joule Tomson value is used. It would be more energy efficient if a turbo expander was used to take advantage of the pressure differential and help minimize the cost of compression by reducing the energy requirements of the system.

In conclusion, from the research completed it is clear that, the successful development of membrane technology for natural gas dehydration as a competitively viable alternative to conventional glycol dehydrators faces two substantial challenges. First, when the polymers that are highly selective for water/methane are made into industrial thin film composite membranes the majority of transport resistance to water can come from the supporting microporous and paper layers instead of the selective layer. This factor causes a significant decrease in the apparent water permeance and H₂O/CH₄ selectivity of the composite membranes. The second factor is that the separation id restricted by moderate feed to permeate pressure ratios. Vacuum in the permeance side alongside the use of sweep gas is favored for successful natural gas dehydration. However, detailed design with accurate transport model and field tests are required to verify that membranes are a profitable alternative to natural gas dehydration using triethylene glycol.

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