1. Introduction

Until recently, most of the natural gas production came from the conventional reservoirs, typically trapped in multiple, relatively small porous zones in rock formations such as sandstones, siltstones, and carbonates, and relatively easy to recover. Unconventional gas, on the other hand, is obtained from low permeability reservoirs in coals, tight sand formations, and shale, where the accumulation of gas tends to diffuse and spread over large geographical areas, making it more difficult to recover. Improvements in horizontal drilling combined with recent advancements in hydraulic fracturing techniques have allowed access to large volumes of shale gas that were previously uneconomical to produce.

The production of natural gas from shale formation is one of the fastest growing segments of the U.S. oil and gas industry today. The U.S. Energy Information Administration (EIA), Annual Energy Outlook 2013 (AEO2013) [1] Early Release Overview projects a substantial increase in natural gas production and predicts lower natural gas prices in the future facilitated by growing shale gas production. A decade ago, the natural gas production from the shale formation accounted for about 2% of the total U.S. natural gas production, but today it represents approximately 34% of the total U.S. natural gas production and is projected to be above 50% of the total U.S. natural gas production by the year 2040. The EIA reports U.S. natural gas production to increase from 23 trillion cubic feet (Tcf) in 2011 to 33.1 Tcf in 2040 (1 cubic feet = 0.0283 cubic meter), a 44% increase. Almost all of this increase in domestic natural gas production is due to projected growth in the shale gas, which will grow from 7.85 Tcf in 2011 to 16.7 Tcf in 2040. Figure 1 provides the data extracted from the EIA, AEO2013 [1] indicates the history and projections for U.S. dry natural gas production between 1990 and 2040. The data clearly shows expected growth in shale gas
production will exceed 50% of the total U.S. dry gas production by 2040.

The increasing natural gas production from extensive shale gas resources has contributed to a lower natural gas prices (referenced as U.S. Henry Hub price projections). The average natural gas price levels in the U.S. remained below $3 per million Btu (1 Btu = 1.055kJ) in 2012 and projected Henry Hub spot natural gas prices (2011 dollars) remain below $4 per million Btu through 2018 and will reach $5.40 per million Btu in 2030 and $7.83 per million Btu in 2040.

Natural gas is the cleanest burning fossil fuel, primarily due to its combustion produces low levels of carbon dioxide (CO₂) emissions. The combined cycle power generation from natural gas produces half the amount of CO₂ compared to coal based power generation and 30% less emissions than fuel-oil based generation. Shale gas development in the U.S. has great importance in meeting future energy needs as well as alternative energy strategies in reducing greenhouse gas (GHG) emissions.

The lower natural gas prices with lower emissions facilitated by shale gas production, is projected to spur increase in consumption in the electric power and industrial production sectors over the next 15 years. Due to the lower material and energy cost, the consumption in the industrial production sector, specifically bulk chemicals and primary metal industries is projected to grow more rapidly. The bulk chemicals also benefit from the increased NGL production from shale gas. Even with the increased consumption of natural gas in the U.S. domestic market, the shale gas production is projected to outpace domestic consumption by 2020, spurring the net export of natural gas. The U.S. export of LNG from domestic sources is projected to increase after 2020.

The production of shale gas from the ground and delivering it to the market requires considerable additional infrastructure. The infrastructure due to increased shale gas production is similar to other gas production facilities. The shale gas supply chain includes wells, gas gathering, gas treatment, NGL extraction and fractionation facilities as well as gas and liquid transport pipelines. The shale gas chain infrastructure along with the downstream industrial sector has made considerable contribution to the recent U.S. economic development. The sections below provide the overview of the shale gas production, the U.S. and the global shale gas resources, and its production techniques. In addition, the sections below also describe applicable gas purification technologies for contaminants removal from the shale gas and NGL extraction that are necessary for the end use of the shale gas and in the development of its co-products for the downstream industrial sector.

2. Shale Gas — General Overview

Shale gas refers to natural gas that is trapped within the shale formations. Shale is a fine-grained sedimentary rock that can provide rich sources of petroleum and natural gas. Sedimentary rocks are rocks formed by the accumulation of sediments at the earth surface and within bodies of water. Common sedimentary rocks include sandstone, limestone and shale. Modern Shale Gas [2] provides excellent information on the shale gas formation in various shale plays in the U.S. and their geotechnical description.

The recent improvements in horizontal drilling techniques combined with advances in hydraulic fracturing (or fracking) methods have greatly improved the efficiencies and economics in shale gas production. Horizontal well drilling is a key to changing the flow pattern in the reservoir to a distance of 3,000 to 10,000 feet. In hydraulic fracturing, a mixture of hydraulic fluid with propping agents and additives is pumped at high pressure into the well bore. The high hydraulic fluid pressure creates fractures in the reservoir and causes the fractures to grow.

The fracturing fluid is 90% water, 9% propping agent, and less than 1% of functional additives containing pH adjusting agent, biocides, clay stabilizer, scale and corrosion inhibitors, gelling agent, friction reducer, surfactants, acid, etc. A blender mixes the fluid with propping agent (generally sand) and other additives and supplies the fracture fluid slurry to high pressure pumps. The fracturing pumps increase the pressure from a few hundred pounds per square inch (psi) to over 20,000 psi, depending on the depth of the formation and friction in the well bore. The pressurized mixture causes the rock layer to crack, pushing the earth apart so a fracture forms and propagates to unlock the natural gas trapped in the rocks allowing it to flow from the shale into the well.

Figure 2 provides a diagram of a typical hydraulic fracturing operation illustration in shale gas. The hydraulic fracturing
operations utilizes between 2 to 4 million gallons of water depending on the type of shale formation. After drilling and fracturing of the well are completed, water is produced along with the natural gas. Some of the returned water is fracture fluid and some is natural formation water. Regardless of the source, these produced waters that move through the wellhead with the gas represent a stream that must be managed.

States, local governments and shale operators are pursuing the pollution prevention by reduce, re-use and recycle by both traditional and innovative approaches that include underground injection, treatment and discharge and recycling. New water treatment technologies have been developed for the reuse of the produced water and minimize use of resources.

Estimates of the technically recoverable resources (TRR) for the shale plays in the lower 48 states in the U.S. is at 862 Tcf. EIA [4] recently assessed preliminary geologic and reservoir characterization of shale basins and formation(s) for the 14 regions outside the U.S. The initial shale gas TRR estimates for shale gas basins in 32 countries, containing almost 70 shale gas formations in these 14 regions outside the U.S., is 5,760 Tcf. This is more than six times EIA's 862 Tcf estimate for the U.S. shale gas. This together with the U.S. shale gas estimates put the total world resources at 6,622 Tcf. These are moderately “risked” conservative estimates. This indicates there is significant potential for shale gas that could play an increasing role in the global natural gas market. Additional infrastructure in developing these resources from the wellhead to the overall gas processing facilities will have major economic impacts in the years ahead.

The infrastructure requirement in the development of shale gas is generally similar to the conventional gas gathering and processing infrastructure. The main difference is in the type of gas contaminants, constituents and substantial quantity of produced water returned back from the wells as a result of large quantity of water utilized in the hydraulic fracturing. Figure 3 provides an overall block diagram of the infrastructure requirement in gathering and processing of shale gas value chain.

The shale gas gathering and liquid (mainly water) separation from the gas is generally part of the well head facilities and provide a separation between well head and downstream gas processing facilities. The large quantity of produced water and any hydrocarbon condensate is separated at the well head facility before diverting the gas to the gas processing facilities. As mentioned in the previous section, the hydraulic fracturing operation adds a large quantity of water to the wells and they become part of the produced water in addition to any formation water that may be present. As mentioned earlier, the water produced must be managed properly using pollution prevention measures such as reduce, re-use and recycle using both traditional and innovative approaches.

The shale gas processing facility is generally a dedicated processing and separation facility that begins with the gas purification or removal of acid gases (CO₂, H₂S and other organic sulfur compounds such as COS, CS₂ etc.) contained in the natural gas. If large amount of sulfur contaminants are present, the facility may require a sulfur recovery unit to recover elemental sulfur from the off gas stream of this process. Where the amount of sulfur is small, the off gases can be either incinerated or vented from the process to the atmosphere. The sections below further describe the gas purification technologies intended for shale gas treatment. The natural gas is processed further to remove water and mercury from the gas prior to any heavier hydrocarbon removal to meet the pipeline quality gas requiring dew point and...
heating value specifications, generally at 1100 Btu per standard cubic feet (Scf).

Natural gas is a key resource having lower emissions compared to other fossil fuel for electrical power production and residential use as well as vital source material for chemical and petrochemical feed stock. Once the impurities are removed from the shale gas, the NGL extraction can have significant implications in reshaping the chemicals Industry. The NGL production and fractionation of NGL into ethane, propane, butanes and heavier hydrocarbons (light naphtha) as co-products of natural gas has significant added value and impact on the downstream energy sector. The ethane, as mentioned earlier is a precursor to petrochemical production. The additional section below describes the NGL extraction technology utilized in efficiently extracting these higher value co-products in the end use of shale gas. The lean pipeline quality gas mostly consisting of methane is delivered to the transmission pipeline for electrical power generation, residential use as well as feed stock to the gas based chemicals including ammonia, urea, methanol etc. In addition, available low price natural gas can be liquefied to LNG for energy export and if economics permit, natural gas can be reformed to synthesis gas, a source for gas to liquids (GTL) conversion in producing high quality naphtha, diesel etc.

4. Shale Gas Purification

Natural gas from the wells almost always requires some level of purification to make it suitable for the end use. Shale gas is no different in that regard. Numerous gas purification technologies have been developed over the last fifty years to remove acid gas from a variety of gas streams. The main acid gas contaminants in the natural gas stream are CO$_2$ and H$_2$S and to a lesser degree the organic sulfur components such as COS and mercaptans (RSH). Removal of the acid gas contaminants from the natural gas is required for corrosion control, to meet gas and/or liquid product specifications, to prevent formation of CO$_2$ solids (freeze-out) at low temperatures in the downstream processes, prevent poisoning of catalysts and to meet environmental requirements. The acid gas content varies greatly with each natural gas stream. It is important to understand the acid gas components and their content in the inlet natural gas stream and required specifications in the treated gas to allow proper design and selection of the technology.

Shale gas found in the U.S. contains moderate levels of CO$_2$. It ranges from less than 1 mole% to over 3 mole%. The H$_2$S concentration levels from most U.S. shale gas have been generally low, ranging from less than 100 parts per million by volume (ppmv) to as much as 750 ppmv. Although the H$_2$S content is low, it is still high enough to require treatment to meet pipeline gas specification of less than 4 ppmv. In most cases shale gas treatment is required to remove the H$_2$S. The pipeline specification for CO$_2$ varies depending on the pipeline, typically a maximum of 2 mole% with some pipelines allowing a maximum of 3 mole%. However, the downstream cryogenic NGL extraction may require CO$_2$ levels below 1.5% in order to avoid any CO$_2$ solids formation (freeze-out) in the process.

The above requirement generally sets the scope for acid gas removal process and technology selection. There are many acid gas removal technologies to remove CO$_2$ from the natural gas. They include chemical and physical solvent based re-generable processes, membrane based CO$_2$ / methane separation using polymeric membranes, cryogenic processes for CO$_2$ / methane separation, re-generable solid-bed absorbents such as molecular sieve and non-re-generable processes such caustic wash. These processes as well as hybrid of these processes can be applied for acid gas removal depending on their efficiency and cost effectiveness for a specific application. Additional description for these processes and their application can be found in GPSA [5], Kohl and Riesenfeld [6], and also Shaw and Hughes [7].

The chemical solvent based process using aqueous amine is the primary one of interest for acid gas removal from natural gas. The solvent based process is re-generable and there are many commercial installations using these solvents. Figure 4 provides a simplified process scheme, representing a typical aqueous amine based process.

![Figure 4 Simplified Process Schematics - Amine Solvent Based Acid Gas Removal Process](image-url)
referred to as a stripper) from the top where depending on the H₂S content and local environmental requirement is diverted to the sulfur recovery plant when a larger quantity of H₂S is present or sent to a thermal oxidizer. The lean regenerated amine solvent is pumped back to the absorber column via a lean/rich exchanger (to recover heat), a lean amine cooler and amine filters.

The selection of the solvent and specific design is important for the shale gas treatment. The shale gas described above has low concentration of H₂S and higher concentration of CO₂. It is important to understand the use of selective H₂S removal to ensure low CO₂ to H₂S ratio in the stripped acid gas in the amine regenerator to sulfur plant. This requires proper selection of the solvent and understanding of the absorber design to limit the CO₂ absorption. Figure 5 provides various solvents characteristics for acid gas removal extracted from GPSA [5] that can help in the preliminary selection of aqueous amine or physical solvent. The guidelines presented here can be utilized in the solvent selection. The acid gas removal process design can affect the entire gas processing facility including methods selected for the acid gas disposal, sulfur recovery, gas dehydration, NGL extraction, fractionation and liquids treating downstream of the fractionation. Some of these factors to be considered are as follows:

- Air emissions requirement, specifically for sulfur compounds disposal
- Type and concentration of impurities in the shale gas
- Gas pipeline specifications
- Acid gas selectivity requirements for downstream sulfur unit
- Disposal of byproducts, considered hazardous chemicals in most cases
- Consideration for downstream processing and liquid products specifications
- Pressure, temperatures and volume of the sour inlet gas
- Capital, operating (utility) and technology license/royalty cost

It is essential to have an extended and accurate analysis of the shale gas to identify if organic sulfur components such as COS, CS₂ etc. are present. These components, even in a small quantity, can have a significant impact on the process design of the acid gas removal and downstream processing facilities. For most shale gas processing, selective H₂S removal is preferred to meet the pipeline specification as well as reducing the CO₂ to a desired level. The process solvent selection must offer selectivity for the downstream sulfur unit as well as lower the overall solvent circulation rate to reduce utility consumptions. MDEA and MDEA based formulated solvents will generally meet these conditions. However, there are challenges in the design of the MDEA solvent based process. These challenges can be overcome by having basic process understanding in the design for the selective H₂S removal from the shale gas.

The amine based process is a chemical reaction between the acid gases and the aqueous solvent. Reaction of CO₂ in the MDEA solvent is much slower due to the fact that CO₂ first dissolves in water to form carbonic acid and then it reacts with MDEA. The reaction between CO₂ and water is a slow reaction and affected by the reaction temperature, residence time and to some extent MDEA concentration. On the other hand, the reaction between H₂S and amine is direct and fast. It is generally equilibrium limited. The understanding of difference in reactivity between these two acid gas components is a key in design of the selective H₂S removal system using MDEA. The following basic process parameters will provide optimum design with required flexibility in the design of the amine absorber system operation, where the absorption of CO₂ must be minimized to a desired level:

- Optimize amine temperature
- Optimize amine concentration
- Optimize tray design by a combination of residence time and number of trays
- Provide multiple feed points for the for lean solvent to the absorber
- Minimize solution circulation rate

The temperature control is one of the most important factors in controlling the CO₂ reaction. Higher temperature in the absorber promotes faster reaction between CO₂ and amine.
Lower temperature will minimize the reaction between the CO$_2$ and water. The higher temperature may also shift the equilibrium between the H$_2$S and amine and slip H$_2$S that is undesirable. Albiol and Shah [8] developed a modified amine process called MINISOL$^\text{TM}$ showing a way to control the absorber temperature. Their experience has shown that MDEA based process can be designed to slip substantial amount of CO$_2$ by controlling the absorber temperature while lowering the amine circulation rate and also meeting the pipeline H$_2$S specifications.

The amine concentration is also important in reducing the water content of the amine solution. As described above, the reaction of CO$_2$ requires water to form the carbonic acid before it can react with the MDEA. The higher concentration of MDEA solution reduces the available water and therefore minimize the reaction between the water and CO$_2$ reducing its pick-up in the solution. The solution concentration of up to 50wt% MDEA can be operated before the solution viscosity can adversely affect the mass transfer in the absorber column.

The column tray design is always critical for mass transfer between the acid gas and the MDEA solution. The absorber diameter is generally controlled by high vapor loading. The lower tray liquid loading in the absorber presents various challenges in the gas liquid contact time and associated mass transfer. Today the mass transfer based simulation software tools are available in the market and the designer must understand the geometry of the tray to enhance the control of residence time and optimize the amine absorber design. Weiland [9,10] presented benefits of mass transfer rate based simulation and tray operating regime for the amine absorbers. It highlights the importance of column tray design and the use of mass transfer based simulation in the system design where the selective H$_2$S removal is desired.

The overall amine circulation rate also has impact to the overall mass transfer in the absorber column. In the column designed with trays, higher circulation rate increases the height of the liquid on each tray, as the weir creates a flow obstruction. The amine stacks up and provides larger surface area for CO$_2$ absorption. The more liquid in the column will provide higher gas/liquid interface for the CO$_2$ to be absorbed and will reduce the CO$_2$ slip from the absorber.

The process parameters described above must be taken into consideration during the design of the acid gas removal system, especially in the shale gas purification using MDEA solvent.

Over the last twenty five years, MDEA based formulated solvents have been developed by various companies, i.e. Dow, Union Carbide, BASF, Huntsman etc. Use of these proprietary formulated solvents may provide enhanced selectivity in acid gas removal, generally at a higher solvent cost but sometimes offer advantages over generic MDEA. They must be evaluated for their cost benefit during the design of the acid gas removal units. They can provide benefits of reduced circulation rate with lower energy requirements, reduced corrosion etc. The formulated solvents are generally MDEA based solvents with additives such as pH suppressants, corrosion inhibitors etc.

In addition to the formulated MDEA based solvents, sterically hindered amine has also been used to treat sour gas. These are specialty amines constructed by a process defined as steric hindrance. The actual structure of the amine is formed to accommodate specific process requirement. This type of amine and the associated technology is different than the formulated solvents, which create the desired formulations by blending different components in the amine such as MDEA. An example of sterically hindered amine is FLEXORB SETM solvent, marketed by Exxon Research and Engineering Company. It is developed to selectively remove H$_2$S from natural gas in presence of CO$_2$ [11].

5. NGL Extraction

The recovery of hydrocarbon liquids from the natural gas stream ranges from a simple dew point control to deep ethane extraction. The desired level of liquids recovery has significant impact on the process selection, complexity and cost of the processing facility. The term NGL is a general term which applies to liquids recovered from the natural gas and refers to ethane and heavier compounds. The term liquefied petroleum gas (LPG) describes hydrocarbon mixtures with propane and butanes. The gas processing facilities in the U.S. today produce a single NGL (ethane plus) product, which is then sent to the fractionation facility to make products such as a purity ethane, ethane -propane mix (EP mix), commercial propane, iso and normal butanes and gasoline (light naphtha).

The NGL extraction development has evolved over the last century from the lean oil absorption process developed to extract butanes and heavier components from the gas to mechanical refrigeration processes to extract propane and heavier components and finally the modern day cryogenic turbo-expander processes to extract ethane and heavier components from the natural gas.

GPSA [5] provides depth of history and process development in this area. Figure 6 provides one of the many versions of cryogenic turbo-expander process. The specific process in this figure is called GasSub-cooled (GSP) process, where the process uses high pressure dry feed gas to produce the necessary refrigeration by expansion across the turbine (turbo-expander). The turbo-expander recovers the useful work from this gas expansion, typically driving a centrifugal compressor to compress the lean residue gas from the process. This expansion is nearly isentropic and lowers the gas temperature significantly in comparison to the expansion across the valve (called Joule Thompson (J-T) adiabatic expansion).

In this process the high pressure dry inlet gas is first chilled using the low pressure cold lean residue gas and used for side
heating of the demethanizer column also recovering refrigeration from the cold liquids. Additionally, with richer gas feed, sometimes mechanical refrigeration is utilized to supplement gas chilling.

The chilled gas is sent to the cold separator where the condensed liquid is separated, flashed and fed to the middle part of the demethanizer column. The cold vapor from the separator is split into two. A small portion of the cold high pressure gas is sent to an overhead exchanger where it is totally condensed with the demethanizer overhead stream. This stream is then flashed to the top of the demethanizer providing reflux to the column. The remaining gas from the cold separator is expanded in the turbo-expander and then fed to the demethanizer several stages below the top of the column. The demethanizer column separates the methane from the ethane and heavier liquids at the bottom. The cold overhead methane rich lean residue gas stream is heat exchanged to recover the refrigeration prior to compressing in the turbo-expander driven compressor.

The process is completely heat integrated to maximize gas chilling of the high pressure dry inlet gas stream and very efficient providing high ethane and heavier component recovery from the natural gas. Due to the cryogenic nature of the process the gas has to be bone dry to avoid any hydrate related issues. The molecular sieve (aluminosilicates) solid desiccant type gas dehydrators are commonly utilized to remove water from the natural gas. Also the gas is treated to remove any traces of mercury presence in the gas to avoid corrosion to the brazed aluminum heat exchangers utilized in the cryogenic services.

### 6. General Conclusion

The economic expansion fueled by the advancement in drilling technologies combined with hydraulic fracturing to extract shale gas will have a dramatic impact on the future U.S. energy picture. The production of natural gas from the shale gas formation is one of the fastest growing segments in the U.S. The projected increase in shale gas production is significant and has helped transform the energy picture in the U.S. towards becoming energy independent as well as a net energy export country over the next decade.

The paper has presented an overview of the shale gas production and infrastructure installation associated with gas gathering, gas pipelines and gas processing facilities. The growth that has resulted from the shale gas development and production has attracted billions of dollars in direct investment in this sector having enormous impact fueling the U.S. economy. It has also generated various additional impacts in the downstream chemical market and beyond, including ammonia, urea and methanol production. The value added co-products of shale gas, such as ethane and heavier hydrocarbons have fueled the investment in the U.S. petrochemical industry. The availability of low cost shale gas has also had a profound effect on the manufacturing in energy intensive sectors such as steel, glass, rubber, aluminum and papers. Obviously the low cost natural gas has also helped increase investment in the electric power and reducing the emissions of GHG. The country has taken a 180 degree turn in the LNG industry where previously the U.S. was expecting an increase in import of LNG is now converting the LNG regasification terminals with liquefaction facilities for LNG export commencing over the next five to six years.

The paper also presented details of gas purification process and technologies considerations in the design of the facilities associated with the shale gas production to make it suitable for end use. The NGL extraction process was discussed to provide the importance of the co-products of shale gas as these end products will have tremendous value added effect along the natural gas value chain. There is no doubt that the significant increase in the NGL production could drive change across the U.S. chemicals industry in transforming the U.S. balance of trade as ethylene capacity comes on line. Recent studies by EIA has identified worldwide resources of shale gas and the results show the potential for exploiting these resources can be enormous with advances in the shale gas drilling and hydraulic fracturing technologies.

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