Technologies for Upgrading of Carbon Dioxide-Rich Natural Gases: Challenges and Recent Advances

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ABSTRACT

An overview of gas process technologies for CO_2 separation from natural gas and process technologies based on absorption, adsorption and membrane separation is considered. For each technology, the fundamental separation mechanism accompanying their operational criteria is described. Amine absorption technologies for acid gas treating are well-established in the natural gas industry.

Keywords: natural gas sweetening, upgrading, absorption, membrane, adsorption

1. Introduction

According to the International Energy Outlook 2010 on its June 2011 release, natural gas was reported to be one of the main energy sources for industrial and electrical power generation applications [1].

The growth in the global demand for natural gas has led to a re-evaluation of the development potential of unconventional, stranded and contaminated gas reserves that were previously considered economically unviable. The estimated world volumes of sub-quality natural gas reserves, including sour natural gas, are significant. Sub-quality natural gas reserves

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are defined as gas fields containing more than 2% CO_2, 4% N_2 and 4ppm hydrogen sulphide (H_2S) [2]. Additional gas processing challenges arise from new environmental regulations that may call for capture and sequestration of CO_2 from gas fields.

As one of the major contaminates in natural gas feeds, carbon dioxide must optimally be removed as it reduces the energy content of the gas and affect its selling price. Moreover, it becomes acidic and corrosive in the presence of water that has a potential to damage the pipeline and the equipment system. The presence of CO_2 in natural gas remains one of the challenging gas separation problems in process engineering for CO_2/CH_4 systems. Therefore, the removal of CO_2 from the natural gas through the purification processes is vital for an improvement in the quality of the product.

The major operations that can be used in natural gas processing and LNG production are shown in Fig. 1. Common process operations include inlet gas compression, acid gas removal, dehydration, LPG/NGL recovery and hydrocarbon dew-point control, nitrogen rejection, outlet compression and liquefaction. Depending on the available markets, feed gas properties, product specifications and the gas flow rate, the units identified in Fig. 1 may not all be required.

In conventional gas processing H_2S and CO_2 are removed in an acid gas removal unit (AGRU) using aqueous amine absorption processes. The sweetened gas leaving the amine process is saturated with water, so typically the AGRU is located upstream of the dehydration facilities. The final sections of the gas liquefaction plant (main cryogenic heat exchange (MCHE) in Fig. 1) can operate at temperatures as low as -161.1^{o}C, and therefore, it is essential that components that could freeze, and cause blockages in the cryogenic equipment, at low temperatures are removed from feed to the cryogenic plant. In addition to CO_2, components that could freeze in the cryogenic plant include water (typically removed to less than 0.1 ppmv), heavier paraffinic hydrocarbons and aromatics such as benzene [3].

This review provides an overview of gas processing technologies for CO_2 removal from natural gas as a solution for efficient domestic and commercial utilization of low-grade natural gases. The subsequent sections of this review describe the core concepts of absorption, membrane and adsorption. Distillation processes are not included here as their range of application is beyond the typical cases of natural gas processing.

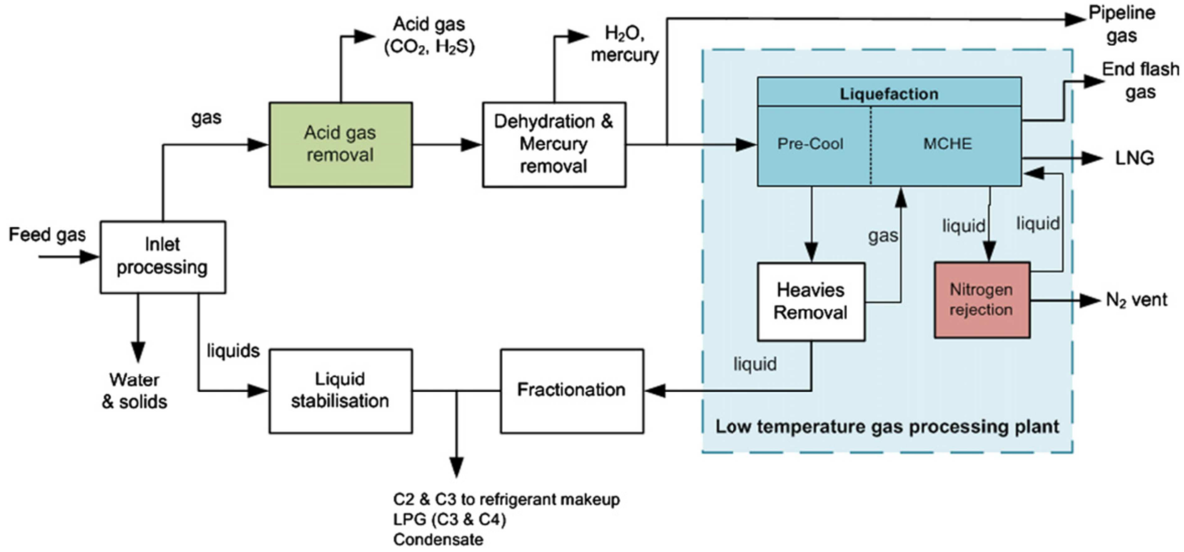

Figure 1- Conventional gas processing operations in a typical natural gas plant

(MCHE= main cryogenic heat exchanger) [3]

2. Separation Techniques

Separation processes can be designed to exploit differences in the molecular properties or the thermodynamic and transport properties of the components in the mixture. Molecular properties that could be exploited to achieve a separation of CO_2/CH_4 include the differences in kinetic diameter, polarizability, quadrupole and dipole moments of the molecules. Thermodynamic and transport properties that could be exploited include vapor pressure and boiling points, solubility, adsorption capacity and diffusivity. Based on these properties of the components to be separated, the primary operations for the separation and purification of gases apply one of the following inherent separation mechanisms [4]:

- Phase creation by heat transfer and/or shaft work to or from the mixture
- Absorption in a liquid or solid sorbent
- Adsorption on a solid
- Permeation through a membrane
- Chemical conversion to another compound

Capturing and separation of CO_2 from gas streams are essential parameters for the carbon management for CO_2 sequestration from environment. A wide range of technologies based on physical and chemical processes currently exist for CO_2 separation from a gas stream. The choice of a suitable technology depends on the characteristics of gas stream.

Facing the vast range of applicable technologies, the process designers' challenge lies in selecting the optimal technology. Figure 2 proposed a selection chart that considered the content of acid gases in the feed and product streams.

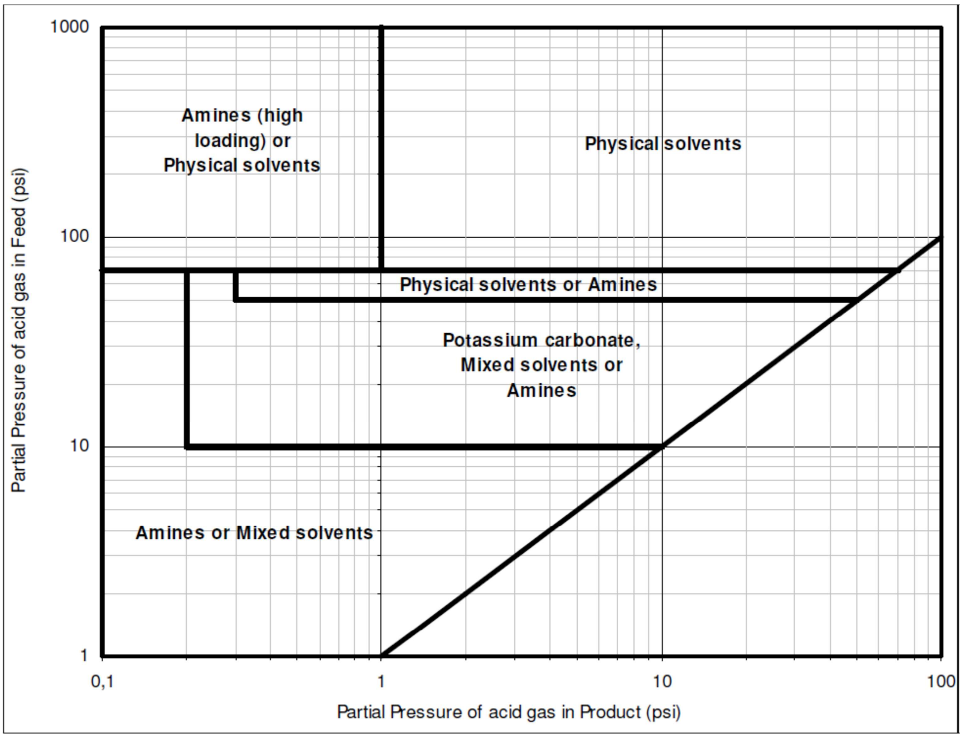

Figure 2- Gas sweetening technology selection chart [5]

Factors such as nature and amount of contaminants in the feed gas, the targeted removal capacity, amount of hydrocarbon in the gas, pipeline specification, capital and operating cost, the flow rate and condition of the feed gas (temperature, pressure, water content) to be processed and desired selectivity are the major factors that should also be considered in the selection of process technology for CO_2/CH_4 separation. Process selection is also influenced by the available disposal routes for the removed contaminants, which may include re-injection of CO_2 for enhanced oil recovery (EOR) or enhanced gas recovery (EGR), and venting to atmosphere. It is worth mentioning that for upgrading natural gas the candidate separation process must be tolerant toward handling high feed flow rates and also must have low energy consumption to be economically feasible.

2. 1. Absorption

Absorption could be performed as chemical or physical processes. The basic principle of chemical absorption is neutralization reaction in which absorbent react with CO_2 in the gas. Strong and weak alkaline solutions are commonly used absorbents. KOH and NaOH are examples of strong alkaline solutions, and alcohol amines (such as MEA, DEA, TEA and MDEA) and aqueous ammonia ($NH_3.H_2O$) are examples of weak alkaline solutions. The applicability of strong alkaline solution is limited due to its strong corrosion to equipment. The alcohol amines usually suffer from the disadvantage of high energy requirement for regeneration, easy oxidation/degradation by SO_2 and O_2 in flue gas and system corrosion [6]. Aqueous ammonia has the advantage of high-absorption efficiency, high-absorption capacity, low-energy requirement for absorbent regeneration and wide distribution of resources. In Table 1, advantages and disadvantages of chemical absorption by different alkaline solutions are categorized.

Physical absorption takes place at high CO_2 partial pressures. This process is not economical for streams with CO_2 content lower than 15 vol%. In physical absorption, organic solvent is used to physically, rather than chemically, absorb CO_2. In this process, CO_2 removal is based on its solubility within the solvents which depends on the partial pressure and temperature of the feed gas. Higher CO_2 partial pressure and lower temperature favor the solubility of CO_2 in absorbent. The solvents are regenerated by increasing temperature or decreasing pressure. In comparison with chemical solvents, the interaction between CO_2 and absorbent is weak. Physical absorption process and related solvents for CO_2 removal are commercially available. Selexol process is based on dimethyl ethers of polyethylene glycol (DMPEG), a Union Carbide liquid glycol-based solvent, and has been used since 1969. Glycol is effective for CO_2 capturing at high concentration. Rectisol process is based on low temperature methanol (cold methanol). Glycol carbonate is another interesting solvent because of its high selectivity for CO_2 but it has relatively low capacity. Propylene carbonate (FLUOR process) and N-methyl-2-pyrrolidone (NMP-Purisol) are other physical solvents [7].

Table 1- Advantages and disadvantages of alkaline approaches for CO_2 capture.

Process	Advantage	Disadvantage
Strong alkaline/alkaline metal solution (KOH, NaOH solution)	– Fast reaction rate – Large absorption capability – High absorption efficiency	– Cost of absorbent – Strong corrosion to equipment – Product treatment and disposal
Weak alkaline ($NH_3.H_2O$)	– Large absorption capability and high loading capacity – Low energy requirement for absorbent regeneration – Utilization of products as fertilizer – Wide distribution of absorbent	– Easy to volatilize and leak – Thermal instability of products – Corrosion to equipment
Aqueous ammines (MEA, DEA, TEA, MDEA)	– Less volatility – Good stability of absorbent – Enhancement role used as additive	– Absorption efficiency – High energy consumption for regeneration – Easy degradation by SO_2 and O_2 in flue gas – Resulting in system corrosion

2. 2. Membrane

Membrane separation technology is a low cost process when high purity gas streams are not fundamental. Membranes can separate carbon dioxide from a gas stream by size exclusion or by chemical affinity. Chemical affinity membranes are often impregnated with a scrubbing solution or chemical functional group (e.g., amine) selective for carbon dioxide. A large body of research has been conducted on the properties of carbon dioxide selective membranes based on inorganic materials such as zeolites, alumina, carbon, and silica. Higher separation energy efficiency relative to equilibrium-based processes, no waste streams production, existence of commercial references, no regeneration energy required, high packing density which requires small installations and increasing mass transfer area in a given volume are several advantages of membrane separation process [8].

On the other hand, the treatment of an enormous flow rate of CO_2 containing gas requires a very large membrane area and increases the cost of this technology.

Organic (polymeric) and inorganic (zeolite, ceramic and silica) membranes are of particular interest in CO_2 separation. Polymeric membranes separate gases based on solution-diffusion mechanism. Low cost, high separation performance, ease of synthesis and mechanical stability are their advantages [9]. An important limitation of polymeric membrane is its application for a high-temperature gas stream as it cannot be applied without cooling of the gas stream in order not to destroy the membrane.

2. 3. Adsorption

Adsorption is also considered a feasible process for CO_2 capture at an industrial scale. It is a selective process in which molecules contained in liquid or gaseous mixtures adhere on a solid surface, the adsorbent. These molecules, even in small concentrations in the streams, can be captured by these selective materials. The properties of the adsorbed particles (molecular size, molecular weight and polarity) and the adsorbent surface (polarity, pore size and spacing) determine the adsorption quality. Adsorption can be either physical (physisorption) or chemical (chemisorption).

Several adsorbents have been proposed for CO_2 capture, including carbon fiber monolithic adsorbents, activated carbon fiber-phenolic resin composites, melamine- formaldehyde highly porous adsorbents, amine immobilized adsorbents, red mud, steam-activated anthracite, activated carbon, lithium zirconate, lithium silicate, alumina, metallic oxides and zeolites among others. Adsorption-based systems such as Xebec's rapid cycle pressure-swing adsorption (PSA) process is emerging processes for processing of high CO_2 concentration gases and for developing remote gas fields [10, 11].

3. Industrial-scale case studies

Some of the most important large-scale integrated CCS (carbon capture and sequestration) projects relative to gas industry currently in operation are [12]:

- "In Salah CO_2 Injection" is a fully operational onshore gas field in Algeria with CO_2 injection. CO_2 is separated from produced gas using amine capture technology and re-injected in the producing hydrocarbon reservoir zones. Since 2004, about 1 Mt of CO_2 annually has been captured during natural gas extraction and injected into the Krechba geologic formation at a depth of 1800m.
- "Sleipner CO_2 Injection" is a fully operational offshore gas field with CO_2 injection initiated in 1996 in Norway. CO_2 is separated from produced gas and re-injected in the Utsira saline aquifer (800–1000 m below ocean floor) above the hydrocarbon reservoir zones. CO_2 capture is done using amine technology.
- "Snøhvit CO_2 Injection" is a fully operational offshore gas field in Norway with CO_2 injection. The LNG plant is located onshore. CO_2 is necessarily separated by amine technology to produce liquefied natural gas (LNG) and then CO_2 is injected in a saline aquifer below the hydrocarbon reservoir zones offshore at a rate of 700000 t/a into the Tubåen sandstone formation 2600 m under the seabed for storage.

4. Conclusion

To answer the question: “which method fits the project requirements for CO_2 separation best?”, one should consider the whole gas processing scheme and site conditions, and not only the sweetening technology itself.

Chemical absorption method has many obvious advantages such as high efficiency, high absorption capacity, low cost and technical maturity. These solvents are usually preferred to physical ones. Physical solvents required low regeneration energy, but they have low absorption capacity and selectivity for CO_2 separation. Physical absorption is not economical for gas streams with CO_2 concentration lower than 15 vol%.

Adsorption is suitable for separating CO_2 from low flow rate stream. Although, chemical adsorbents have high capacity and selectivity, but their regeneration is difficult. Physical adsorption is the most suitable for CO_2 capture at high pressures and low temperatures.

Membrane separation is suitable for high pressure stream with high concentration (>10vol%). Inorganic membranes have high thermal and chemical stability but their selectivity is lower than polymeric ones. Polymeric membranes are very selective for CO_2 separation but they have low thermal stability. Glassy polymeric membranes have higher selectivity, while the rubbery polymeric membranes have higher thermal stability. Membrane processes are efficient for gas streams with high CO_2 concentration.

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