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Natural Gas Purification Technologies – Major Advances for CO$_2$ Separation and Future Directions

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1. Introduction

In an effort to satisfy the rising global demand for energy and at the same time to combat the environmental impacts such as global greenhouse gas (GHG) emissions, it's worth searching for potential energy alternatives. As a base line for most approaches, the issues of producing sufficient quantity of energy with high quality, economical viability and environmental sustainability are the concern of the present. One of such vital components of the world's supply of energy that has fulfilled the aforementioned requirement is natural gas.

In addition to its primary importance as a fuel, natural gas is also a source of hydrocarbons for petrochemical feed stocks. Many researches have been undertaking on natural gas field as the presence of high component of methane in natural gas contributes for the production of other potential products such as syngas and high purity hydrogen.

Although natural gas is mostly considered as a "clean" fuel as compared to other fossil fuels, the natural gas found in reservoirs deposit is not necessarily "clean" and free of impurities. Natural gas consists primarily of methane as the prevailing element but it also contains considerable amounts of light and heavier hydrocarbons as well as contaminating compounds of CO$_2$, N$_2$, Hg, He, H$_2$S and etc. Thus, the impurities must be removed to meet the pipe-line quality standard specifications as a consumer fuel, enhance the calorific value of the natural gas, avoid pipelines and equipment corrosion and further overcome related process bottle necks.

In this chapter, the major advances, process advantages and limitations for the existing technologies in natural gas purification including absorption, adsorption, cryogenic and membrane processes are discussed. Moreover, special emphasis on the removal technologies of CO$_2$ from the natural gas is presented since CO$_2$ is the largest contaminant found in natural gas and the major contributor for the global GHG emissions. Comparisons in terms of advantages and disadvantages between these technologies are also described. Emerging concepts for new approaches in natural gas separation are highlighted. Finally, the future research and development directions of natural gas processing technologies are also presented.

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1.1 Natural gas consumption statistics

In consideration of the state of the art green technology requirements in promoting low-and zero-emission through the wise use of natural resources for the available reserves, natural gas becomes one of the most attractive, fastest and the premium growing fuel of world primary energy consumption (Economides and Wood 2009).

According to the technical report that was released on June 2011 by the International Energy Outlook 2010, the global utilization of natural gas raises to 44% from the reference year 2007 (108 trillion cubic feet) to the predicted year of 2035 (156 trillion cubic feet). In 2008, the need for natural gas was lowered due to the global economic recession that affects the global fuel markets, and in the following year, the worldwide natural gas utilization was reduced approximately by 1.1% (Energy Information and Administration 2011).

Nevertheless, the worldwide need for natural gas has revived as the global economies starts to make progress from the economic recession. Accordingly, the spending of natural gas rise on average by 1.8 percent per annum as of the year 2007 to the predicted year of 2020. However, far from the predicted year 2020 to 2035, the increase in natural gas utilization of natural gas is estimated to slow down to 0.9 percent per annum on average, due to the high prices on the natural gas product and its resources that will be introduced to the worldwide sell. Natural gas, also called "the prince of hydrocarbons" as it has many applications. The proportion of the natural gas consumed for energy production in major fields including industrial, commercial, residential, transportation and in generating electricity for the year 2009 is shown on Fig. 1.
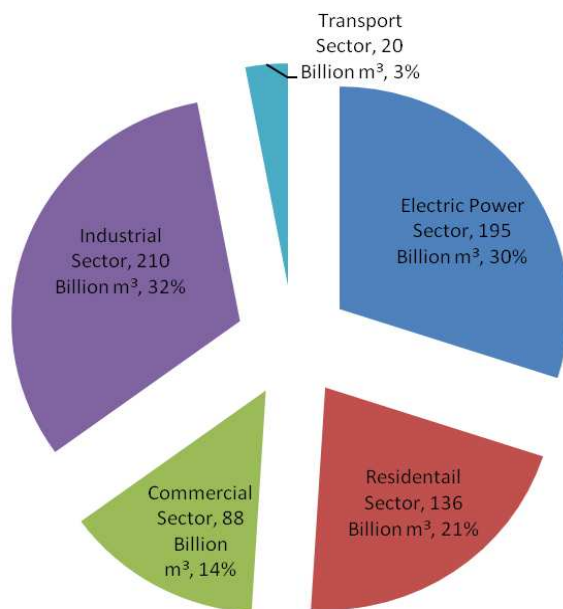

Fig. 1. Natural gas consumption statistics by different sectors
(Energy Information and Administration 2011)

Again, 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. From the total worldwide natural gas consumption statistics for the year 2007, the industrial field shared almost 40 percent and it is predicted to maintain that share through 2035. In applications for electric power field, natural gas is usually preferred for new power plants. Moreover, when combusting natural gas, it usually emits less CO$_2$ than does other fuels such as petroleum or coal so it is expected that the use of natural gas will be encouraged by government decision and policy makers to at least reduce the impact of GHG (Energy Information and Administration 2011).

1.2 Theories of formation of natural gas

Like other non-renewable fossil fuels, natural gas is essentially formed from the decomposition of living matters such as plants, animals and micro-organisms that lived over millions of years ago and became an inanimate mixture of gases. Although there are various theories about the origin of fossil fuels, the most widely accepted theory states that fossil fuels are usually formed when organic matters are decayed and compressed under the earth's crust at high pressure and for a very long time. This kind of formation is technically referred to as thermogenic methane. This type of natural gas is formed by the decomposition process of the piled and compressed organic matters that are covered in mud, sediment and debris at high temperature beneath the crust of the earth. In another way, natural gas can also be formed by the action of tiny methane-producing microorganisms and it is technically termed as biogenic methane. In this case, methane formation usually takes place close to the earth's surface and the methane produced is usually dissipated into the atmosphere. However, in some cases, this methane can be trapped underground and recovered as natural gas. As a third theory, natural gas is formed by abiogenic processes where this process takes place at extremely underneath the earth's crust, where hydrogen-rich gases and carbon molecules are dominant. These gases may interact with minerals found in the underground in the absence of oxygen by the time the gases gradually rise towards the surface of the earth. In such processes reaction will take place and forms gaseous compounds such as nitrogen, carbon dioxide, oxygen, water and inert gases like argon. Hence, the condition will form methane deposits at very high pressure, similar to that of the thermogenic methane (NaturalGas.org 2010).

1.3 Composition of natural gas

The natural gas processed at the wells will have different range of composition depending on type, depth, and location of the underground reservoirs of porous sedimentary deposit and the geology of the area. Most often, oil and natural gas are found together in a reservoir. When the natural gas is produced from oil wells, it is categorized as associated with (dissolved in) crude oil or non-associated.

It is apparent that two gas wells producing from the same reservoir may have different compositions. Table 1 shows the composition of natural gas reservoirs in some part of the world. Further, the composition of the gas produced from a given reservoir may differ with time as the small hydrocarbon molecules (two to eight carbons) in addition to methane that existed in a gaseous state at underground pressures will become liquid (condense) at normal atmospheric pressure in the reservoir. Generally, they are called condensates or natural gas

Component	Reservoir				
	Groningen (Netherlands)	Laeq (France)	Uch (Pakistan)	Uthmaniyah (Saudi Arabia)	Ardjuna (Indonesia)
CH_4	81.3	69	27.3	55.5	65.7
C_2H_6	2.9	3	0.7	18	8.5
C_3H_8	0.4	0.9	0.3	9.8	14.5
C_4H_{10}	0.1	0.5	0.3	4.5	5.1
C_{5+}	0.1	0.5	-	1.6	0.8
N_2	14.3	1.5	25.2	0.2	1.3
H_2S	-	15.3	-	1.5	-
CO_2	0.9	9.3	46.2	8.9	4.1

Table 1. Composition of natural gas reservoirs in some parts of the world in volume percent basis (Rojey 1997; Bahadori, Mokhatab et al. 2007; Bakar and Ali 2010)

liquids (NGLs). This usually happens in a retrograde condensate reservoir (Beggs 1984; Bahadori, Mokhatab et al. 2007).

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 the selling price of the natural gas. Moreover, it becomes acidic and corrosive in the presence of water that has a potential to damage the pipeline and the equipment system. In addition, when the issue of transportation of the natural gas to a very far distance is a concern, the use of pipelines will be too expensive so that Liquefied Natural Gas (LNG), Gas to Liquid (GTL) and chemicals are considered to be an alternative option. In LNG processing plant, while cooling the natural gas to a very low temperature, the CO_2 can be frozen and block pipeline systems and cause transportation drawback. Hence, 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 (Dortmundt and Doshi 1999).

As a gaseous fossil fuel, natural gas is relatively low in energy content per unit volume and emits lower quantities of green house gases (GHG) than other fossil fuels (Pascoli, Femia et al. 2001). However, when compared with other hydrocarbon energy sources, it is the most hydrogen-rich and has higher energy conversion efficiencies (Economides and Wood 2009).

Natural gas consists primarily of methane (70-90% of the total component) and other light and heavier hydrocarbons. The impurities present in natural gas need to be removed to meet the pipeline quality standard (NaturalGas.org 2010).

The allowable amounts of common impurities in U.S. for the delivery of the natural gas to the pipe line are given on Table 2 (Al-Juaied 2004; Baker 2004).

This standard may vary from pipeline to pipeline grids depends on the pipeline's system design. Generally, the following standards are used for natural gas specification in pipeline grid (Tobin J., Shambaugh P. et al. 2006). The natural gas should be (i) within a specific Btu

Components	U.S. pipe line specification
CO_2	<2 mol%
H_2S	<4 ppm
H_2O	<0.1 g/m³ (<120 ppm)
C_{3+}	950-1050 Btu/scf dew point -20 °C
Total inerts (N_2,He, Ar, etc)	< 4 mol%

Table 2. U.S. pipeline composition specifications for natural gas delivery
(Al-Juaied 2004; Baker 2004)

content range (1,305 Btu per cubic feet, +/- 50 Btu) (ii) delivered at a specified hydrocarbon dew point temperature level (below which any vaporized gas liquid in the mix will tend to condense at pipeline pressure (iii) contains no more than trace amounts of elements such as hydrogen sulfide, carbon dioxide, nitrogen, water vapor, and oxygen (iv) free of particulate solids and liquid water that could be detrimental to the pipeline or its ancillary operating equipment.

Comparatively carbon dioxide, that is produced from oil and coal, a GHG linked to global warming, has approximately higher production rate (1.4 to 1.75 times) than does from natural gas (Kidnay, Parrish et al. 2006).

1.4 Major processes in natural gas processing plant

The processing of wellhead natural gas into pipeline-quality dry natural gas can be quite complex and usually involves several processes. Most often, the number of gas treatment steps and the type of techniques used in the process of creating pipeline-quality natural gas depends on the source and makeup of the wellhead production stream. A typical natural gas processing plant whose simplified schematic representation shown in Fig. 2 consists
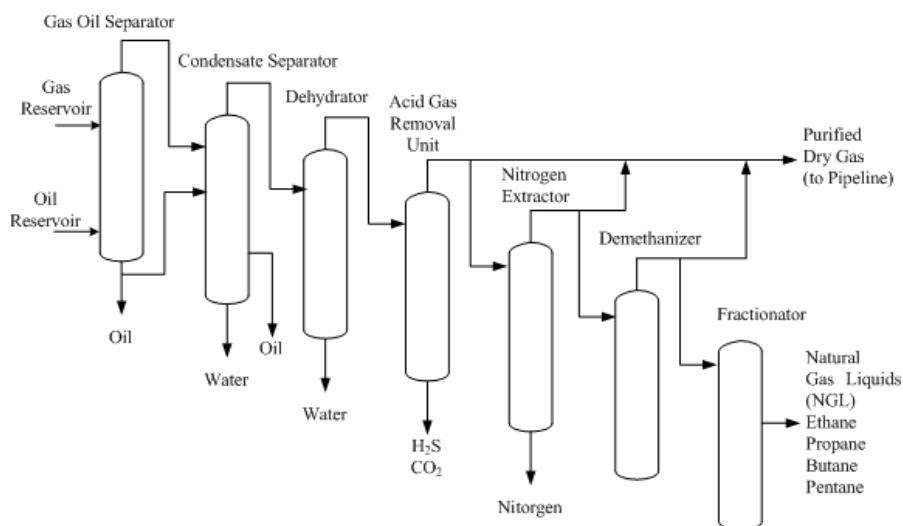

Fig. 2. Simplified schematic representation of a gas processing plant
(Tobin J., Shambaugh P. et al. 2006)

mainly of the following processes: (i) gas oil separator (treatment unit); (ii) condensate separator; (iii) dehydrator; (iv) acid gas removal unit; (v) nitrogen extractor or Nitrogen rejection unit (NRU) and (vi) fractionator.

Brief descriptions about the major unit operations are provided as follows.

Gas-oil separators: are used to separate the gas stream and the crude oil at the top and bottom part of the cylindrical shell respectively by the action of pressure at the wellhead where gravity separates the gas hydrocarbons from the heavier oil.

Condensate separators: are used to remove condensates from the gas stream by mechanical separators at the wellhead. In condensate treatment section, two main operations, namely water washing and condensate stabilization are performed. Based on the quality of the associated water, the condensate may require water wash to remove salts and additives (Tobin J., Shambaugh P. et al. 2006).

Dehydrators: are used to remove water vapor using dehydration process so that the natural gas will be free from the formation of hydrates, corrosion problem and dew point. In this treatment, process of absorption using ethylene glycol is used to remove water and other particles from the feed stream. As another option, adsorption process can also be used for water removal using dry-bed dehydration towers (Tobin J., Shambaugh P. et al. 2006).

Acid gas removal units: are used to remove contaminates in the dry gas such as CO_2, H_2S, some remaining water vapor, inert gases such as helium, and oxygen. The use of alkanolamines or Benfield solution processes is mostly common to absorb CO_2 and H_2S from the feed gas (Tobin J., Shambaugh P. et al. 2006).

Nitrogen extractor or Nitrogen rejection unit: are used to remove nitrogen from the stream using two common ways. In the first type, nitrogen is cryogenically separated from the gas stream by the difference in their boiling point. In the second type, separation of methane from nitrogen takes place using physical absorption process. Usually regeneration is done by reducing the pressure. If there were trace amounts of inert gases like Helium then pressure swing adsorption unit can be used to extract them from the gas stream (Tobin J., Shambaugh P. et al. 2006).

Demethanizer: are used to separate methane from NGLs using cryogenic processing or absorption techniques. The demethanization process can take place in the plant or as nitrogen extraction process. As compared to absorption method, the cryogenic method is more efficient for the lighter liquids separation, such as ethane (Tobin J., Shambaugh P. et al. 2006).

Fractionators: are used to separate the NGLs present in the gas stream by varying the volatility of the hydrocarbons present in the stream. In fractionation, the NGLs after the demethanizer is subjected to rise through towers and heated to increase the temperature of the gas stream in stages, assisting the vapor and liquid phases thoroughly contacted, allowing the components to vaporize and condense easily and separate and flow into specific holding tanks (Tobin J., Shambaugh P. et al. 2006).

2. Acid gas removal technologies for natural gas purification

2.1 Overview on acid gas removal technologies for natural gas purification

Acid gas removal processes, also commonly known as gas sweetening processes are used to purify the natural gas from the acid gases such as CO_2 and H_2S. The technologies that are

widely used to treat the natural gas include absorption processes, adsorption processes, cryogenic condensation and membranes. The technologies and their improvement have been developed over the years to treat certain types of gas with the aim of optimizing capital cost and operating cost, meet gas specifications and environmental purposes (Ebenezer and Gudmunsson 2006).

Comparative to the other natural gas separation techniques, the membrane process is a viable energy-saving alternate gas separation since it does not require any phase transformation. All the processes except membrane separation involves a change in the state of phase of the penetrant specious, where the desired penetrant is selectively transferred from gaseous state to liquid or solid state (Rojey 1997). Moreover, the necessary process equipment for membrane separation is very simple with no moving parts, compact, relatively easy to operate and control, and also easy to scale-up (Stern 1994).

2.2 Process selection factors

The processes that are used to remove acid gas are broad and the existing technologies are many that effective selection of process becomes a critical concern. This is because each of the processes has their own advantages and limitations relatives to others. Although common decisions in selecting an acid gas removal process can generally be simplified, factors such as nature and amount of contaminants in the feed gas, the amount of every contaminants present in feed gas and the targeted removal capacity, amount of hydrocarbon in the gas, pipeline specification, capital and operating cost, amount of gas to be processed, desired selectivity, conditions at which the feed gas is available for processing are the major factors that should also be considered (Dortmundt and Doshi 1999).

As highlighted on section 1.2.1, the aforementioned gas purification processes are briefly summarized in the following sections.

3. Absorption process

3.1 Basic separation principles for absorption process

Absorption process is one of the most important unit operations in natural gas purification process where a component of a gaseous phase is contacted with a liquid in which it is preferentially soluble.

Absorption is usually carried out in a countercurrent tower (column), through which liquid descends and gas ascends.

As per the needed surface area for gas-liquid contact, the absorption tower may be fitted with required trays, filled with packing, or fitted with sprays or other internals.

As overall selection criteria, the characteristics of a good solvent for absorption process fulfils the following main features: high gas solubility, high solvent selectivity, high volatility, low effects on product and environment, high chemical stability, low cost and more availability, non corrosive, low viscosity, non flammable and low freezing point.

At equilibrium conditions, solubility of gases is referred as the quantity of gas dissolved in a given quantity of solvent. Further at equilibrium, the partial pressure (fugacity) of a component in the gas is equal to the fugacity of the same component in the liquid. This

defines the equilibrium thermodynamic criterion for the relation of the concentration of a component in the gas and its corresponding concentration in the liquid (Meyers 2001).

As the important fundamental principles for physical absorption are solubility and mass transfer, the principles of reaction equilibria and reaction kinetics are for chemical absorption.

Based on the theoretical principles of mass transfer, the rate at which the equilibrium is attained when the gas (as a solute) is transferred into the solvent, no net transfer of material occurs between the phases. However, diffusion of materials between the phases will occur when a system is not in equilibrium. Thus, this ascertains that the driving force for diffusion of materials between the phases occur as far from the equilibrium (Meyers 2001).

When the gas (as a solute) is absorbed into a solution containing a reagent that reacts chemically with it, the amount of absorption (concentration profile) becomes dependent on the reaction kinetics and the concentration of the reacting reagent in the liquid (Meyers 2001).

The reverse process (which is also termed as stripping process, desorption, or regeneration), is employed when it is needed to remove the absorbed gases from the solvent for the purpose of recovery of the gas or the solvent or both. In the process of absorption, the selective solvent (absorbent) in a plate of packed column is contracted countercurrently with the gas to be processed (absorbate). As applied to gas purification process and based on the nature of interaction of absorbent and absorbate, absorption process is generally divided into physical and chemical absorption. In physical absorption, the desired gas component being absorbed (absorbate) is more soluble in the liquid solvent (absorbent) than other components in the gas phase but does not react chemically with the absorbent. Whereas in chemical absorption, the absorbate react chemically with the absorbent or a component within the absorbent. When the absorbent reaches its equilibrium level, regeneration step will take place by reducing the partial pressure in the gas phase and by thermal or chemical gradient for the case of physical and chemical absorption respectively (Kohl and Nielsen 1997; Scott 1998).

For cases where the removal of CO_2 is only needed in large quantities, or when only partial removal is required, the use of a hot carbonate solution or one of the physical solvents is preferred for economical advantages. The details on each of the absorption techniques for typical acid gases mainly for CO_2 separation are described in the next sections.

3.2 Physical absorption

Physical absorption processes are the type of absorption processes where the solvent interacts only physically with the dissolved gas. In this process, the solvent is used as an absorbent with thermodynamic properties such that the relative absorption of CO_2 is more favored over the other components of the gas mixture.

Mostly, physical solvent systems are used when the feed gas is characterized by high CO_2 partial pressure and low temperatures. Although heavy hydrocarbon restricts the wide use of physical solvent, its absorption capacity can be higher than chemical solvents. In addition, low CO_2 partial pressures as well as low outlet pressure of the product stream may also discourage the application of physical solvents (Ebenezer and Gudmunsson 2006).

Removal of CO_2 from the feed gas by physical solvent absorption is based on the solubility of CO_2 within the solvents. The partial pressure and the temperature of the feed gas are the

two major factors that determine the solubility of CO_2. Although there are too many physical solvent processes for the removal of CO_2 from natural gas, not all the processes available are capable of removing CO_2 to meet LNG specification of 50-100 ppmv of <2.5% of CO_2 in the product stream (Ebenezer and Gudmunsson 2006).

In physical absorption, the interaction between CO_2 and the absorbent is weak relative to chemical solvents, decreasing the energy requirement for regeneration. Regeneration of solvents is assisted by either heating, pressure reduction or a combination of both.

Mostly, physical solvent scrubbing of CO_2 is well established. Selexol, a liquid glycol-based solvent, has been used for decades to process natural gas, both for bulk CO_2 removal and H_2S removal (Davison, Freund et al. 2001). Glycol is effective for capturing both CO_2 and H_2S at higher concentration. However, the CO_2 is released at near atmospheric pressure, requiring recompression for transportation and geologic storage. The Rectisol process, based on low temperature methanol, is another physical solvent process that has been used for removing CO_2. Glycerol carbonate is interesting because of its high selectivity for CO_2, but it has a relatively low capacity (Kovvali and Sirkar 2002).

3.3 Chemical absorption

In natural gas purification plant, chemical absorption processes are used to remove acid gases such as CO_2 in the gas stream by the action of exothermic reaction of the solvent with the gases.

Many alkanolamines are most widely used as the chemical solvent gas treating process for acid gas removal in the natural gas and petroleum processing industries. These processes use a solvent, either an alkanolamine or an alkali-salt (hot potassium carbonate processes) in an aqueous solution. The common amine based solvents used for the absorption process are monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) that reacts with the acid gas (CO_2 and H_2S) to form a complex or bond. H_2S, CO_2 and SO_2 are termed as acid gases since they dissociate to form a weak acidic solution when they come into contact with water or an aqueous medium. These amines are known as weak organic bases.

The basicity is provided by the amine function, and it provides reactivity to remove the acid gases. The hydroxyl groups serve to increase the solubility of amine in water. This effect reduces the vapor pressure of the amines so that less is lost out the top of the absorber or stripper (Glasscock 1990).

Table 3 shows the absorption capacity and some characteristics of commonly used amines for acid gases removal processes (Kohl and Nielsen 1997; Ritter and Ebner 2007).

A simplified schematic representation for the flow of a typical gas treating operation using amine solvents is shown in Fig. 3 (Kohl and Nielsen 1997; Al-Juaied 2004).

In the typical process, a sour gas (H_2S and/or CO_2) is introduced to absorber from its bottom at high-pressure and goes to rise up and counter currently contacts an aqueous alkanolamine solution that is routed to the top of the absorber. The resulting amine solution that contains high CO_2 is then transported to the heat exchangers to raise its temperature. Then, it is directed to the top of a regenerator (stripper) to countercurrently contact steam at high temperature and low pressure. Afterwards, the steam strips the CO_2 and H_2S from
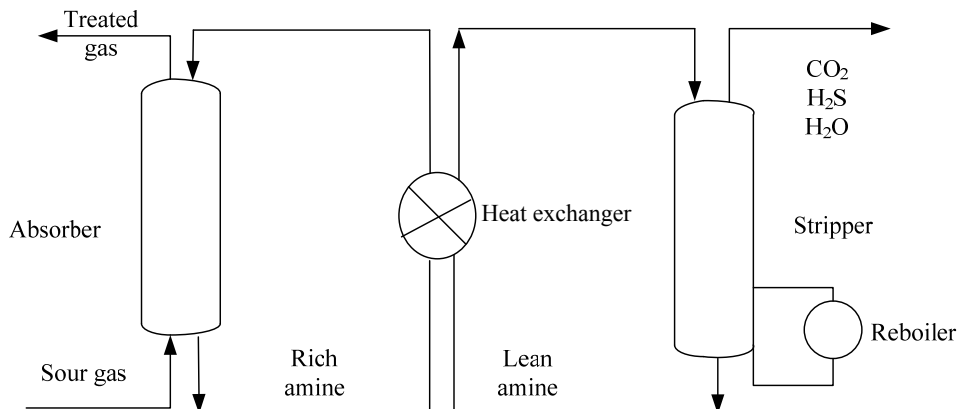
Fig. 3. Schematic representation for the flow of a typical gas treating operation using amine solvents (Kohl and Nielsen 1997; Al-Juaied 2004)

Name of amines	Vapour pressure (mmHg)	Relative acid gas capacity (%)	Remarks
Ethanolamine/ Monoethanolamine (MEA)	1.05	100	Good thermal stability, slow losses of alkanolamine but difficult to use MEA to meet pipeline specifications for H_2S.
Diethanolamine (DEA)	0.058	58	Lower capacity than MEA, reacts more slowly.
Triethanolamine (TEA)	0.0063	41	Low reactivity toward H_2S.
Hydroxyethanolamine/ Diglycolamine (DGA)	0.016	58	Same reactivity and capacity as DEA, with a lower vapour pressure and lower evaporation losses.
Diisopropanolamine (DIPA)	0.01	46	Selective for H_2S removal over CO_2 removal.
Methyldiethanolamine (MDEA)	0.0061	51	Selectively removes H_2S in the presence of CO_2, has good capacity, good reactivity, and very low vapour pressure, a preferred solvent for gas treating.

Table 3. Absorption capacity and some characteristics of commonly used amines for acid gases removal processes (Kohl and Nielsen 1997; Ritter and Ebner 2007)

solution and the lean alkanolamine solution is routed through the heat exchanger, where it is cooled, and reintroduced at the top of absorber (Al-Juaied 2004).

As the process proceeds, the complex or bond is subsequently reversed in the regenerator at elevated temperatures and reduced acid gas partial pressures releasing the acid gas and regenerating the solvent for reuse. These are well suited for low pressure applications where the acid gas partial pressures are low and low levels of acid gas are desired in the residue gas since their acid gas removal capacity is relatively high and insensitive to acid gas partial pressures as compared to physical solvents (Kohl and Nielsen 1997).

In most oil refineries sector, since stripped gas is mostly H$_2$S, much of which often comes from hydrodesulfurization (sulfur-removing process). The clause process is then used to convert the H$_2$S-rich stripped gas to elemental sulfur. In some plants, it is common to share a common regenerator unit for more than one amine absorber unit (Kohl and Nielsen 1997).

Recently, 2-amino-2-methyl-1-propanol (AMP) as another group of alkanolamines has received great deal of focus as it needs less energy for their regeneration. Moreover, blending of alkanolamines has also been researched as to obtain their potential synergy than the individual favorable features, e.g. high absorption capability coupled with thermal energy demand for regeneration (Rodriguez, Mello et al. 2011).

Generally, the chemical solvent processes are characterized by a relatively high heat of acid gas absorption and require a substantial amount of heat for regeneration.

As an overall, Table 4 shows the comparison of chemical and physical solvent absorption process for acid gas removal (Ritter and Ebner 2007).

	Chemical Absorption		Physical Solvent Absorption
	Alkanolamine	Inorganic Carbonate	
Type of absorbents	MEA,DEA,DGA,MDEA, DIPA	K$_2$CO$_3$, K$_2$CO$_3$-MEA, K$_2$CO$_3$-DEA	Selexol, Rectisol, Purisol
CO$_2$ absorption mechanism	Chemical reaction CO$_2$: 2RNH$_2$+CO$_2$+H$_2$O↔(RNH$_3$)$_2$CO$_3$ (RNH$_3$)$_2$CO$_3$+CO$_2$+H$_2$O↔2RNH$_3$HCO$_3$	Chemical reaction CO$_2$: Na$_2$CO$_3$+CO$_2$+H$_2$O↔2NaHCO$_3$	Physical dissolution
Operating gauge pressure, mmHg	Insensitive to pressure	> 10,337.76	12,922.2-51,688
Operating Temp., ^{o}C	37.78-204.44	93.33-121.11	Ambient temperature
Absorbent Recovery	Reboiled stripper	Stripper	Flash, reboiler, or steam stripper
Swing variables (Temp. or Pressure)	Temperature principally	Both, but pressure principally	Pressure principally
Selectivity CO$_2$ vs. H$_2$S	Only MDEA selective for H$_2$S	May be selective for H$_2$S	Some selectivity for H$_2$S
Meets ppmv CO$_2$	Yes	Yes	Yes
Utility Cost	High	Medium	Low to medium

Table 4. Comparison of the major acid gas absorption processes (Ritter and Ebner 2007)

3.4 Limitation and challenges

The limitations of absorption process are briefly described as flows. The solvent used in absorption process such as amines and Benfield solution causes corrosion of the units (Polasek and Bullin 1984). When the solvent react with some corrosion inhibitors, it will cause erosion of the unit, high tendency for foaming and solid suspension thus reduce CO_2 solvent loading and require injection of antifoaming agents to reduce the surface tension of the solvent and to ensure better contact between the solvent and the CO_2, the regenerated solution leaving the stripper is at its saturated temperature and partially vaporize in the pump suction, resulting in vibration and excessive wear of the pump impellers. Moreover, since all of the solvents cannot be recycled back to the absorber column, the disposal of the solvents causes environmental hazards and thus showed the common disadvantages of using the absorption process (Bord, Cretier et al. 2004; Ebenezer and Gudmunsson 2006).

4. Adsorption process

4.1 Basic separation principles for adsorption process

In gas separation application, the process of adsorption is described as the adhesion or retention of selective components of feed gas stream brought into contact to the surface of certain solid adsorbent as the result of the force of field at the surface.

As the surface of an adsorbing material may exhibit different affinities for the various components of a fluid, it offers a straightforward means of purification (removal of undesirable components from a fluid mixture) as well as a potentially useful method of bulk separation (separation of a mixture into two or more streams of enhanced value). Bulk separation is defined as having the concentration of the adsorbed component above 10% by weight of the gas stream while for purification the concentration of adsorbed component is generally <2% by weight of the gas stream in the feed (Kerry 2007).

Although adsorption process is rarely applied for bulk separation of CO_2 from CH_4, there are kinetics-based adsorption processes that have been implemented in USA for the recovery of methane from landfill gas. These gases mainly comprises of methane (50-65%), carbon dioxide (35-50%), a trace amount of nitrogen and sulfur compounds. In this process, carbon molecular sieve is used as the adsorbent. In use of this process, it can be possible to recover more than 90% methane with 87-89% purity (Yang 1997).

One of the successful application for bulk separation of CO_2 from CH_4 is performed by using Engelhard molecular gate, a commercial brand name adsorbent developed by Engelhard Corporation.

The first application of molecular gate CO_2 removal system is at the Tidelands Oil Production Company operated facility in Long Beach, California. The feed source for this unit is hydrocarbon rich associated gas from enhanced oil recovery section. The feed more typically operates at 30-40% of CO_2 and the adsorbent able to reduce CO_2 level less than 2% (Ritter and Ebner 2007).

Depending on the nature and strength of the surface forces, adsorptive gas separation process can be divided into two types: physical adsorption and chemisorption.

Chemisorption can be considered as the formation of a chemical bond between the sorbate and the solid surface (covalent interaction of CO_2 and the surface of the adsorbent) that

gives scope for much larger increases in adsorption capacity. Such interactions are strong, highly specific, and often not easily reversible. Chemisorption systems are sometimes used for removing trace concentrations of contaminants, but the difficulty of regeneration makes such systems unsuitable for most process applications (Meyers 2001).

In most operations, adsorption processes depend on physical adsorption. The forces of physical adsorption are weaker (a combination of Van der Waals forces and electrostatic forces) than the forces of chemisorption so the heats of physical adsorption are lower and the adsorbent is more easily regenerated as no covalent bonds are formed and heat is released upon adsorption. During capture, the chemical potential of the adsorbed CO_2 is lower than the chemical potential of CO_2 in the gas mixture. Several different types of force are involved. For nonpolar systems the major contribution is generally from dispersion-repulsion (van der Waals) forces, which are a fundamental property of all matter. When the surface is polar, depending on the nature of the sorbate molecule, there may also be important contributions from polarization, dipole, and quadrupole interactions. Selective adsorption of a polar species such as water or a quadrupolar species such as CO_2 from a mixture with other nonpolar species can therefore be accomplished by using a polar adsorbent. Indeed, adjustment of surface polarity is one of the main ways of tailoring adsorbent selectivity (Meyers 2001).

Physical adsorption at a surface is so fast, and the kinetics of physical adsorption are usually controlled by mass or heat transfer rather than by the intrinsic rate of the surface process (Meyers 2001).

Most of the separation processes is based upon equilibrium mechanism and the separation is accomplished by the adsorption equilibrium capacity difference of the adsorbent among the adsorbate.

The primary requirement for an economic adsorption separation process is an adsorbent with sufficient selectivity, capacity and service life. Adsorption selectivity may depend either on a difference in adsorption equilibrium or, less commonly, on a difference in kinetics. Kinetic selectivity is generally possible mainly with microporous or biporous adsorbents such as pelleted zeolites or carbon molecular sieves (Meyers 2001). These adsorbents offer three types of resistances to mass transfer: the external resistance of the fluid film, the diffusion resistance associated with transport through the macropores, and the intracrystalline or micropore diffusional resistance (Meyers 2001; Meyers 2011).

Thus the aforementioned resistances (one or their combined effects of resistance) will control the rate depending on the particular system and the conditions.

Since adsorption is a surface phenomenon, an adsorbent should have a high surface area to volume ratio. The main advantage of physical adsorption methods is its low energy requirement for the regeneration of the sorbent material with short period of time associated with the change in pressure.

The widely used adsorption processes includes the metal oxide (metal organic frame works), molecular sieves (zeolites, activated carbon) and promoted hydrotalcites based processes. Zeolite systems can produce nearly pure streams of CO_2, but have high energy expenses due to vacuum pumps and dehumidification equipment. As most effective

adsorbent, the use of hydrotalcites at high temperatures (177-327°C) is widely for adsorption of CO_2 in or near combustion or gasification chambers. However, more study is still required to decrease the pressure difference requirement and enhance the capacity of current adsorbents (Hermann, Bosshar et al. 2005).

Commercial adsorbents that show ultraporosity have been used for the selective separation of gases, and included activated carbons, charcoal, activated clays, silica gel, activated alumina, and crystalline aluminosilicate zeolites.

The major advantages of using adsorption processes are simplicity of operation, the relative capability of the molecular sieve beds to withstand mechanical degradation and the possibility of simultaneous dehydration of gases and acid removal.

Once saturation of the adsorbent is reached, regeneration is carried out by either applying heat or by lowering pressure (concentration). Based on regeneration methods, adsorption process is most commonly divided into temperature swing adsorption (TSA), pressure swing adsorption (PSA) and displacement desorption.

Table 5 shows typical loading capacities of some commercial adsorbents towards acid gases with their corresponding regeneration methods. As an overall, the choice of adsorption methods depends on economic factor as well as technical considerations.

The next section briefly describes the aforementioned regeneration methods for adsorption processes.

Adsorbent	Adsorbate	T (°C)	P (mmHg)	Loading (mol/kg)	Regeneration Method
Activated carbon	CO_2	25-300	500	1.5-2.0@25 °C 0.1-0.2@300 °C	PSA
5A zeolite	CO_2	25-250	500	~ 3.0@25 °C 0.2@250 °C	PSA
Titanosilicates	CO_2	25-200	760-6x10^5	-	PSA
HTlc (K-promoted)	CO_2	300-400	200-700	0.4-0.7	PSA
Solid amine (supported PEI)	CO_2	75	760	1.5 - 3.0	PSA
Double-layer hydroxides	CO_2	375	230	1.5	PSA
Alumina (un-doped)	CO_2	400	500	0.06	PSA
Alumina (doped w/Li_2O)	CO_2	400	500	0.52	PSA
alumina(basic)	CO_2	300	500	0.3	PSA
Li zirconate	CO_2	500	760	3.4-4.5	TSA
CaO	CO_2	500	150	4-8@500 °C 7@500 °C	TSA

Table 5. Typical CO_2 loading capacities of some adsorbents at operating conditions (Ritter and Ebner 2007)

4.2 Thermal swing adsorption

The use of cyclic thermal swing processes (TSA) is widely applicable for the purification operations such as removal of CO_2 from natural gas or drying. In TSA, desorption is achieved by increasing the temperature of the adsorption bed by applying heat to the bed or more commonly by purging with a hot purge gas. At higher temperatures the adsorption equilibrium constant is reduced so that even quite strongly adsorbed species can be removed with a comparatively small purge gas volume. TSA is generally used for purification of the process such as drying or removal of CO_2 from natural gas (Meyers 2001).

Thermal swing adsorption is very reliable to remove minor component. The limitation in thermal swing adsorption process is the adsorption cycle time that is required to cool down the bed. Other obstacles are the high energy requirements and large heat loss (Mersmann, Kind et al. 2011).

In practice, in most two-bed purification processes, the desorption step controls the cycle, either directly or through the heat balance. Initial design of the regeneration cycle is commonly based on the assumption that during desorption the column approaches equilibrium. However, at the low concentrations that will prevail during the later steps of desorption, kinetic effects may be important, so more detailed understanding of the kinetics is necessary (Meyers 2001).

The rate at which the temperature is raised for regeneration is another important factor in the regeneration of molecular sieve driers. When this condition is too fast relative to the rate of moisture removal (drying), the probability of rapid desorption of moisture from the initial section of the bed will be there as it will be in contact with the hot desorbent gas, followed by condensation of liquid water in the cooler regions at some distance from the inlet. And the consequences will be serious for adsorbent life. To overcome the possibility of fluidizing the bed, the system will need to be operated in the down flow mode with up flow desorption since the gas velocity during adsorption is normally higher than that of desorption. Usually, the maximum up flow velocity is normally limited to 80% of the minimum fluidization velocity, while velocities as high as 1.8 times minimum fluidization can be tolerated in down flow (Meyers 2001).

When the adsorbent is regenerated by the TSA (when the equilibrium is favourable for this regeneration method) and unloaded by heating provided indirectly by an embedded heat transfer exchanger or directly by a hot regeneration gas or by both. The residual loading depends on the maximum temperature and a preconcentration of the possibly recircled gas and of the kinetic approach to equilibrium. Mostly the temperature swing adsorption is applied on molecular sieves which are loaded with H_2O, SO_2 and CO_2. In such conditions, the heats of adsorption are very high ($\Delta H > 30 kJ/mol$) for polar adsorptives adsorbed on adsorbents with electrical charges like zeolites. Moreover, this TSA process is also applied on the regeneration of activated carbon, zeolites, and silica gel loaded with hydrocarbons present in natural gas when the heat of adsorption is higher than 30 kJ/mol (Mersmann, Kind et al. 2011).

4.3 Pressure swing adsorption

Pressure swing adsorption (PSA) is one of the most known industrial processes for gas separation. PSA is well known a technology for the removal of CO_2 from gaseous streams

containing methane In such process, the removal of CO_2 from natural gas streams by adsorption processes are based on materials with selective adsorption to CO_2 by different equilibrium capacities or by differences in uptake rates (Cavenati, Carlos et al. 2006).

In PSA, regeneration is carried out by lowering the operating partial pressure to desorb the adsorbate (Kerry 2007). This can be obtained either by depressurization or by evacuation or by both. PSA is more suitable for bulk separation. Moreover, PSA is also used for drying of air and industrial gases. Air prepurification (purification of air prior to cryogenic distillation by removal of CO_2, water, and hydrocarbons) is also at developing stage for PSA (Yang and Wiley 2003).

As the most important decision in any adsorption-based technology is the adsorbent selection, zeolites as microporous materials that adsorb CO_2 strongly, are mostly used in PSA processes. Zeolites have good records for separation of CO_2 than activated carbons in the PSA (Cavenati, Carlos et al. 2006).

The PSA process is applied when there is a need for an essential reduction of the loading to be achieved by a certain pressure drop. This mainly depends on the loading as a function of the partial pressure at the operating temperature.

In a typical adsorption process, each bed in a PSA plant undergoes adsorption and regeneration cycle steps. These steps include 1) pressurization, 2) high pressure feed, 3) co-current depressurization, 4) countercurrent depressurization, 5) countercurrent purge (light reflux), and 6) several equalization (pressurization/depressurization) steps between two beds (Ritter and Ebner 2007).

While purge gas stripping depends on reducing the partial pressure by dilution with an inert purge gas, a pressure swing process desorption is achieved simply by reducing the total pressure. This generally requires a rather large purge volume, so such a process would normally be used only in special circumstances.

One of the important features of such processes is that the less strongly adsorbed species (the raffinate product) can be recovered at high purity but at relatively low fractional recovery, while the more strongly adsorbed species (the extract product) is always recovered in less pure form during the blowdown and purge steps. This type of process is therefore especially suitable for gaseous separations when the feed is inexpensive and the less strongly adsorbed species is the required product. All three major industrial applications of PSA (air drying, air separation, and hydrogen purification) fulfill these requirements (Meyers 2001).

Moreover, PSA systems are well suited to rapid cycling, making the process more preferable in obtaining relatively large throughput with relatively small adsorbent beds. However, the energy efficiency of such processes is not high, and since mechanical energy is usually more expensive than heat, PSA systems are generally not economical for large-scale operations. However, their process advantage lies in their compactness and simplicity, making them ideal for applications such as the production of medical oxygen in the home or in hospitals in remote areas. Nevertheless, with recent improvements in process efficiency, PSA processes are economically competitive with cryogenic distillation for oxygen production rates up to about 250 tons/day (Meyers 2001).

Engelhard Corporation is well known for its development of a typical PSA process to remove H$_2$O, CO$_2$, and heavier hydrocarbons from methane using their Molecular Gate adsorbent technology. Its adsorbents are comprised of titanium silicate molecular sieves that were originally developed to remove only N$_2$ from natural gas by kinetic separation. This class of materials was subsequently found to provide interestingly higher kinetic and adsorption selectivities for CO$_2$ and H$_2$O, exceeding those of more widely known aluminosilicate molecular sieves. A typical PSA system using the Molecular Gate adsorbent can separate CO$_2$ from CH$_4$ rich gas streams at feed absolute pressures between 5168.88 and 41,351.02 mmHg producing a product stream containing CH$_4$ at concentrations of > 90 vol%. This commercial technology is able to process gas streams containing up to 30 vol% CO$_2$ with favorable economics (Ritter and Ebner 2007).

The major advantages of PSA system are low capital and maintenance costs, high purity product, rapid shutdown and start-up characteristics, lack of corrosions problems, absence of heat requirement and pipe insulation and comparative straight forward operation.

Although the simple two-bed PSA cycle is widely used in small-scale units that achieve economic operations on a larger scale, it is necessary to improve the energy efficiency of the process. This can be accomplished by using multiple-bed systems in which blowdown and repressurization take place in several stages in such a way that the high-pressure enriched gas at the end of the adsorption step in one column is used to pressurize partially on the second column and so on. In contrast, PSA has a limitation as it requires high pressure and vacuum pressure that contribute to high operating cost (Meyers 2001).

4.4 Displacement desorption

Displacement desorption, is similar to purge gas stripping as the temperature and pressure are maintained constant, but instead of an inert purge, an adsorbable species is used to displace the adsorbed component from the bed similar to displacement chromatography. Displacement desorption is usually used when desorption by pressure swing or thermal swing fails to be practical.

Steam stripping process can be considered as a combination of thermal swing and displacement desorption as it is mostly used in the regeneration of solvent recovery system using an activated carbon adsorbent.

In a typical displacement desorption, the displacing component should be adsorbed somewhat less strongly than the preferentially adsorbed species so that the adsorption-desorption equilibrium can be shifted by varying the concentration of the desorbent. Such processes run more or less isothermally and offer a useful alternative to thermal swing processes for strongly adsorbed species when thermal swing would require temperatures high enough to cause cracking, coking, or rapid aging of the adsorbent (Meyers 2001).

4.5 Limitation and challenges

As compared to other methods, for adsorption to be economical, ideal adsorbents should have high transfer rates, high regenerability and high capacity that allow for thermal swing adsorption (TSA) or low pressure swing adsorption (PSA).

At the adsorption equilibria, the loading usually decreases with increasing temperature for a given partial pressure or concentration of the adsorptive in the fluid. In an isothermal system, the loading decreases with decreasing partial pressure or concentration. A further regeneration process is based on the replacement of the adsorbate by another adsorptive with a greater affinity to the adsorbent (Mersmann, Kind et al. 2011).

As an overall, the advantages and limitations of the aforementioned desorption techniques on the choice of the regeneration methods are summarised on Table 6 (Meyers 2001).

Method	Advantages	Limitations
Thermal swing	Good for strongly adsorbed species, since small change in temperature gives large change in adsorbate; desorbate can be recovered at high concentration; applicable to both gases and liquids	Thermal aging of adsorbent; heat loss means inefficiency in energy usage; unsuitable for rapid cycling, so adsorbent cannot be used with maximum efficiency; in liquid systems, high latent heat of interstitial liquid must be added.
Pressure swing	Good where weakly adsorbed species is required in high purity; rapid cycling, efficient use of adsorbent	Very low pressure may be required; mechanical energy more expensive than heat; desorbate recovered at low purity
Displacement desorption	Good for strongly held species; avoids risk of cracking reactions during regeneration; avoids thermal aging of adsorbent	Product separation and recovery needed. (choice of desorbent is crucial)

Table 6. Advantages and limitations of the regeneration method (Meyers 2001)

5. Cryogenic process

5.1 Basic separation principle for cryogenic process

Cryogenic separation (also known as low temperature distillation) uses a very low temperature (-73.30 °C) for purifying gas mixtures in the separation process (Ebenezer and Gudmunsson 2006).

The major industrial application of low-temperature processes involves the separation and purification of gases. Much of the commercial oxygen and nitrogen, and all the neon, argon, krypton, and xenon, are obtained by the distillation of liquid air (Meyers 2001).

Commercial helium is separated from helium-bearing natural gas by a well-established low-temperature process. Cryogenics has also been used commercially to separate hydrogen from various sources of impure hydrogen (Meyers 2001).

The cryogenic method is better at extraction of the lighter liquids, such as ethane, than is the alternative absorption method. Essentially, cryogenic processing consists of lowering the temperature of the gas stream to around -84.44 °C. While there are several ways to perform this function the turbo expander process is most effective, using external refrigerants to chill the gas stream. The quick drop in temperature that the expander is capable of producing condenses the hydrocarbons in the gas stream, but maintains methane in its gaseous form (Tobin J., Shambaugh P. et al. 2006).

While cryogenic separation is used commercially to liquefy and purify CO_2 from streams that have high CO_2 concentrations (typically greater than 50-70 percent), it has not been applied to large scale CO_2 capture from flue gas due to the low concentration of CO_2 that makes the application of this technique not economical. Cryogenic separation can separate CO_2 from other gases using pressure and temperature control resulting in solid or liquid CO_2 particulate matter and other contaminants are also removed in the process. Cryogenics use condensation of gases as the main principle. When CO_2 is cooled below its boiling point, it begins to condense and separate and turns into a liquid state. Differences in boiling points cause the gases to separate because each gas will turn to a liquid at a different point, but separation into pure components can also be influenced by the composition of the gas being cooled (Tobin J., Shambaugh P. et al. 2006).

The advantages of this process are the suitability to liquefy and purify the feed gas with high concentration of CO_2 and for producing a liquid CO_2 ready for transportation by pipeline and does not require compression since there is no additional chemicals used.

5.2 Limitation and challenges

The main disadvantage of cryogenic separation is that the process is highly energy intensive for regeneration and can significantly decrease the overall plant efficiency when applied to streams with low CO_2 concentration. Moreover, tendency for blockage of process equipment is high and some cryogenic fluids are flammable and toxic such as (acetylene, ethane) (Ebenezer and Gudmunsson 2006).

6. Membrane process

6.1 Basic principle of membrane process

In essence, gas separation membranes are thin films that selectively transport gases through the membrane based on differences in permeabilities of the species flowing through the membrane. The permeability of gases in a membrane is related as a function of membrane properties (physical and chemical structure), the nature of the permeant species (size, shape, and polarity), and the interaction between membrane and permeant species (Stern 1994; Burggraaf 1996; Shekhawat, Luebke et al. 2003).

The membrane properties and the nature of the permeant species determine the diffusional characteristics of a penetrant gas through a given membrane. The interaction between membrane and permeant, refers to the sorptivity or solubility of the gas in the membrane. The permeability coefficient (or permeability) of a penetrant is the product of the solubility coefficient or the sorptivity (thermodynamic parameter) and the diffusion coefficient (kinetic parameter). The permeability coefficient denotes the rate at which a penetrant traverses a membrane. The solubility (sorptivity coefficient) is a measurement of the amount of gas sorbed by the membrane when equilibrated with a given pressure of gas at a given temperature. The diffusion coefficient indicates how fast a penetrant is transported through the membrane in the absence of obstructive sorption.

The selectivity of the membrane to specific gas or liquid molecules is subject to the ability of the molecules to diffuse through the membrane. The permselectivity or ideal separation factor is simply the ratio of the pure gas permeability of the gases being separated.

Membranes utilized in separations need to possess both high selectivity and high permeation. The higher the permeability, the less membrane area is required for a given separation and therefore the lower the membrane cost. The higher the selectivity is the lower the losses of methane and therefore the higher the volume of the product that can be recovered (Porter 1990; Shekhawat, Luebke et al. 2003).

Gas transport through porous membranes takes place through a number of mechanisms, such as molecular sieving, Knudsen diffusion, surface diffusion, capillary condensation and micropore diffusion. Brief descriptions of these mechanisms are provided as follows.

Molecular diffusion: In molecular diffusion, the mean free path of the gas molecules is smaller than the pore size and diffusion occurs primarily through molecule-molecule collisions. Here, the driving force is the composition gradient. If a pressure gradient is applied in such pore regimes bulk (laminar) flow occurs, the transport is described by *Poiseuille flow* or viscous flow (De Lange, Keizer et al. 1995; Javaid 2005).

Knudsen diffusion: This mode of transport is significant when the mean free path of the gas molecules is greater than the pore size. In such situations, the collisions of the molecules with the pore wall are more frequent than the collisions among molecules. Separation selectivities with this mechanism are proportional to the ratio of the inverse square root of the molecular weights (De Lange, Keizer et al. 1995; Javaid 2005).

Surface diffusion: It takes place when the permeating species exhibit a strong affinity for the membrane surface and adsorb along the pore walls. In this mechanism, separation occurs due to the differences in the amount of adsorption of the permeating species. Surface diffusion often occurs in parallel with other transport mechanisms such as Knudsen diffusion (De Lange, Keizer et al. 1995; Javaid 2005).

The activation energy for the diffusion is strongly correlated with the heat of adsorption. Since it is assumed that diffusion takes place by molecules which jump from one site to another, the activation energy is a fraction of heat adsorption (Gilliland, Baddour et al. 1974). This implies that: a) strongly adsorbed molecules, and b) the total flux will decrease as the temperature is increased since the increased diffusivity is overruled by the decrease in surface concentration (De Lange, Keizer et al. 1995).

Capillary condensation: It is one form of surface flow where one of the gases is a condensable gas. Typically in mesopores and small macropores, at certain critical relative pressures as determined by the Kelvin equation, the pore gets completely filled by the condensed gas. Due to the formation of menisci at both ends of the pore, transport can take place through hydrodynamic flow generated by capillary pressure difference between the two ends. This mechanism of gas transport can be considered as the limiting case adsorption process when the pressure is increased. Theoretically capillary condensation can be used to achieve very high selectivities, as the formation of the liquid layer of the condensable gas will block and prevent the flow of the non-condensable gas (Javaid 2005).

Configurational or micropore diffusion: This type of diffusion may be considered as the limiting value of surface diffusion where the pore size becomes comparable to the molecular size. In this mechanism, diffusion is perceived as an "activated" process and separation is a strong function of molecular shape, molecular size, pore size, and the interactions between the pore wall and gas molecules. This type of mechanism is dominant in microporous inorganic membranes such as zeolite and carbon molecular sieves membranes (Javaid 2005).

In another dimension, membranes can be coupled with a solvent to capture desired gases such as CO_2 and the process is known as membrane gas absorption. In such process, the CO_2 diffuses between the pores in the membrane and is then absorbed by the solvent. The membrane maintains the surface area between gas and liquid phases. This type of membrane is used when the CO_2 has a low partial pressure, such as in flue gases, because the driving force for gas separation is small.

Unlike the gas separating membrane discussed earlier, the membrane gas absorption process does not undergo separation of the CO_2 from other feed gases, but rather function as a barrier between the liquid and gas with permeability through the pores.

As opposed to the traditional solvent absorption process whereby the solvent and the gas flow together and lead to transport problems such as foaming and channeling, the physical separation of the gas flow from the liquid flow through membrane absorption eliminates these problems.

Although a range of configurations exists either simply as gas separation devices or incorporating liquid absorption stages, the process has not yet been applied on a large scale and there are challenges related to the composition and temperature of the feed gases such as flue gases.

Currently, most researches are focussed on developing effective solvents and optimising the reaction time. The general advantages of the membranes process and mainly for the removal of CO_2 from natural gas includes: enhanced weight and space efficiency which make it more applicable for off shore environment, high adaptability to variation of CO_2 content in the feed gas and separation at low pressure and temperature, easy to combine with other separation process and use of other chemicals is not required, periodic removal and handling of spent solvent or adsorbent making the system more environmental friendly, relatively no moving parts make the process more flexible to operate, control and also easy to scale-up, low maintenance requirement, reduced energy consumption unless compression used, and low capital costs. However, it has some limitations as the separated CO_2 is at low pressure, it needs additional energy for compression of the feed gas to and meet pipeline pressure standard. Hence, economics remains a challenge while working towards pipeline specifications (Ebenezer and Gudmunsson 2006).

6.2 Membrane selection for natural gas separation

For more than two decades membranes have been known to constitute a mature technology that has been applied in natural gas processing. Currently membranes are used for CO_2 removal from natural gas at processing rates from million standard cubic feet per day (MMSCFD) to 250 MMSCFD. New units are also in design or construction stage to handle volumes up to 500 MMSCFD (Sridhar, Smitha et al. 2007).

The important criteria for selecting membrane materials for gas separation are based on the following key factors (a) intrinsic membrane permselectivity (b) ability of the membrane material to resist swelling induced plasticization (chemical resistance, which is quite rare but mostly fulfilled by inorganic membranes) and (c) ability to process the membrane material into a useful asymmetric morphology with good mechanical strength under adverse thermal and feed mixture conditions. The polymer membrane material should have good interaction and sorption capacity preferably with one of the components of the

mixture for an effective separation. Molecular structure, specific nature and arrangement of chemical groups attached to the main chain are also some of the important factors, which affect the membrane properties and hence, their performance. Molecular weight distribution and membrane polarity are other parameters of interest for the development of novel membranes in natural gas separation.

Nowadays, the control of gas permeability and permselectivity of membrane material has attracted the attention of a large number of membrane researchers all over the world, from industrial sectors as well as academic laboratories.

In addition, knowledge and understanding of the scientific factors such as thermodynamics, mass transfer kinetics and surface science are equally important to control the complex morphologies that are needed for an efficient use of advanced materials in asymmetric and composite membranes. Furthermore, the behaviour of membranes with respect to various feed mixtures under practically realistic operating conditions using analytical techniques need also be understood.

In the field of removal of acid gases from natural gas, a feed stream constituting CH_4, CO_2 and H_2S must be dealt with an integration of three relevant areas such as material selection, membrane synthesis and system configuration.

A clear choice of membrane materials not only render high permeability ratios, but also yield good permeabilities. The specific membrane chemistry is also equally important which depends upon the type of separation to be achieved. Therefore, membrane material selection is an area of high significance.

With a few exceptions and based on the materials that the membranes were made from, gas separating membranes can be broadly categorized into the following major categories: polymeric, inorganic and mixed matrix. The following sections briefly explain about the aforementioned gas separating membranes and further address the current challenges in the area.

6.3 Polymeric membranes

Polymeric membranes are most commercially used for the bulk separation of gases in many processes such as recovery of nitrogen from air, separation of oxygen-nitrogen mixture and hydrocarbons in petrochemical industries and also purification of natural gas. With regards to the separation of CO_2 from gas streams, primarily for natural gas sweetening, these membranes selectively transmit CO_2 versus CH_4. The driving force for the separation is pressure gradient across the membrane. As such, compression is required for the feed gas in order to provide the driving force for permeation, and the separated CO_2 is at low pressure and it requires additional compression to meet pipeline pressure requirements (Pandey and Chauhan 2001; Sridhar, Smitha et al. 2007; Bernardo, Drioli et al. 2009).

The two types of polymeric membranes that are commercially available for gas separations are glassy and rubbery membranes. Glassy membranes are rigid and glass-like, and operate below their glass transition temperatures. On the other hand, rubbery membranes are flexible, soft and operate above their glass transition temperatures. Mostly, rubbery polymers show a high permeability, but a low selectivity, whereas glassy polymers exhibit a low permeability but a high selectivity. Glassy polymeric membranes dominate industrial

membrane separations because of their high gas selectivities, along with good mechanical properties.

Based on structure, gas separation membranes can be classified as microporous membranes or nonporous dense membranes. Microporous membranes have a rigid, highly voided structure with randomly distributed, interconnected pores on the order of 0.01 to 10 µm in diameter. Nonporous, dense membranes consist of a dense film through which permeants are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is related directly to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material. Thus, nonporous, dense membranes can separate permeants of similar size if their concentration in the membrane material (that is, their solubility) differs significantly. Most gas separation processes use dense membranes to perform the separation. Usually these membranes have an anisotropic structure to improve the flux (Baker 2004).

In dense polymeric materials, solution-diffusion is widely accepted to be the main mechanism of transport. This mechanism is generally considered to be a three-step process. In the first step, the gas molecules are absorbed by the membrane surface on the upstream end. This is followed by the diffusion of the gas molecules through the polymer matrix. In the final step, the gas molecules evaporate on the downstream end. In glassy polymers, the sorption of gases becomes a complex process, which has been described by a combination of Henry's law and Langmuir expressions. This has been referred to as "dual mode sorption theory". Diffusion in glassy polymers is usually an activated process and Arrhenius relations may be used to express the permeability, diffusivity, and solubility coefficients (Kesting and Fritzsche 1993; Al-Juaied 2004).

Generally, polymeric membranes have been known for their excellent intrinsic transport properties, high processability and their low cost. However, a limit in the trade-off between permeability and selectivity as described by Robeson's "upper bound" (Fig. 4) has been seemingly reached by most polymeric membrane materials (Robeson 1991; Xiao, Low et al. 2009).
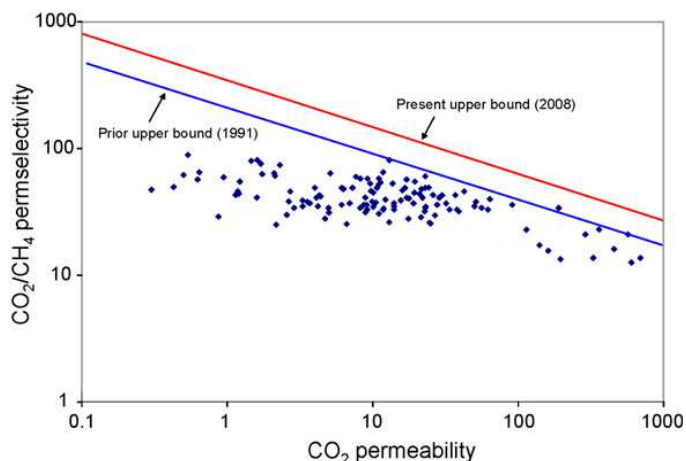

Fig. 4. Robeson's trade-off curve for carbon dioxide/natural gas pair (Xiao, Low et al. 2009)

Thus, the current research trend has focused on pushing the polymer performance above the upper bound and into the economically attractive region as showed by inorganic membranes.

6.4 Inorganic membranes

Inorganic membranes (also known as ceramic membranes) are used for gas separation due to their superior thermal, mechanical and chemical stability, good erosion resistance, insensitivity to bacterial action and a long operational life (Caro, Noack et al. 2000).

Microporous and dense membranes are the two types of inorganic membranes that are suitable for high-temperature gas separation applications.

Dense, nonporous inorganic membranes are made of polycrystalline ceramic material, in particular made of perovskites, palladium and its alloys, silver, nickel and stabilized solid electrolytes (zirconia). Mostly, they have been used or evaluated for separating gaseous components in laboratory work to characterize membrane properties. They are prepared as unsupported ones as well as thin films on porous supports. Application of dense membranes is primarily for highly selective separation of hydrogen (i.e.H_2 through Pd) and oxygen (i.e.O_2 through perovskites); transport occurs via charged particles. Dense membranes are impermeable to all gases except for a very limited number of gases that can permeate the material or can be incorporated into the structure of the membrane and transported through the material However, their applications are rarely been used in membrane separation processes because of their low permeability as they have relatively thick membranes which limited their application for practical separation processes as compared to porous inorganic membranes (Ismail and David 2001; Baker 2004).

Microporous inorganic membranes made of glass, metal, alumina, zirconia, zeolite and carbon membranes are commercially used as porous inorganic membranes. Other inorganic materials, such as cordierite, silicon carbide, silicon nitride, titania, mullite, tin oxide and mica also have been used to produce porous inorganic membranes. These membranes vary greatly in pore size, support material and configuration. A microporous ceramic membrane system generally consists of a macroporous ceramic support, some ceramic intermediate layers, and eventually a highly selective top layer. The support provides mechanical strength to the system. The intermediate layers bridge the gap between the large pores of the support and the small pores of the top layer. The top layer has separating capacities (Baker 2004).

Although inorganic membranes are more expensive than polymeric membranes, they possess advantages of temperature and wear resistance, well-defined stable pore structure, chemically inertness, and better selectivity than the polymeric membranes. However, due to the lack of technology to form continuous and defect-free membranes, high cost of production and handling issues e.g., brittleness, the commercial applications of inorganic membranes are still limited. For example, according to (Vu 2001; Baker 2004), a zeolite membrane module would cost around US$ 3000/m^2 of active membrane area compared to US$ 20/m^2 for existing gas-separation polymeric hollow-fiber membrane modules (Vu 2001; Baker 2004).

Later development has shown that there is a need to find cheap precursors and secure mechanical strength in order to make them an economically better choice. The development following the pyrolyzed carbon membranes was actually one step back, now trying to combine the excellent separation properties of the inorganic membranes with the more robust polymers (Pabby 2008).

Comparison in terms of the advantages and limitations of inorganic membranes over polymeric membranes are given on Table 7 (Caro, Noack et al. 2000).

Advantages for inorganic membranes	Limitation for inorganic membranes
High stability at high temperatures	High capital costs
High resistance to harsh environments	Brittleness (membrane cracking) due to extremely high sensitivity of membranes to temperature gradient
High resistance to high pressure drops	Low membrane surface per module volume
High resistance to microbiological degradation	Challenging in achieving high selectivities in large scale microporous membranes
Ease of cleanability after fouling	Generally low permeability of the highly selective (dense) membranes at medium temperatures
Ease of catalytic activation	Challenging for proper sealing of membrane to module at high temperatures

Table 7. Advantages and limitations of inorganic membranes over polymeric membranes (Caro, Noack et al. 2000)

Thus, the trend showed that the other alternative is the development of mixed matrix composite membranes which is a cost-effective membrane that combines homogeneously interpenetrating polymeric and inorganic particle matrices for high permeability and selectivity well above the upper-bound limit (Sridhar, Smitha et al. 2007).

6.5 Mixed matrix membranes

As discussed in previous sections, because of the economic competitiveness and the present challenges of aggressive environments for gas separating membranes, it is desirable to synthesize more durable membrane materials having higher selectivity and permeability with low cost and these have been an important goals of recent researches (Koros and Mahajan 2001).

In view of this situation, it remains a need for a new approach called mixed matrix membranes (MMMs) which is considered to be the most practical approach with the potential for future applications. It is also highly desirable to provide an alternative cost-effective membrane which combines homogeneously interpenetrating polymeric matrices for ease of processibility and inorganic particle for high permeability and selectivity well above the upper-bound limit (Shekhawat, Luebke et al. 2003).

The molecular-sieve type fillers used in mixed matrix membranes (MMMs) such as zeolite and carbon molecular sieve (CMS) are capable to discriminate between different molecules present in the feed mixture, usually on the basis of size and shape of molecules (Pal 2007; Shimekit, Mukhtar et al. 2009).

Gas transport through a mixed matrix membrane is considered as complex phenomena. Due to its heterogeneity, a number of theoretical permeation models have been used to predict the permeation properties of mixed matrix (heterogeneous) membranes as a function of the permeabilities of the continuous and dispersed phases (Hashemifard, Ismail et al. 2010).

Generally, permeation in MMMs occurs by a combination of diffusion through the polymer phase and diffusion through the permeable zeolite particles. The relative permeation rates through the two phases are determined by their intrinsic permeabilities (Baker 2004). The available models used in the prediction of the permeability of gases in mixed matrix membrane can be referred from (Shimekit, Mukhtar et al. 2011).

(Baker 2004; Shimekit, Mukhtar et al. 2011) states that CO_2 separation from natural gas are at the developing stages. Currently, significant growth in these applications, driven by the development of better membranes and process designs is occurring. For example, UNOCAL corporation offshore platform membrane systems and others such as cellulose acetate membranes have been widely used for the removal of carbon dioxide from natural gas for more than two decades mainly at small gas processing plants (less than 5 MMSCFD)(Baker 2002; Baker 2004).

Based on the current trend, the market for the separation of acid gases by membranes can be divided as follows: (1) Very small systems (less than 5 MMSCFD). At such flow rate, membrane units are very attractive and usually, the permeate gas is used or flared as fuel. Moreover, the system is a simple bank of membrane modules. (2) Small systems (5-40 MMSCFD). Two-stage membrane systems are used to reduce methane loss. In this gas flow range, amine and membrane systems compete and the choice depends on site specific factors. (3) Medium to large systems (more than 40 MMSCFD). In this range, membrane systems are too expensive to compete with amine plants. However, a number of large membrane systems have been installed on offshore platforms, at carbon dioxide oilfield flood operations, or where site-specific factors particularly favor membranes (Baker 2002).

6.6 Limitation and challenges

The application of membranes today for CO_2 separation in natural gas processing is mainly used for moderate-volume gas streams. For large-volume gas streams, membrane separation today cannot yet compete with the standard amine absorption as the flux and selectivity of the membranes are too low for processing large gas volumes.

Membranes are used in situations where the produced gas contains high levels of CO_2. However, a key sensitivity with these current membranes is that they must be protected from the heavier C_{5+} hydrocarbons present in wet natural gas streams. Exposure to these compounds immediately degrades performance and can cause irreversible damage to the membranes.

Thus, in order to fully exploit the use of membranes in natural gas purification, development of more selective, higher-flux and cost effective new membranes are still critical concerns. And hence, the outcome will make membrane processes much more competitive with other technologies such as amine absorption for large scale systems (Baker 2004).

7. Comparison of natural gas purification technologies for acid gas removal

In the previous sections the widely used natural gas purification technologies for the removal of acid gases from product natural gas streams have been discussed in detail. In the following section, an attempt is made to compare and summarize the aforementioned technologies briefly.

Absorption by physical solvents is mostly not recommended at low partial pressures as the compression of the gas for physical absorption is relatively no economical. In general, the economics of CO_2 separation is strongly influenced by the partial pressure of CO_2 in the feed natural gas. However, if the gas is available at high pressure, physical solvents might be a better choice than chemical solvents. While physical solvents can often be stripped of impurities by reducing the pressure without the application of heat, regeneration of chemical solvents is achieved by the application of heat. Mostly, physical solvents tend to be favored over chemical solvents when the concentration of acid gases or other impurities is very high. Unlike chemical solvents, physical solvents are non-corrosive, requiring only carbon steel construction. The concentration of heavy hydrocarbons in the feed gas also affects the choice of gas treating solvent. If the concentration of heavy hydrocarbons is high, a physical solvent may not be the best option due to higher co-absorption of hydrocarbons, particularly pentanes plus. Unlike synthesis gases, where there aren't appreciable quantities of hydrocarbons, natural gases can be a problem for physical solvents as the result of hydrocarbon co-absorption. This makes physical solvents particularly applicable to synthesis gas treating (Burr and Lyddon 2008).

Although adsorption technique is restricted to small gas stream and moderate pressure due to complexity of the design, the use of PSA technology is mostly used in shut-in natural gas wells that usually contained too much N$_2$. As a typical example, titanosilcate adsorbent (Engelhard Corporation) combined with a PSA process in a vacuum swing adsorption are used to remove N$_2$ and/or CO_2 from natural gas feed streams (Ritter and Ebner 2007).

When the natural gas well contains high CO_2 and H$_2$S, the use membrane process is most preferable at high pressure. CO_2 separation is accomplished by pressure-driven mass transfer through a permeable membrane where separation is due to the differences in permeation rate of different gas penetrants. Although the acid gas is usually recovered at low pressure, high purity product containing approximately 95% CO_2 can be achieved with one or two stages, depending upon feed gas pressure and percent recovery. Economic considerations may dictate additional capital and incremental energy requirements to increase feed pressure and/or utilize two-stage separation with recompression of gas from the first stage.

Cryogenic process, as compared to other methods of separating CO_2, it has the advantage that the CO_2 can be obtained at relatively high pressure. However, this advantage may be offset by the large refrigeration requirement. In such regards, the need of special materials is critical for cryogenic process.

The overall comparison of the widely used natural gas purification technologies with regards to acid gas removal are summarized in Table 8.

Although the choice of acid gas removal technology depends on the needs of the gas processor, the current market trend showed that membranes have also proven their usefulness to compete with absorption (amines) technology. Nevertheless, the absorption technology based on amine treatment is still an efficient method although the amine units are large and heavy. Table 9 compares amines and membranes for CO_2 removal systems (Baker 2004).

Process	Advantages	Disadvantages
Absorption	• Widely used technology for efficient (50-100) % removal of acid gases (CO_2 and H_2S).	• Not economical as high partial pressure is needed while using physical solvents. • Long time requirement for purifying acid gas as low partial pressure is needed while using chemical solvents.
Adsorption	• High purity of products can be achieved. • Ease of adsorbent relocation to remote fields when equipment size becomes a concern.	• Recovery of products is lower • Relatively single pure product
Membrane	• Simplicity, versatility, low capital investment and operation. • Stability at high pressure • High recovery of products • Good weight and space efficiency • Less environmental impact.	• Recompression of permeate • Moderate purity
Cryogenic	• Relatively higher recovery compared to other process • Relatively high purity products	• Highly energy intensive for regeneration • Not economical to scale down to very small size. • Unease of operation under different feed stream as it consists of highly integrated, enclosed system.

Table 8. Overall comparisons of natural gas purification technologies

Operating Issues	Amines	Membranes
User Comfort Level	Very familiar	Still considered new technology
Hydrocarbon Losses	Very low	Losses depend upon conditions
Meets Low CO_2 Spec.	Yes (ppm levels)	No (<2% economics are challenging)
Meets Low H_2S Spec.	Yes (<4 ppm)	Sometimes
Energy Consumption	Moderate to high	Low, unless compression used
Operating Cost	Moderate	Low to moderate
Maintenance Cost	Low to moderate	Low, unless compression used
Ease of Operation	Relatively complex	Relatively simple
Environmental Impact	Moderate	Low
Dehydration	Product gas saturated	Product gas dehydrated
Capital Cost Issues		
Delivery Time	Long for large systems	Modular construction is faster
On-Site Installation Time	Long	Short for skid-mounted equipment
Pretreatment Costs	Low	Low to moderate
Recycle Compression	Not used	Use depends upon conditions

Table 9. Comparison of Amines and Membranes for CO_2 Removal Systems (Baker 2004)

In the next sections, potential hybrid separation processes in natural gas processes are briefly presented.

7.1 Hybrid separation processes

In hybrid separation processes, an integration of one process is used with other separation process or processes in which the basic functioning of one process is joined with another physical or chemical process in a single unit operation (Bernardo, Drioli et al. 2009).

A properly designed hybrid process will balance the drawbacks of the specific process and favourably combine their advantages. It is anticipated that the result will be a better separation, contributing to a sustainable process improvement by allowing the reduction of investment and operational costs (Bernardo, Drioli et al. 2009).

As has been described in the previous sections and in spite of the greater potential of membranes for commercial application towards bulk removal of CO$_2$ in high-pressure natural gas streams with high CO$_2$ content, the technology faces some limitations as compared with other techniques especially when the CO$_2$ concentration is low. And it may be necessary to use another process (e.g., amine based or cryogenic system) to create a hybrid system (Tabe-Mohammadi 1999). Hence, this motivates researchers to look for an alternative technologies aimed at filling its technology gaps through the use of hybrid separation process.

Some researchers (Bhide, Voskericyan et al. 1998) also report that a membrane-amine hybrid system would be economical in comparison to an amine system alone or a membrane system alone for various conditions, such as low CO$_2$ compositions, and a recent study confirms the economic feasibility of another membrane-amine system design (Falk-Pedersen and Dannstrom 1997).

A study with a membrane-cryogenic distillation hybrid system also shows favourable economics as well (Vu 2001).

The integration of membranes with other separation processes such as PSA are also well-established in the chemical and petrochemical industries (Choe, Auvil et al. 1987; Doshi 1987; Doshi, Werner et al. 1989; Doshi and Dolan 1995; Feng, Pan et al. 1998). Membrane permeation can be an effective aid in the pressurization and high-pressure adsorption steps of a typical PSA process; the pressure difference available from the PSA can be used for operating the membrane incorporated into the blowdown step of the PSA cycle (Esteves and Mota 2007). Usually, the integration of membranes with PSA is considered in H$_2$ separation, while hybrid membranes + amine absorption are applied to the CO$_2$ separation. Cost comparison for membrane and absorption (diethanolamine) process showed that the membrane process is more economical for CO$_2$ feed concentrations in the range 5-40 mol % (Bhide, Voskericyan et al. 1998). It does ascertain that when the feed contains other gases such as H$_2$S, the operating cost for removing the additional gases also increases. In such cases, use of hybrid membrane processes (membranes for bulk separation of CO$_2$ and H$_2$S and gas-absorption processes for purification) is economically feasible (Bhide, Voskericyan et al. 1998). A hybrid system comprising of Cynara membranes and amine absorption is operating since 1994 in Mallet (Texas, U.S.A.) to perform the bulk removal of CO$_2$ from associated gas (90% CO$_2$ and heavy hydrocarbons), before downstream treating. The membrane system offered a 30% reduction in operating cost when compared with a methyl

diethanolamine (MDEA) system and significantly reduced the size of the subsequent operations (Blizzard, Parro et al. 2005; Bernardo, Drioli et al. 2009).

The combination of membrane processes with another process (most commonly with amine units) for bulk removal of CO_2 offers an economical advantage over amine technologies. However, this process has also the limitation of being complex as it is a combination of two processes (Baker 2004).

8. Conclusions and future directions

In general, this chapter attempted to address a comprehensive assessment on the fundamental technologies that are widely used for natural gas purification (gas sweetening) processes namely: absorption, adsorption, membranes and cryogenics. More specifically, the removal of acid gases mainly of carbon dioxide (CO_2) from the natural gas has been given special emphasis aimed at increasing the heating value of natural gas, reducing pipe lines and equipment corrosion during transportation, storage and distribution and meeting environmental requirements. A comparative study on the aforementioned technologies was also made on the basis of their advantages and limitations. Furthermore, the economical competitive advantages of using hybrid separation processes over single gas separation processes havebeen discussed.

In the next section, potential research directions and future development opportunities of the promising natural gas purification processes are presented.

8.1 Research and development opportunities for natural gas separation

Research opportunities to improve and implement acid gas removal technologies in natural gas purification field have many drivers, including economical reasons, growing interest among policy makers and regulators, and concerns about GHG emissions.

Understanding of the current state of acid gas removal technologies, the direction of the researches and developments being undertaken and their likely outcomes is the key insight that energy company managers, engineers and planners are required to make informed strategic decisions. Thus, the following section describes the potential research and development activities with regards to the major acid gases separation process mainly on CO_2 separation using natural gas purification technologies and in accordance with what is set by the Chemical Industry Vision 2020 Technology Partnership (Ritter and Ebner 2007).

Absorbents and absorption process development

Although there are quite numerous absorbents available for CO_2 removal process in natural gas processing plant, in the near-future, development of new absorbents and absorption process will continue to be carried out as the need for enhanced capacity and improved heat of absorption will still be the interest of the processing industries for CO_2 removal. Moreover, researches and developments on new regeneration techniques for CO_2 removal from natural gas, as opposed to thermal or vacuum regeneration, need also be conducted at high pressure. Further, there is also a need to research and develop new absorbents that function at elevated temperature gases. More importantly, research and development on absorbents that are stable to contaminants such as amine environments need to be carried

out. Moreover, preferential selective absorbents such as preferential absorption of CO$_2$ over other impurities such as sulfur in the acid gas removal process from natural gas or coal bed methane are some of the research directions with regards to absorption technologies (Ritter and Ebner 2007).

Adsorbents and adsorption process development

As a short-term adsorbent development research direction for CO$_2$ removal from natural gas, the focus of the current research interest are mostly on the development of high-capacity (~ 3-4 mol/kg) CO$_2$-selective adsorbents that can function at elevated pressures and operating temperatures. There are also related avenue of research that attempted to comp up with new designs for PSA cycle that have potentials to use the newly developed or the available CO$_2$ selective adsorbents (temperature swing adsorption or integrated PSA-TSA cycles). For example, development of new PSA cycles that used the idea of heavy reflux to show that CO$_2$ as a heavy product is more important than that of H$_2$ (light product). The issue of thermal energy management while designing the TSA and its hybrid cycle with PSA is also categorized in this research area to improve the overall efficiency of the removal of CO$_2$ from natural gas processing plant.

In the long-term, the research direction for the removal of CO$_2$ from natural gas using adsorption process will focus on fabrication of new, structurally modified adsorbents that can be used for the integration of gas-liquid absorption with PSA that is commonly known as rapid cycle PSA and improved design of the CO$_2$ removal process. Moreover, detail studies on how to reduce the cycling time in the rapid PSA process need to be conducted. Further studies on the adsorbent particle size, surface adsorption properties, and mass transfer limitations for enhanced removal of CO$_2$ from natural gas need to be addressed.

Once the novel adsorbent materials with enhanced adsorption capacity have been fabricated, the next studies will direct on development of temperature swing adsorption and/or integration of gas-liquid absorption with pressure swing adsorption using recently improved materials. Afterwards, further studies to quantify their effect on cycling time and bed sizes for a stressed TSA/PSA cycle will follow. The development of integration of gas-liquid absorption with pressure swing adsorption, studies for the improvement of CO$_2$ removal using the reaction processes that can improve the sorption for natural gas purification need equally be searched (Ritter and Ebner 2007).

Membranes and membrane process

In the near-term the research and development directions for the removal of CO$_2$ using membrane technologies will advance in areas such as: development of CO$_2$ permselective polymeric glassy or rubbery membranes that has a selectivity of CO$_2$ over H$_2$ with the range of 16-25, with high flux and high temperature stability, development of polymeric glassy or rubbery membranes for CO$_2$/CH$_4$ that can have selectivity of more than 50, high resistance for plasticization and stability towards heavy oil. More research is also need to be carried out on the development of facilitated transport membranes for enhanced CO$_2$ selectivity with higher resistance for adverse environments and service life. Although economical challenges are still there for the development of CO$_2$ permselective inorganic membranes, new inorganic membranes that can achieve higher selectivity (> 15-20%) under harsh environments need to be developed. Furthermore, enhanced permselective CO$_2$ surface flow membranes with higher CO$_2$ selectivity over H$_2$, N$_2$, and CH$_4$ need to be researched,

development of CO_2 selective mixed-matrix membranes with higher selectivity, permeance and stability, development of CO_2 permselective hollow fiber membrane contactors with improved permeance and strength for natural gas purification are some of the typical future research directions.

In the near future, new membrane materials for CO_2 removal from natural gas will need to be given more focus so that membranes can be fabricated to have enhanced selectivity of CO_2 (> 100%), operating at high temperatures and pressures and with resistance to fouling and cracking or embrittlement.

Further in the long-term, the intensification of processes such as hybrid technologies using highly selective CO_2 adsorbent and membrane with high permeability for H_2 processes for the development of H_2 production (e.g., for steam methane reforming) will be the interest of researchers. Moreover, the extension of the results from the newly developed CO_2 adsorbent and membrane technologies will further be researched for their compatibility to be integrated into gasification combined cycle (IGCC) and other related technologies that targets for CO_2 sequestration as a long term prospect (Ritter and Ebner 2007).

In general, the potential of the hybrid processes over single processes for the removal of CO_2 from the natural gas in industrial scale need to be fully exploited through detail understanding of design methodologies and process flows. In this regards, modeling of the newly developed processes, new models for accurate prediction of permeation of gases in the newly developed processes such as (mixed matrix membranes and hybrid systems) along with molecular dynamics studies and module performance models can be recommended for further research direction.

9. Acknowledgments

10. References

Al-Juaied, M. A. (May 2004). Carbon dioxide removal from natural gas by membranes in the presence of heavy hydrocarbons and by Aqueous Diglycolamine®/Morpholine, PhD thesis, pp. 1-424, The University of Texas at Austin, Texas

Bahadori, A., S. Mokhatab, et al. (2007). Rapidly estimating natural gas compressibility factor. *Journal of Natural Gas Chemistry,* Vol. 16, No. 4, pp. 349-353

Bakar, W. A. W. A. and R. Ali. (2010). Natural Gas, In: *natural gas*, Primož Potočnik, pp. (1-616), Sciyo, Retrieved from
http://www.intechopen.com/articles/show/title/natural-gas.

Baker, R. W. (2002). Future directions of membrane gas separation technology. *Industrial & Engineering Chemistry Research,* Vol. 41, No. 6, pp. 1393-1411

Baker, R. W. (2004). *Membrane Technology and Applications* (2nd edition), John Wiley & Sons, ISBN 0-470-85445-6, West Sussex

Beggs, H. D. (1984). *Gas Production Operations*, OGCI Publications, ISBN 0-930972-06-6, Oklahoma

Bernardo, P., E. Drioli, et al. (2009). Membrane gas separation: a review/state of the art. *Industrial & Engineering Chemistry Research,* Vol. 48, No. 10, pp. 4638-4663

Bhide, B. D., A. Voskericyan, et al. (1998). Hybrid processes for the removal of acid gases from natural gas. *Journal of Membrane Science,* Vol. 140, No. 1, pp. 27-49

Blizzard, G., D. Parro, et al. (2005). Mallet gas processing facility uses membranes to efficiently separate CO$_2$. *Oil and Gas Journal,* Vol. 103, No. 14, pp. 48-53

Bord, N., G. Cretier, et al. (2004). Determination of diethanolamine or N-methyldiethanolamine in high ammonium concentration matrices by capillary electrophoresis with indirect UV detection: application to the analysis of refinery process waters. *Analytical and Bioanalytical Chemistry,* Vol. 380, No. 2, pp. 325-332

Burggraaf, A. J. (1996). Important characteristics of inorganic membranes. *Membrane Science and Technology,* Vol. 4, pp. 21-34

Burr, B. and L. Lyddon (2008). A Comparison of Physical Solvents for Acid Gas Removal, In: *options for acid gas removal,* 11.08.11, Available from:
http://www.bre.com/portals/0/technicalarticles/A%20Comparison%20of%20Physical%20Solvents%20for%20Acid%20Gas%20Removal%20REVISED.pdf

Caro, J., M. Noack, et al. (2000). Zeolite membranes-state of their development and perspective. *Microporous and Mesoporous Materials*, Vol. 38, No. 1, pp. 3-24

Cavenati, S., A. Carlos, et al. (2006). Removal of carbon dioxide from natural gas by vacuum pressure swing adsorption. *Energy & fuels*, Vol. 20, No. 6, pp. 2648-2659

Choe, J. S., S. R. Auvil, et al. (1987). Process for separating components of a gas stream, Google Patents 4701187

Davison, J., P. Freund, et al. (February 2001). Putting carbon back into the ground (1st edition), IEA Greenhouse Gas R&D Programme, ISBN 1 898373 28, Cheltenham

De Lange, R. S. A., K. Keizer, et al. (1995). Analysis and theory of gas transport in microporous sol-gel derived ceramic membranes. *Journal of Membrane Science, Vol.* 104, No. No. (1-2), pp. 81-100

Dortmundt, D. and K. Doshi (1999). Recent Developments in CO$_2$ Removal Membrane Technology, In: *design consideration*, 16.08.11, Available from:
http://www.membrane-guide.com/download/CO2-removal-membranes.pdf

Doshi, K. J. (1987). Enhanced gas separation process, Google Patents, 4690695

Doshi, K. J. and W. B. Dolan (1995). Process for the rejection of CO$_2$ from natural gas, Google Patents, 5411721

Doshi, K. J., R. G. Werner, et al. (1989). Integrated membrane/PSA process and system, Google Patents, 4863492

Ebenezer, S. A. and J. S. Gudmunsson (December 2006). Removal of Carbon Dioxide from Natural Gas for LPG Production, In: *carbon dioxide removal processes,* 21.08.11, Available from:
http://www.ipt.ntnu.no/~jsg/studenter/prosjekt/Salako2005.pdf

Economides, M. J. and D. A. Wood (2009). The state of natural gas. *Journal of Natural Gas Science and Engineering*, Vol. 1, No. 1-2, pp. 1-13

Energy Information, A. and U. S. E. I. Administration (2011). International Energy Outlook 2011, In: *Natural gas*, 22.08.11, Available from:
http://205.254.135.7/forecasts/ieo/pdf/0484(2011).pdf

Esteves, I. A. A. C. and J. P. B. Mota (2007). Gas separation by a novel hybrid membrane/pressure swing adsorption process. *Industrial & Engineering Chemistry Research,* Vol. 46, No. 17, pp. 5723-5733

Falk-Pedersen, O. and H. Dannstrom (1997). Separation of carbon dioxide from offshore gas turbine exhaust. *Energy Conversion and Management,* Vol. 38, No. S81-S86

Feng, X., C. Y. Pan, et al. (1998). Integrated membrane/adsorption process for gas separation. *Chemical Engineering Science,* Vol. 53, No. 9, pp. 1689-1698

Gilliland, E. R., R. F. Baddour, et al. (1974). Diffusion on surfaces. I. Effect of concentration on the diffusivity of physically adsorbed gases. *Industrial & Engineering Chemistry Fundamentals,* Vol. 13, No. 2. pp. 95-100

Glasscock, D. A. (1990). Modeling and experimental study of carbon dioxide absorption into aqueous alkanolamines, PhD thesis, pp. (1-292), The University of Texas at Austin, Texas

Hashemifard, S. A., A. F. Ismail, et al. (2010). Prediction of gas permeability in mixed matrix membranes using theoretical models. *Journal of Membrane Science,* Vol. 347, No. 1-2, pp. 53-61

Hermann, W., P. Bosshar, et al. (2005). An Assessment of Carbon Capture Technology and Research Opportunities, In: *Physical Adsorption*, 25.08.11, Available from: http://gcep.stanford.edu/pdfs/assessments/carbon_capture_assessment.pdf

Ismail, A. F. and L. I. B. David (2001). A review on the latest development of carbon membranes for gas separation. *Journal of Membrane Science,* Vol. 193, No. 1, pp. 1-18

Javaid, A. (2005). Membranes for solubility-based gas separation applications. *Chemical Engineering Journal*, Vol. 112, No. 1-3, pp. 219-226

Kerry, F. G. (2007). *Industrial Gas Handbook: Gas Separation and Purification*, CRC, ISBN 978-0-8493-9005-0, New York

Kesting, R. E. and A. K. Fritzsche (1993). *Polymeric Gas Separation Membranes*, Wiley, ISBN 978-0-4715-6931-2, New York

Kidnay, A. J., W. Parrish, et al. (2006). *Fundamentals of Natural Gas Processing*, CRC, ISBN 978-0-8493-3406-1, New York

Kohl, A. L. and R. B. Nielsen (1997). Gas Purification (5th edition), Gulf Professional Publishing, ISBN 978-0-8841-5220-0, Texas

Koros, W. J. and R. Mahajan (2001). Pushing the limits on possibilities for large scale gas separation: which strategies? *Journal of Membrane Science,* Vol. 181, No. 1, pp. 141-141

Kovvali, A. S. and K. K. Sirkar (2002). Carbon dioxide separation with novel solvents as liquid membranes. *Industrial & Engineering Chemistry Research,* Vol. 41, No. 9, pp. 2287-2295

Mersmann, A., M. Kind, et al. (2011). *Thermal Separation Technology Principles, Methods, Process Design*, Springer, ISBN 978-3-642-12524-9, New York

Meyers, R. A. (2001). *Chemical Engineering. Encyclopedia of Physical Science and Technology* (3rd edition), Ramtech, Inc. California

NaturalGas.org. (2010). Overview of Natural Gas, In: *Background,* 22.06.11, Available from:http://www.naturalgas.org/overview/background.asp

Pabby, A. K. (2008). *Handbook of Membrane Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications* (1st edition), CRC, ISBN 978-0-849-39549-9, New York

Pal, R. (2007). New models for thermal conductivity of particulate composites. *Journal of Reinforced Plastics and Composites*, Vol. 26, No. 7, pp. 643

Pandey, P. and R. S. Chauhan (2001). Membranes for gas separation. *Progress in Polymer Science*, Vol. 26, No. 6, pp. 853-893

Pascoli, S. D., A. Femia, et al. (2001). Natural gas, cars and the environment. A (relatively) 'clean' and cheap fuel looking for users. *Ecological Economics,* Vol. 38, No. 2, pp. 179-189

Polasek, J. and J. Bullin (1984). Selecting amines for sweetening units. *Energy Progress,* Vol. 4, No. 3, pp. 146-149

Porter, M. C. (1990). *Handbook of Industrial Membrane Technology*, Noyes Publications, ISBN 08155-1205-8, New Jersey

Ritter, J. A. and A. D. Ebner (2007). Carbon Dioxide Separation Technology: R&D Needs For the Chemical and Petrochemical Industries, In: *Recommendation for future R&D,* 22.06.11, Available from:
http://www.chemicalvision2020.org/pdfs/CO2_Separation_Report_V2020_final.pdf

Robeson, L. M. (1991). Correlation of separation factor versus permeability for polymeric membranes. *Journal of Membrane Science*, Vol. 62, No. 2, pp.165-185

Rodriguez, H., L. Mello, et al. (2011). Absorption of Carbon Dioxide into Aqueous Solutions of Alkanolamines in a Wetted Wall Column with Film Promoter. *Chemical Engineering Transactions*, Vol. 25, No, 51, pp. 51-56

Rojey, A. (1997). *Natural Gas: Production, Processing, Transport*, Editions Technip, ISBN 2-7108-0693-2, Paris

Scott, K. (1998). *Handbook of Industrial Membranes,* Elsevier science publishers, ISBN 1-8561-7233-3, Oxford

Shekhawat, D., D. R. Luebke, et al. (2003). A Review of Carbon Dioxide Selective Membranes: A Topical Report, In: *CO₂ selective membranes,* 13.07.11, Available from: http://www.osti.gov/bridge/product.biblio.jsp?osti_id=819990

Shimekit, B., H. Mukhtar, et al. (2009). Ceramic membranes for the separation of carbon dioxide: A review. *Transaction of Indian Ceramic Society*, Vol. 68, No. 3, pp. 115-138

Shimekit, B., H. Mukhtar, et al. (2011). Prediction of the relative permeability of gases in mixed matrix membranes. *Journal of Membrane Science*, Vol. 373, No. 1-2, pp.152-159

Sridhar, S., B. Smitha, et al. (2007). Separation of carbon dioxide from natural gas mixtures through polymeric membranes-a review. *Separation & Purification Reviews*, Vol. 36, No. 2, pp, 113-174

Stern, A. (1994). Polymers for gas separations: the next decade. *Journal of Membrane Science,* Vol. 94, No. 1, pp. 1-65

Tabe-Mohammadi, A. (1999). A review of the applications of membrane separation technology in natural gas treatment. *Separation Science and Technology,* Vol. 34, No. 10, pp, 2095-2111

Tobin J., Shambaugh P., et al. (2006). The Crucial Link between Natural Gas Production and its Transportation to Market In: *Stages in the production of pipeline-quality natural gas and NGLs.* 13.07.11, Available from: http://lba.legis.state.ak.us/sga/doc_log/2006-01-01_eia_publication_natural_gas_processing.pdf

Vu, D. Q. (2001). Formation and Characterization of Asymmetric Carbon Molecular Sieve and Mixed Matrix Membranes for Natural Gas Purification, PhD thesis, pp. 1-362, The University of Texas at Austin, Texas

Xiao, Y., B. T. Low, et al. (2009). The strategies of molecular architecture and modification of polyimide-based membranes for CO_2 removal from natural gas-A review. *Progress in Polymer Science*, Vol. 34, No. 6, pp. 561-580

Yang, R. (1997). *Gas Separation by Adsorption Processes,* Imperial College Press, ISBN 9781860940477, Singapore

Yang, R. T. and J. Wiley (2003). *Adsorbents: fundamentals and applications*, John Wiley & Sons, ISBN 9780471297413, New Jersey
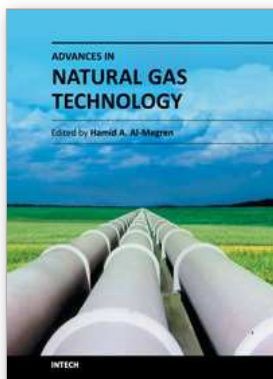
Advances in Natural Gas Technology

Edited by Dr. Hamid Al-Megren

Natural gas is a vital component of the world's supply of energy and an important source of many bulk chemicals and speciality chemicals. It is one of the cleanest, safest, and most useful of all energy sources, and helps to meet the world's rising demand for cleaner energy into the future. However, exploring, producing and bringing gas to the user or converting gas into desired chemicals is a systematical engineering project, and every step requires thorough understanding of gas and the surrounding environment. Any advances in the process link could make a step change in gas industry. There have been increasing efforts in gas industry in recent years. With state-of-the-art contributions by leading experts in the field, this book addressed the technology advances in natural gas industry.

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