

CO₂ Capture and Usage: Harnessing the CO₂ Content in Natural Gas for Environmental and Economic Gains

Emmanuel O. Agiaye and Mohammed Othman, Nigerian Agip Oil Company

Summary

Carbon dioxide (CO₂) capture and usage (CCU) is currently a global topical issue, and is viewed as one possible route to reduction of CO₂ concentrations in the atmosphere. The core issues facing the world in current times—development, economy, and environment—are identified as being dependent on the provision of clean, efficient, affordable, and reliable energy services. Currently, the world is highly dependent on fossil fuels for provision of energy services, and the amount of which renewable energies can sufficiently replace is minimal. The deployment of appropriate CO₂-separation technologies for the processing of natural gas is viewed as an abatement measure toward global CO₂-emissions reduction. Selection of the optimum technology among the several separation technologies for a particular separation need requires special attention to harness the economic and environmental benefits. The captured CO₂ would also require appropriate disposal or usage so as to sequester or “delay” its re-entry into the atmosphere. These challenges of CCU— involving natural gas particularly during processing, which has become an area of intense research—shall be discussed in the paper with respect to the selected technique for CO₂ capture. A typical natural-gas-production scenario in Nigeria shall be analyzed for potential CO₂ capture. Further discussion shall be on the identification of the recovered CO₂ gas-usage framework, such as CO₂ flooding [in enhanced oil recovery (EOR)], for additional revenue generation, assessment of the CO₂ savings, and the contribution to the clean development mechanism (CDM).

Introduction

The separation of CO₂ from the gas stream is currently a global issue. The increasing amounts of greenhouse gases (GHGs) in the atmosphere in recent years, considered to be partly responsible for climate change, have been a serious global concern, and CO₂ gas has been identified to as a major contributor of GHGs. Several postulations have proposed a long-term global stabilization of CO₂ concentrations in the atmosphere to be a possible panacea for curtailing climate change and global warming. The use of fossil fuels inclusive of natural gas currently dominate the source of global energy supply, which are considered capable of meeting the world’s increasing energy needs up to 84% by 2030 (IEA 2008, page 47) from the current demand of approximately 81% (IEA 2012, page 10). CO₂ emission to the atmosphere from combustion of fossil fuels (coal, oil, and natural gas) and during production/processing of natural gas is considered to be the major cause of high CO₂ volumes in the atmosphere. It has been outlined that energy scenarios involving the use of clean-energy technologies can result in a more than 50% reduction in global CO₂ emissions up to 2050 (IEA 2010) with the deployment of carbon capture and sequestration (CCS), inclusive of industry and

power generation, as capable of contributing up to 19% in CO₂ reductions (IEA 2008, page 69). These are not withstanding the assessment performed by IEA (2012) with respect to “high potential CO₂ emissions” found with global “carbon reserves,” and thereby outlining the deployment of CCS as the major technology required for sustaining the projected demand on fossils. “The assessment has attributed almost 63% to coal, 22% to oil and 15% to gas in CO₂ emissions potential locked in these reserves.” The case of CO₂ in natural gas represents a typical scenario for a number of oil and gas companies faced with the enormous challenge of reduced energy level of sales gas making it subquality or when disposal by flaring increases the source of CO₂ emissions to the atmosphere. However, the amount of natural gas flared globally has been shown to contribute approximately 1.2% of the global CO₂ emissions, which is given to be more than one-half of the certified emissions reductions under the Kyoto Protocol (ICF International 2006).

There are several technologies and techniques now available for separation of CO₂ (or acid gases) from gas mixture, either as flue gas from power plants or from natural gas. In addition to deployment of these technologies, the captured or separated CO₂ must be disposed of in such a manner as to prevent it from seeping back into the atmosphere. This is required to achieve the aims of the CDM from the use of fossil fuels. Among the fossil fuels, natural gas has been shown to contain the least amount of CO₂ emitted per tonnage of fuel burnt as compared with coal and oil. In addition to the CO₂ emitted during combustion, natural gas on production also contains a certain amount of impurities, including CO₂ gas. The maximum level of CO₂ permitted in natural-gas fuel is typically less than 3%. Hence, all natural gas is treated to remove the solids and free liquids and to reduce water-vapor content to acceptable levels and, especially, to meet pipeline specifications. Hence, natural gas must be purified through the removal of CO₂ and other acid gases and impurities (where present) because these impurities can form acids in the presence of water to corrode pipelines and other equipment. In addition, higher concentrations of CO₂ in natural gas reduce the heating value or energy level, which is below pipeline specifications, necessitating its removal before distribution to the end consumer. Natural gas has been a main source in meeting the world’s energy demand, contributing an estimated 23.81% in 2010 to the world energy supply mix (Rufford et al. 2012, page 123). This contribution is projected to increase because natural gas is considered the cleaner fossil fuel compared with coal and oil. The deployment of appropriate CO₂-capture technology in processing natural gas stands to improve its value as the cleaner fossil fuel. In this paper, a brief review of related acid-gas separation processes will be reviewed and recommendations will be presented. Economic opportunities by use of the captured CO₂ for additional revenue generation through EOR by CO₂ flooding, as well as appropriate transportation and storage infrastructure, will be reviewed.

CO₂-Capture Technologies

There are different techniques or technologies available today that are used for the separation of CO₂ from natural gas or from flue

Property	CH ₄	CO ₂	N ₂
Kinetic diameter (Å)	3.80	3.30	3.64
Normal boiling point [K (°C)]	111.7 (–161.45)	–	77.3 (–195.85)
Critical temperature [K (°C)]	3.80 (–269.35)	304.1 (30.95)	126.2 (–46.95)
Critical pressure [psi (bar)]	667.2 (46)	1,070.4 (73.8)	493.1 (34)
ΔH_{vap} at NBP (KJ/mol)	8.17	26.1	5.58
Polarizability (Å ³)	2.448	2.507	1.710
Quadrupole moment (DÅ)	0.02	4.3	1.54

Table 1—Physical properties of CH₄, CO₂, and N₂ (Rufford et al. 2012; Scholes et al. 2008, page 54).

gas (from power plants). The type of separation process required in any particular case is often affected by the specifications of the product gas and the amount and composition of the gas mixture. As simple as it may seem, the selection of the optimum technology suitable for the separation process may become an issue as a result of a number of factors. This is because no one technology can perfectly suit all the conditions required for separation. Hence, each is associated with its advantages and disadvantages. Typical factors that may be considered for the separation of CO₂ from natural gas include

- The CO₂ content in the product gas, which is typically required at less than 2%
- The presence and concentration of other impurities in the feed gas, such as H₂S and water content
- The presence and concentration of heavy hydrocarbon (HC) ends, contaminants, and water vapor
- The conditions available for processing the gas, such as the pressure, temperature, and volume of the feed gas

However, the choice of a CO₂-capture technology could be simplified by “exploiting the differences in the molecular properties or the thermodynamic and transport properties of the components in the mixture” (Rufford et al. 2012, page 125). **Table 1** shows the physical properties of a gas mixture [methane (CH₄), CO₂, and nitrogen (N₂)] that can be exploited by use of the molecular-properties approach to achieve separation of these gases.

Thermodynamic and transport properties can also be used to achieve separation by use of properties such as solubility, adsorption capacity, diffusivity, vapor pressure, and boiling points.

On the basis of the molecular or thermodynamic and transport properties of the gas components to be separated (Rufford et al. 2012, page 125), approximately five separation mechanisms are usually applied, with which a suitable separation process could be selected. Generally, selection of the appropriate separation process depends more on its characteristic separation power (SP) to achieve the desired gas specifications in addition to its economic viability in terms of the separated-products value.

The following five separation mechanisms are commonly applied in any of the separation processes:

- Absorption—involves absorption in a liquid or solid sorbent through diffusion into the liquid or solid absorbing medium (for instance, amine absorption of CO₂ in a scrubber process).

- Adsorption on a solid—involves the gas component to be separated, binding to the surface of a solid adsorbent such as activated carbon, silica gel, zeolites, and finely divided platinum. A typical example of an adsorption mechanism is the molecular-sieves-separation process for natural-gas purification.
- Permeation mechanism—involves separating components by use of the principle of solubility diffusion to permeate through a membrane.
- Chemical conversion to another compound—for instance, the steam-reformation process of natural gas to produce H₂ and CO₂, otherwise known as hydrogen economy.
- Phase creation by heat transfer—to (or from) the gas mixture, which involves use of phenomena such as condensation, desublimation, or distillation.

The separation mechanisms as outlined in the preceding are each characterized by a major property known as selectivity with respect to the components to be separated. In particular, the equilibrium selectivity of the feed stream is usually a very important property for the evaluation of absorption and adsorption separation processes. In membrane-permeation mechanisms, selectivity, for instance, is applied in the analysis of the process-separation capability, depending on the concentrations of the permeate (CO₂-rich gas) and feed stream. The performance of a separation process can therefore be viewed as governed by the selectivity behavior of the separation mechanism and engineering decisions leading to the selection and implementation of the separation process. Typical engineering decisions include aspects that will enhance or maximize the process efficiency, such as mitigation decisions of CO₂ plasticization of membranes. The separation-process performance, which is dependent on selectivity behavior, could therefore be related to the SP that is used to quantify the performance of the entire separation process in terms of the feed-gas compositions (Seader and Henley 2006). In **Table 2**, typical inherent selectivity values are shown as applicable to the separation mechanisms of the most common separation technologies, especially for natural-gas-sweetening applications. The SP of each of the technologies is also given. The values show estimation of the inherent selectivity and SP required to produce typical pipeline-quality gas to less than 2% CO₂ from a natural-gas feed mixture of 5% CO₂ (Rufford et al. 2012, page 126). From the table, one can easily notice the higher inherent

Process	Separating Agent	Typical Inherent Equilibrium Selectivity ($\alpha_{\text{CO}_2\text{-CH}_4}$)	Typical Process SP ($SP_{\text{CO}_2\text{-CH}_4}$)
Membrane permeation – CO ₂ selective	Membrane	15–20	20–40
Adsorption—CO ₂ selective	Solid adsorbent	2.0–8.5	6.0–22
Amine absorption (MDEA)	Liquid absorbent	860	3,300
Physical solvent (Chilled CH ₄)	Liquid absorbent	318	1,900

MDEA = methylenedioxyethylamphetamine.

Table 2—The inherent equilibrium selectivity and SP for the separation of CO₂ from CH₄ (Rufford et al. 2012).

selectivity values with respect to CO₂-component separation in the process mechanisms of absorption by use of chemical-amine absorption and physical-solvent absorption as compared with the membrane-permeation and -adsorption processes. The higher SP values are also an indication that the absorption mechanisms are possibly better in separation of CO₂ gas from natural gas.

Given that considerations for inherent selectivity or SP alone are not enough to determine the appropriate separation technology for gas separation, other design steps are usually to be taken by the design engineer through good-engineering practice toward the selection of the optimum and most-economical separation process. In the case of natural-gas purification involving the removal of CO₂, other factors worthy of consideration include

- The assessment of the level of contaminants and impurities in the feed composition and requirement for removal level to meet end-use specifications.
- The feed-gas conditions, such as temperature, pressure, water content, and flow rate.
- The method of removal of other acid gases other than CO₂, such as H₂S present in the feed gas. This requires the engineer to decide on the choice of either the selective- or the simultaneous-removal method or the appropriate separation mechanism to achieve an optimum process.
- The method of disposal or market usage of the separated component(s). Typical instances could include finding a market for the captured CO₂ for additional revenue generation, reinjection of the CO₂ for EOR, and venting of N₂ to atmosphere or N₂ generation.

A detailed cost and performance analysis, which can ultimately lead to the determination of the best separation process under given conditions, can thereby be performed by use of the preceding selection factors.

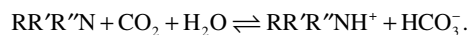
Absorption in a Liquid (or Solid) Sorbent

Absorption is referred to as “the transfer of a component of gas phase (CO₂, H₂S) into a liquid (or solid) phase in which it is soluble” (Kohl and Nielsen 1997, page 1). The process involves passing a gas mixture through a liquid (or solid) such that one or more components of the gas mixture are dissolved selectively to provide a solution with the liquid (or solid). The gas component (the solute), forming solution with the liquid or solid (the sorbent), is said to be absorbed by the sorbent. This absorption mechanism has been used in many commercial gas-separation processes worldwide, especially in oil and gas operations, and is generally carried out in conventional industrial pressure vessels known as contactors, where a mass transfer by direct contact and dispersion of one phase within another takes place (Dindore 2003, page 4). Depending on whether there is a chemical or physical reaction between the solute and the sorbent, absorption processes are basically available as chemical absorption and physical absorption, respectively.

The basic process in chemical absorption in CO₂ capture from natural gas involves the reaction of the CO₂ with the sorbent to form weakly bonded intermediate compounds. On application of heat, the CO₂ is released from the compound, thereby regenerating the sorbent. The chemical solvents are somewhat favored at lower partial pressures (60 to 100 psia) above which physical solvents are preferable (Freireich and Tennyson 1977).

Some of the common chemical-absorption processes for acid-gas treating (particularly CO₂ capture from natural gas) in the industry are as follows:

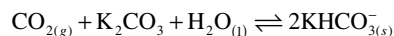
- Aqueous amine processes derived from ammonia (NH₃): For instance, a tertiary amine process, such as MDEA (Rufford et al. 2012, page 128)



In the preceding simplified reaction, the tertiary amine (sorbent) reacts exothermically with the CO₂ in the natural-gas

stream, usually at high pressure and low temperature, to form a carbamate-ion nitrogen/carbon bond, thereby capturing the CO₂ from the gas stream. The carbamate-ion bond is then broken down at a higher temperature and low pressure to endothermically strip the CO₂ in a regeneration process, while the lean amine solution is recycled back for another round of capture. The aqueous amine-based absorption can be achieved by use of primary, secondary, or tertiary amine solvents. Depending on the key requirement for CO₂ capture, tertiary amines have an advantage over secondary and primary amines by regeneration-energy and loading-capacity requirements, whereas the primary and secondary amines are preferred in terms of faster reaction rates with the acid gas (CO₂) (Rackley 2010, page 105).

- Hot-carbonate (alkali salt) systems: Use of hot solutions of potassium carbonate (K₂CO₃) or sodium carbonate (NaCO₃) to remove CO₂ from high-pressure gas streams (Rufford et al. 2012, page 130):



Similar to the amine-based process, the simplified reaction in the preceding gives the absorption of CO₂ in a lean hot-potassium-carbonate stream, usually occurring in a counter-flow arrangement between the hot alkali (sorbent) and the natural-gas stream. The rich alkali solution containing captured CO₂ is then regenerated and recycled back, with the entire process occurring at high temperatures.

- Aqueous ammonia-based absorption: Similar to the amine-based absorption, ammonia-based absorption involves the chemical reaction of ammonia and its derivatives with CO₂ to form a weak bond where CO₂ is removed on application of heat. Compared with the amine-based process, the aqueous ammonia process is shown to have lower energy requirements (Rufford et al. 2012, page 130), thereby lending it to possible significant energy efficiency improvement and lower costs (Rackley 2010, page 105).

Physical absorption involves the selective absorption or separation of CO₂ from the natural-gas stream, where the rate of absorption increases with increasing pressure and at low temperature. The physical-absorption process uses the principle of gas (solute) solubility in the sorbent such that the dissolved volume is proportional to the partial pressure at a given temperature without reacting chemically with the sorbent (Rackley 2010, page 109). Physical-absorption processes are generally favored at acid-gas (CO₂) partial pressures greater than 200 psia (14 bara) (Rufford et al. 2012, page 128). Other factors considered favorable include low concentration of HCs (C₆⁺) and requirement for selective and bulk capture of CO₂ in the gas mixture. The most common physical-absorption processes used in the industry include Selexol[®] (using the union carbide sorbent made of dimethyl ether of polyethylene glycol), Rectisol[®] (using chilled methanol sorbent), and fluor (based on propylene carbonate sorbent) processes.

In both the physical- and chemical-absorption processes, the amount of CO₂ gas to be captured, as well as the CO₂ loading capacity of the sorbent, determines the rate of circulation of the required sorbent; in addition to the energy required to regenerate the sorbent, these form the major cost factors in the absorption processes (Rufford et al. 2012, page 128). Despite the preceding constraints, the chemical-absorption processes with amine solutions, for instance, have been commonly used absorption processes for CO₂ capture and gas sweetening within the natural-gas industry. In comparison with the physical-absorption solvents, the chemical solvents generally have higher energy requirements for regeneration (because the heat of absorption is much higher) and higher acid-gas loading capacity at low/moderate CO₂ partial pressures (Olajire 2010, page 2610). Both physical- and chemical-absorption

processes are suitable process techniques for treating high-volume gas streams containing CO₂ and/or H₂S. However, when the acid-gas partial pressure is low (less than 200 psi), the physical-absorption processes are known to become economically uncompetitive (Kohl and Nielsen 1997, page 4).

The physical- and chemical-absorption processes are further characterized as follows:

- Physical solvents are particularly useful in capturing a higher percentage of CO₂ gas from the total gas stream with a very low heat input compared with the chemical-absorption process (amine or potassium carbonate sorbents), during which substantial heat input, which forms a major cost factor, is required for regeneration of the sorbent. The physical-absorption sorbents, which are nonreactive organic solvents, physically dissolve the acid gas (CO₂ or H₂S) and then strip through reducing the pressure without the application of heat (Kohl and Nielsen 1997, page 1188). The leading physical-absorption technologies used mostly to treat feed gas with very high CO₂ concentrations include Selexol and Rectisol processes (Burr and Lyddon 2008, page 12).
- Commercially available physical solvents have relatively low acid-gas-absorption (loading) capacities, requiring high circulation rates. These usually create room for massive absorption and solvent-regeneration vessels, thereby making physical-absorption technologies unsuitable for use in areas where space constraints exist, such as offshore locations (Rufford et al. 2012, page 130).
- Physical sorbents are known to have affinity for HCs in addition to higher concentrations of acid gas. Hence, their additional absorption capacity for HCs, which is higher than that of chemical sorbents (Shimekit and Mukhtar 2012, page 242), can impact their consideration for application in cases where the feed gas contains HC ends.
- Absorption-based processes, as argued by Shimekit and Mukhtar (2012, page 246), are further limited by corrosion issues in the “units” associated with the solvents, such as amines capable of causing erosion of the units when reacted with corrosion inhibitors. This is in addition to “environmental hazards” caused by the losses associated with the sorbent that occur during regeneration.

Adsorption

According to Kohl and Nielsen (1997, page 2), adsorption, as applied to natural-gas separation, involves the retention of selective components of the feed gas when in contact with a solid adsorbent that has the ability to retain (adsorb) the feed-gas component(s), called the adsorbate. The adsorbate (for instance, CO₂) is then released from the solid adsorbent by either reducing the partial pressure of the gas component or increasing the temperature. The adsorption mechanism for acid-gas removal is an established process technology used in the natural-gas industry to remove the undesirable components from natural gas, such as CO₂, water, mercury, and HCs.

The mechanism of separation in adsorption, which is principally based on physical adsorption, is achieved because the forces (Van der Waal and electrostatic forces) (Shimekit and Mukhtar 2012, page 247) holding the adsorbate on the adsorbent are weaker than the forces of chemical reaction between the adsorbate and adsorbent surface (Kohl and Nielsen 1997, page 2). The basic concepts involved in adsorption-process designs as applied to the removal of gas impurities in a feed stream are mainly the same. In some oil-and-gas-production companies, for instance, the adsorption mechanism that uses the molecular-sieves process (using solid desiccants) is used for the final removal of water (down to 0.1 ppmv) and CO₂ (down to 25 ppmv) from natural gas before its usage for natural-gas-liquid (NGL) production. When feed gas containing CH₄ (nonpolar), water (polar), and CO₂ (nonpolar, but linear) is passed through the molecular sieves, the CO₂ (because it is linear) and

water (which is strongly attracted) are adsorbed by the solid desiccants (a pack of aluminum silicates or zeolites), while the nonpolar components (CH₄) pass on. The dehydrator vessels are then regenerated by increasing the temperature and reducing the total and partial pressure of the system with a hot fuel gas that displaces the water and CO₂, thereby removing them from the system.

The most-common adsorption processes are based on the use of solid desiccants as the sorbents (or adsorbents), such as the molecular-sieve (zeolite), activated-bauxite, activated-alumina, and silica-gel processes. These commonly use any one or more basic cycles, such as the temperature-swing adsorption, which regenerates by use of temperature for regeneration, and pressure-swing adsorption, which regenerates by lowering the partial pressure of the adsorbate (Kohl and Nielsen 1997, pages 1025–1035). Among the solid-desiccants-based-adsorption processes, only the molecular-sieve (zeolite) process finds a wider application in the removal of other gas impurities (acid gas such as CO₂ and H₂S), other than the popular use of gas dehydration (water removal) (Kohl and Nielsen 1997, page 1071; Ebenezer 2005, page 18). However, the molecular-sieve process is characterized by higher regeneration temperatures (Kohl and Nielsen 1997, page 1030) and is suitable for the removal of small concentrations of acid gas from feeds usually containing no more than 2% acid gas, such as CO₂, “because the quantity of adsorbent required to capture greater volumes of CO₂ is large” (Rufford et al. 2012, page 137).

In summary, adsorption processes that use solid desiccant and that are regeneration based for gas purification can be argued to be characterized by requirement for high regeneration temperatures, high pressure drop through the unit, and high initial-investment capital cost. They, however, have inherent advantages for suitability for gas dehydration and acid-gas removal at the same time, have wider capabilities to accommodate fluctuations in feed-gas-flow properties, and are basically free from problems of mechanical degradation and corrosion of units.

Membrane Permeation

The membrane-permeation mechanism for gas-separation processes is new in comparison to some other similar processes, such as amine absorption, adsorption, and cryogenic distillation. Membrane-permeation technologies have been applied to remove acid gases such as CO₂ and H₂S from natural gas and in commercial quantities since the 1980s (Rufford et al. 2012, page 141; Scholes et al. 2012, page 16; Baker and Lokhandwala 2008, page 2). However, the membrane processes to remove CO₂ from natural gas (as compared with their use for removal of other gas components such as NGL, N₂, and H₂S) have been among the most commonly applied processes in industry since commercialization and are considered currently to be the only natural-gas-separation process (CO₂ capture) for which membrane processes are competitive with the conventional technologies, such as amine adsorption (Rufford et al. 2012, page 141). Membrane-permeation technology is a process that involves the use of a membrane (polymeric in nature) to separate gases passing through it by selective permeation of gas components through the polymer. Through the principle of solubility and diffusion, rather than operating as a filter, selective components of the feed gas, such as CO₂, H₂O, and/or H₂S, dissolve into the membrane material, thereby diffusing (or permeating) through it, and are collected from another side of the membrane (as the permeate) at a lower partial pressure, whereas the remaining gas from the feed (known as the residue) does not permeate through the membrane and leaves the membrane unit at a pressure nearly close to that of the feed gas. “Membranes can be fabricated either in a hollow-fiber or spiral-wound format” with three main types of membrane materials available commercially for CO₂ removal, including cellulose acetate, polyimides, and perfluoropolymers (Scholes et al. 2012, page 16).

Industry experience available for the application of membrane technologies as gas-separation techniques have shown them to be particularly advantageous in several ways other than the estab-

Vendor/Licensors	Membrane Material	Module Type	Natural-Gas Separation	Flow Rate (MMscf/D)
Separex™/UOP	Polymeric (cellulose acetate)	Spiral wound	CO ₂ (e.g., 6.5 to 2%)/CH ₄	Up to 680
LPG-Sep™ /MTR	Polymeric	Spiral wound	LPG, NGL / CH ₄	2–50
Z-Top/MTR	Polymeric (perfluoro)	Spiral wound	CO ₂ (< 2%)/CH ₄	1–300
nitroSep™/MTR	Polymeric	Spiral wound	N ₂ (≤ 4%)/CH ₄	0.4–100
PRISM®/APCI	Polymeric (polysulfone)	Hollow fiber	CO ₂ (e.g., 4.5 to 2%)/CH ₄	< 8
CO ₂ membrane/UBE	Polymeric (polyimide)	Hollow fiber	CO ₂ (e.g., 9.6% to < 2%) / CH ₄	14–100

LPG = liquid petroleum gas.

Table 3—Membrane-separation technologies for natural-gas treatment (Rufford et al. 2012, page 141).

lished processes already enumerated. Such advantages as lower capital and operating costs over the investment span of the plant are considered. They are mostly modular in design, and are suitable for skid mounting as compared with the popular amine absorption or molecular-sieves adsorption, where the plants are larger, leading to lower capital investment. Minimal energy for operation, absence of moving parts, and no requirement for solvent replacement all equal lower operating costs. The only major operating cost is that associated with membrane-material replacement, which is performed at approximately 3 to 5 years (Baker and Lokhandwala 2007, page 6), depending on the contaminant level and plasticization effect on the membrane material. Their modularity offers additional advantages of reduced weight and space-efficiency management, which make them particularly suitable for deployment in remote and offshore applications. They also offer design and operational flexibility such that a number of operations can be integrated into one system for gas-purification processes. This means that one system can be designed to remove multiple unwanted components such as water (dehydration), H₂S, CO₂, mercury, and HC ends from the feed gas by integration of operations such as the pretreatment packages.

Some of the major disadvantages known to be associated with the membrane-permeation mechanism include

- CO₂ plasticization phenomena, which necessitate the requirement for a clean feed, usually requiring the addition of pretreatment packages, thereby increasing complexity and cost
- Requirement to compress the low-pressure permeate (CO₂-rich gas) for usage leading to additional energy requirement
- Little economies of scale associated with large installations, which increases the average cost per unit module (Kohl and Nielsen 1997, page 1239)

Considering that the widest application of membrane-permeation mechanisms as gas-separation membranes is during the removal of CO₂ (and H₂S) from natural gas, some emphasis shall be placed in explaining the process technology in detail. Surveys of membrane-separation technologies that have been used in the natural-gas industry are presented in **Table 3**, showing the leading manufacturers and licensors of membrane technologies and their capabilities for separating CO₂ from natural gas (Rufford et al. 2012, page 141). Current installations have been shown to be capable of processing up to 680 MMscf/D for CO₂ inlet concentration ranging from 5 to 70%, while projects of up to 1,200 MMscf/D are currently being developed (Scholes et al. 2012, page 16).

Membrane-Separation Mechanism

Permeation theory, as applied to the membrane-separation mechanism, describes the transport of permeable gases through a membrane material by a solubility diffusion mechanism. By use of differences in permeability and inherent selectivity between the permeable and nonpermeable gases, the permeable gases (CO₂, H₂S, and/or H₂O) dissolving selectively into the surface of the membrane material and diffusing through the membrane layer are

separated from the other side as low-pressure permeate, leaving the nonpermeable (CH₄) at high pressure as residue gas. The solubility diffusion assumptions are summed up in the following equation, according to Fick's law (Baker and Lokhandwala 2007, page 3; Kohl and Nielsen 1997, page 1242):

$$j_i = \frac{D_i k_i \Delta P_i}{l}, \dots\dots\dots(1)$$

where $\Delta P_i = P_{io} - P_{ii}$ and is the partial pressure differential through the membrane; $D_i K_i$ is the membrane permeability measured in barrers, which is a measure of the membrane's ability to permeate gas; j_i is the volume (molar) flux (cm³-STP) of component i ; D_i is the diffusion coefficient; K_i is the gas sorption coefficient (cm³-STP of component i per cm³ of polymer per unit pressure), which is an indication of the number of molecules dissolved in the membrane material; l is the membrane thickness; P_{io} is the partial pressure of component i on the feed side; P_{ii} is the partial pressure of component i on the permeate side; and 1 barrer = 10⁻¹⁰ [cm³(STP)] (cm)/(cm²)(sec)(mmHg).

For a hollow-fiber-type membrane (hollow tubular), the molar volume of gas permeation, j_i , is given by (Kohl and Nielsen 1997, page 1242)

$$j_i = \frac{D_i k_i (2\pi L \Delta P_i)}{\ln\left(\frac{R_o}{R_i}\right)}, \dots\dots\dots(2)$$

where L is the length of the tube, R_o is the effective outer radius of the tube, and R_i is the effective inner radius of the tube.

The typical permeation rates by specific components of a feed gas through commercial membrane materials are given in **Table 4**. According to Kohl and Nielsen (1997), these rates vary with the gas properties and composition.

The membrane selectivity, a_{ij} , as given by the following equation (Baker and Lokhandwala 2007, page 3), gives a measure of the membrane's ability to separate two gases i and j on the basis of the ratio of their permeabilities.

$$a_{ij} = \frac{P_i}{P_j} = \frac{D_i K_i}{D_j K_j} = \left(\frac{D_i/D_j}{K_j/K_i}\right), \dots\dots\dots(3)$$

where a_{ij} is the selectivity or separation factor (SF) between components i and j ; D_i/D_j is the ratio of the diffusion (selectivity) coefficients of the two gases, indicating the relative motion of individual molecules of the two components; and K_j/K_i is the ratio of the sorption (selectivity) coefficients, indicating the relative concentration of components i and j in the membrane material.

Membrane	Permeation Rate (GPU)									
	CO ₂	CH ₄	O ₂	N ₂	H ₂	H ₂ O	H ₂ S	CO	C ₂ H ₆	He
Cellulose acetate	93	3.10	15.5	2.71	202	1550	155	4.65	1.55	232
Polysulfone	93	3.41	15.5	3.10	186	—	—	—	—	—
Polyamide	—	0.78	7.75	0.78	140	—	—	—	—	—
Dow product	1442	—	496	124	2108	—	—	—	—	—
PDMS	—	—	9362	4356	10060	—	—	—	—	—
Permea product	140	6.20	3565	6.2	341	—	—	—	—	—

GPU = gas-permeation unit.

PDMS = Poly(dimethylSiloxane).

Permeation rates (permeance) measured at room temperature and 7 bar.

Table 4—Permeation rates of gases through selected membrane materials (Kohl and Nielsen 1997, page 1243).

From Eqs. 1 through 3, it can be seen that the success of the solubility diffusion mechanism is dependent on the type of membrane material defined by the $\frac{D_i K_i}{l}$ coefficient and the process properties of the feed gas defined by the ΔP_i coefficient. Higher selectivity or SF of component i (such as CO₂) over component j (such as CH₄) translates to higher membrane performance. For instance, typical SF for CO₂/CH₄ ranges from 10 to 50 and is approximately 25 for cellulose acetate material (Kohl and Nielsen 1997, page 1244), which means that CO₂ will permeate selectively 25 times faster than CH₄ in a cellulose acetate material. Apart from the permeability and selectivity considered for the performance of the membrane-permeation process, other factors usually considered include “chemical, thermal and mechanical stability, fouling tendencies, working lifetime, production costs and modularity” (Rufford et al. 2012, page 142). Depending on the component to be separated from the natural-gas mixture, two categories of membrane polymer materials are preferred. The “glassy” polymer materials (such as cellulose acetate, polyimide, perfluoro-polymer) generally separate components by use of differences in size and are a preferred option for CO₂ separation from natural gas. The “rubbery” polymer material (such as ether-amide block copolymer) separates by use of differences in condensability. These materials are depicted in Fig. 1.

Design Considerations for Membranes

Development work has been carried out on a number of membrane-based gas-separation technologies with emphasis on materials, techniques of formation, and module designs of membranes, but the most-popular configurations that have been commercialized are the hollow-fiber and spiral-wound designs because of their high packing density (Rufford et al. 2012, page 141). Figs. 2 and 3 show hollow-fiber and spiral-wound configurations of membranes. Both configurations have been used to develop numerous membrane-module designs, and all are aimed at optimizing the features of gas-flow distribution, pressure drop, and membrane area per unit volume (of gas) (Kohl and Nielsen 1997, page 1249).

In selecting an optimum membrane system for gas purification, some of the key design factors usually considered by the engineer, in addition to higher permeability and selectivity of the component to be separated to ensure higher membrane performance as outlined in the preceding membrane-separation mechanism, include

- Thermal and chemical resistance of the membrane material capable of withstanding the required operating conditions of the feed gas
- Ability of the membrane material to withstand plasticization effects

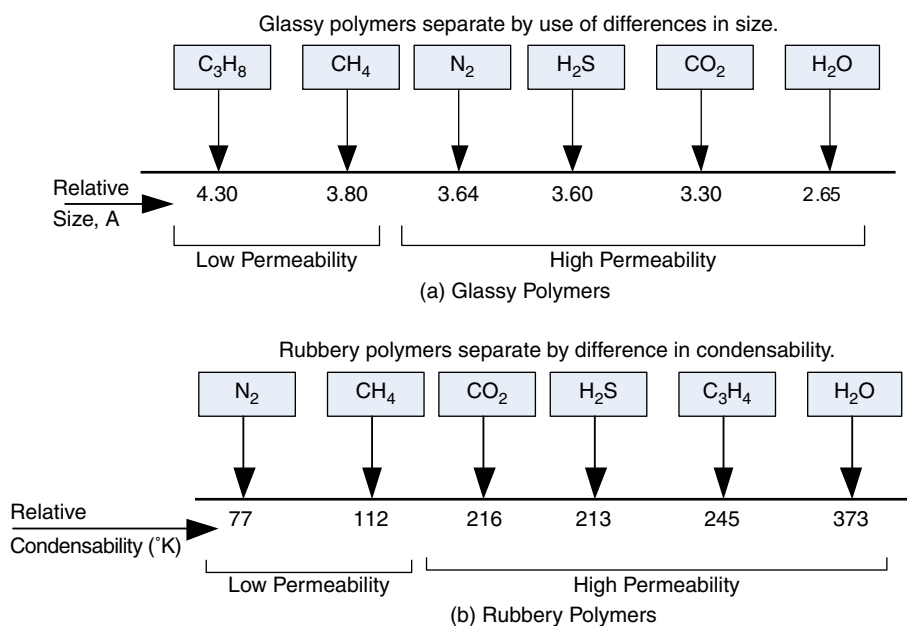
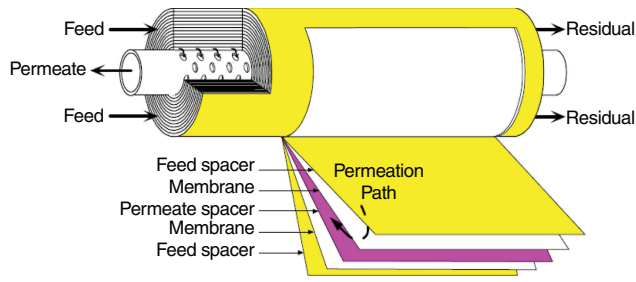


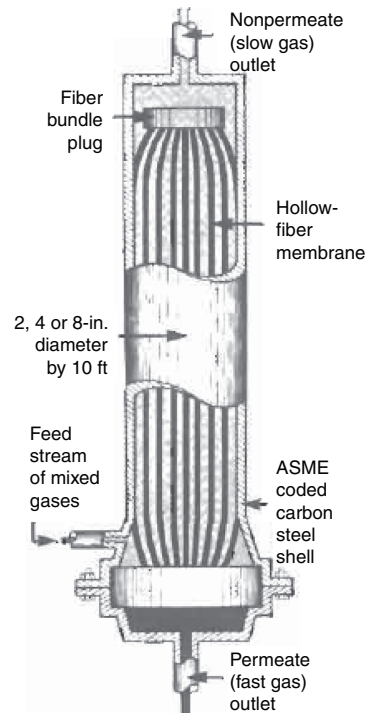
Fig. 1—Separation mechanisms of polymeric materials.



(a) Spiral-wound membrane permeation element (Koch et al. 2011, page 4).



(b) Cellulose acetate membrane plant, which uses the spiral-wound configuration for the removal of CO₂ from natural gas (Baker and Lokhandwala 2008, page 5).



(c) Hollow-fiber membrane-permeation element (Kohl and Nielsen 1997, page 1249).

Fig. 2—Membrane configurations that use the hollow-fiber and spiral-wound designs.

- Cost-effectiveness of the entire process technology, with special consideration given to ease of manufacture of the membrane modules (Brunetti et al. 2010, page 116)

The proper choice of design factors will enhance the durability of the membrane material and the performance, which otherwise could be affected by varying levels of condensable vapors and impurities present in the feed gas. Hence, the life of the membrane material, which according to Kohl and Nielsen (2007, page 1246) is typically between 3 and 7 years, forms a major design consideration in the design of the membrane system, especially with gas separation involving CO₂/CH₄.



Fig. 3—Cellulose acetate membrane plant that uses the spiral-wound configuration.

The presence of the varying levels of condensable vapors and impurities in the feed gas is shown to be capable of inducing plasticization on the membrane material (Ismail and Lorna 2003, page 38).

However, in the case of CO₂/CH₄ separation, the major cause of membrane plasticization, in addition to those causes mentioned in the preceding, is CO₂-induced plasticization, which may occur as a result of permeability increase of CO₂ because of increasing feed pressure above the plasticization pressure. Bos et al. (1999, page 67) defines the plasticization pressure as “the minimum pressure necessary to induce the permeability-increase” of CO₂ through the membrane. Plasticization of the membrane material reduces its selectivity and allows the permeation of CH₄ gas, thereby making the process less economical. However, studies reveal that rubbery polymers are less affected by membrane plasticization compared with glassy polymers (Baker and Lokhandwala 2007, page 6).

One key consideration is the incorporation of a pretreatment-process package into the membrane-permeation process to necessitate the removal of the varying levels of impurities and condensable vapors such as water, oil mist, HCs, and entrained liquids. Other considerations, as suggested by Baker and Lokhandwala (2007, page 6), include crosslinking the membrane material or using polymeric materials, such as nonstick-type perfluoro polymers known to be highly resistant to plasticization, as the selective layer of the membrane.

Phase Creation by Heat Transfer

The phase-creation process involves the condensation or cooling of the feed gas at a certain pressure range to allow phase change of the main separable components of the gas mixture. When applied for the separation of CO₂ from natural gas, it involves cooling the dry feed gas to temperatures sufficiently below 0°C to obtain CO₂ liquid and CH₄ gas, as desired. This is possible considering that, for a typical natural-gas mixture, main components with freezing points include CH₄ (−182°C), CO₂ (−78°C), H₂O (0°C), and N₂

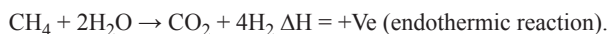
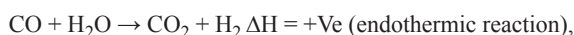
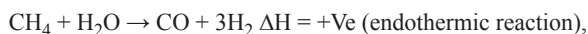
Molar flow (MMscf/D)	180
Feed pressure (barg)	95
Temperature (°C)	37.8
Hydrocarbon dewpoint (°C)	28
Water dewpoint (°C)	25.5
Molecular weight (g/g mol)	19.77
Constituents (%)	
N ₂	0.32
CO ₂	6.5
CH ₄	84.7
C ₂ H ₆	4.5
C ₃ H ₈	1.94
<i>i</i> -C ₄ H ₁₀	0.48
<i>n</i> -C ₄ H ₁₀	0.69
<i>i</i> -C ₅ H ₁₂	0.35
<i>n</i> -C ₅ H ₁₂	0.3
C ₆ H ₁₄	0.15
C ₇ H ₁₆ ⁺	0.07
Total (%)	100.0
Molecular weight C ₇ ⁺	97.57

Table 5—Feed-gas conditions and composition from a production separator unit.

(−196°C), which makes CO₂ to condense out as liquid and CH₄-rich vapor at a pressure and temperature of approximately 870 psig (60 barg) and 212K (−61°C). Rufford et al. (2012, page 125) reports the application of cryogenic distillation as a most commonly used phase-change method for the removal of N₂ from natural gas capable of recovering high-purity CH₄ and N₂. However, the process is particularly useful for cases of high CO₂ or N₂ concentrations in natural gas, and may be a key consideration for applications in remote and offshore locations because refrigerants or solvents will not be required, as is the case of absorption (amine) and adsorption processes that are capable of reducing plant size. A key disadvantage, however, is the considerable energy requirement for achieving cryogenic temperatures at the recommended pressures, which increases cost. There is also the possibility of equipment-channels blockage because of frozen or solid components.

Steam-Reformation Process of Natural Gas

The steam-reformation process of natural gas is one of the chemical-conversion processes of gas separation used to produce other products from natural gas such as methanol, ammonia, and CO₂. It is also a well-established technology used for the production of hydrogen from natural gas. The process is summarized by the following (Gaudernack and Lynam 1998, page 1087):



CO₂-Capture Recommendations for a Typical Gas-Production Plant

Some of the process technologies for CO₂ removal from process gas have been reviewed in the preceding, and a suitable technique for CO₂ capture from natural gas has been determined to be one that will exploit the differences in molecular properties or the thermodynamic and transport properties of CO₂ with respect to CH₄ in the

process gas. Given the gas compositional analysis performed for a typical gas-production facility, the major constituents of the gas mixture from a production separator are estimated as shown in **Table 5**.

From Table 5, one can see a relatively high flow rate of more than 170 MMscf/D of gas, a high pressure of 95 barg (1,378 psig), and a low concentration of HC ends (typically above C₆⁺). In comparing the suitability of the separation processes reviewed given these process conditions, the importance of inherent selectivity or SP as a major governing factor in the performance of the separating mechanism has been highlighted. It is noticed from Table 2 that absorption processes typically have higher inherent selectivities and SPs for CO₂ separation from natural gas as compared with others (such as membrane permeation and adsorption), which could possibly explain why amine absorption (for instance) has been a most commonly applied technique for acid-gas removal from process gas. However, absorption processes have major cost implications in the energy requirement for regeneration of the sorbent with respect to the amount of CO₂ to be removed and the CO₂ loading capacity of the sorbent (amine) in determining the rate of circulation of the sorbent. The adsorption processes, especially those that use solid dessicants and that are regeneration-based processes (for instance, the molecular sieves), are given to be characterized by higher regeneration temperatures and may be suitable for removal of a small concentration of acid gas of not more than 2% because the quantity of adsorbent (such as zeolites and activated carbon) required to remove greater volumes of acid gas is large (Rufford et al. 2012, page 137). However, in addition to their suitability to remove water (dehydration) and CO₂ (acid gas) simultaneously from process gas, they have also been shown to have the potential for energy and capital-investment savings when compared with the conventional absorption (amine) processes. With the foregoing, it can be inferred that for the adsorption-based separation process to be the preferred option for the separation of CO₂ from natural gas, there would be the need for a high partial pressure and low concentration (typically 2%) of CO₂. The membrane-permeation process has been reviewed and shown to have been an accepted natural-gas-treatment technology, especially for the removal of CO₂ from natural gas, with significant advantages compared with the other processes reviewed. It is given to be both economic for gas streams with high feed CO₂ concentration and high pressure as well as low concentrations of other acid gases, such as H₂S. This phenomenon correlates with studies by Scholes et al. (2012, page 21) and Baker and Lokhandwala (2007, page 5), as depicted in **Fig. 4**, indicating the relative comparison of membrane and amine (absorption) in their application suitability. It shows that the membrane process as more competitive in application at very low gas-flow rates (less than 50 MMscf/D).

Because of operational flexibility and ease of incorporation of new membrane developments, membrane systems now in place are capable of processing upwards of 250 MMscf/D of gas. Typical examples are the CO₂-removal systems in Qadirpur and Kadawari, both in Pakistan, which use membrane-permeation technology (Löwenstein 2012, page 10; UNFCCC/CCNUCC 2012).

The Kadawari system is a two-stage unit capable of treating 210 MMscf/D of feed gas at 90 barg with CO₂ content reduced from 12% to less than 3%. The Qadirpur, Pakistan, membrane system is designed to process up to 500 MMscf/D of natural gas at 59 barg from an initial 235 MMscf/D, with CO₂ content reduced from 6.5% to less than 2%. The permeate (CO₂-rich) gas is sold to Engro Power, operating a 220-MW gas-fired plant that uses the permeate gas for power production.

Given the characteristics of the gas-processing facility depicted in Table 5, the following can be affirmed:

- High flow rate of gas of approximately 200 MMscf/D of feed gas.
- Low concentration of CO₂ content, typically 6.5 mol%.
- High feed pressure of up to 103 barg (1,514 psig).
- Hydrocarbon dewpoint of approximately 35°C (95°F).

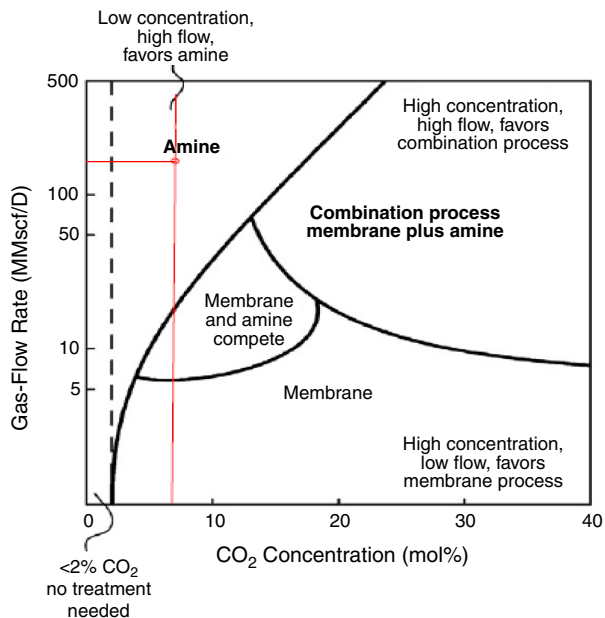


Fig. 4—Comparison of membrane and amine (absorption) processes for CO₂ removal from natural gas (Scholes et al. 2012).

- Use of the permeate (CO₂-rich) gas for additional generation of revenue and contribution to the CDM.
- The flow station is assumed to be located in a relatively remote location with respect to other gas-production facilities, where existing conventional techniques (amine absorption plant and molecular sieves) may have already been used for acid-gas treatment.

From the preceding characteristics, the use of the membrane-permeation process would be considered a more-economical option suitable for the processing of natural gas. Given the need to use permeate (CO₂-rich) gas and increase the profitability index of the investment, an absorption mechanism (commonly the amine process) would not be appropriate for the reasons already enumerated. Phase creation by heat transfer, especially the condensation

mechanism by use of cryogenic temperatures as previously outlined, would not be suitable considering the high energy requirement for achieving cryogenic temperatures. Phase creation is also shown to be a more-suitable method for removal of N₂ from natural gas (Rufford et al. 2012, page 125) compared with CO₂, as depicted in Fig. 1b, which shows the relative condensability temperatures of some natural-gas components. Though each of the acid-gas-removal processes has its own advantages (as already highlighted), the membrane-permeation process had, in recent years, enjoyed the popularity of being increasingly selected for newer projects involving removal of CO₂, especially for applications that had large flows in remote locations. Shown in Table 6 is a summary of characteristics for the main commercial CO₂-removal techniques, which further show the membrane-permeation process as a better-suited method for the removal of CO₂ for the particular case being analyzed. The membrane technique also offers an advantage for wide application in EOR, in which the captured CO₂ is reinjected into the oil well (CO₂ flooding) to enhance oil production for additional revenue generation. This principle (discussed briefly later in the paper) makes the membrane process well-suited for the usage of permeate (CO₂-rich) gas.

The reviewed membrane-permeation process indicated CO₂ plasticization of the membrane material as one of the major factors affecting performance, thereby requiring the addition of a pretreatment unit to facilitate the production of a clean gas feed. The gas-composition scenario discussed previously, for instance, has minimal amounts of HCs (C₆⁺) and little variation in the feed-gas content compared with well-data compositions and analysis, as shown in Table 7. The presence and concentration of HC ends and contaminants in the feed stream affect the performance and reliability of the membrane system and are instrumental in increasing the hydrocarbon dewpoint temperature of the feed-gas stream, which leads to a possible shift in the feed-gas envelope. The pretreatment of the feed gas for the membrane system shall therefore be considered a prerequisite to control of membrane plasticization and condensation of HC ends. The pretreatment configurations for the feed streams into the membrane system vary from minimum (or traditional) to enhanced (or regenerative) systems, with the amount of pretreatment dependent on the type of membrane used and the gas composition to be processed. For instance, a membrane system that uses cellulose acetate material has high sensitivity to water because of higher permeability (approximately 2.65 Armstrong compared with 3.30 Armstrong for CO₂, as depicted in Fig. 1a) and

	Chemical Absorption	Physical Absorption	Adsorption	Membranes Permeation
Process technology	Amines	Solvents	PSA on solid	Permeation
Commercial examples	aMDEA, econamine	Selexol, Rectisol	Molecular gate Xebec PSA	Separex, Z-Top
CO ₂ inlet concentration	≤ 70%	—	≤ 40%	≤ 90%
CO ₂ outlet concentration	≤ 2%	50 ppm possible	50 ppm possible	≤ 2% down to 1%
Simultaneous H ₂ S removal	Yes (depends on solvent)	Yes (most solvents)	Possible	Possible
Typical flow rate (MMscf/D)	Low to >350	100 to 400	≤ 2	Low to >350
Typical operating pressure (barg)	Absorber: 50 to 70	Absorber: 65 to 80	10 to 35	20 to 100
Typical operating temperature (°C)	Regenerator: 150 Absorber: 30 to 60	-73 to ambient	25	< 60 (materials limit)
H ₂ O saturation in outlet residue gas	H ₂ O saturated	Gas dehydrated	Gas dehydrated	Gas dehydrated
CO ₂ outlet pressure (barg)	≈ 0.13	< 5	< 5	< 5
Footprint (plant size)	High	High	Medium	Low
Energy requirements				
Comparative process costs (capital/operating)	High/medium	Medium/low	Medium/low	Medium/low (1-stage) Medium (2+ stages)

PSA = pressure-swing adsorption.

Table 6—Summary of characteristics for the main commercial CO₂-removal techniques (Rufford et al. 2012).

Sampling Point	Well 1	Well 2	Well 3	Well 4	Well 5	Separator Gas Outlet	Sour-Gas KO Drum	Off-Gas Stream	Gas to Pipeline
Sampling temperature (°C)	47.2	38.6	48.8	51.7	56.2	39.6	37.8	16	60.1
Sampling pressure (barg)	103	107	98	99	99.0	97	95	0.2	93
Flow rate (MMscf/D)	86.4	25.3	33.1	15.9	31.0	104.4	174.7	38	174.4
Parameters	Values (mol%)								
N ₂	0.24	0.37	0.45	0.21	0.29	0.29	0.32	0.36	0.28
CO ₂	7.01	4.12	10.16	5.85	4.98	6.07	6.5	28.65	1.055
H ₂ O	0.115	0.082	0.13	0.075	0.101	—	—	0.1671	0.002
C ₁	86.54	82.01	83.82	84.17	88.86	85.21	84.7	68.63	89.783
C ₂	3.98	7.8	3.51	6.14	3.71	4.53	4.5	1.843	5.58
C ₃	1.24	3.54	1.12	2.14	1.19	2.04	1.94	0.282	1.95
<i>i</i> -C ₄	0.28	0.61	0.24	0.49	0.25	0.46	0.48	0.028	0.39
<i>n</i> -C ₄	0.3	0.9	0.29	0.5	0.31	0.66	0.69	0.029	0.52
<i>i</i> -C ₅	0.163	0.27	0.12	0.22	0.13	0.29	0.35	0.0025	0.19
<i>n</i> -C ₅	0.09	0.21	0.09	0.13	0.1	0.25	0.3	0.0014	0.17
C ₆	0.01	0.06	0.04	0.05	0.04	0.13	0.15	0.002	0.05
C ₇ ⁺	0.03	0.03	0.03	0.03	0.04	0.07	0.07	0.005	0.03
Molecular weight (g/g mol)	19.37	20.3	20.14	19.84	18.75	19.9	19.77	18.65	19.29
Specific gravity (air = 1)	0.669	0.701	0.695	0.685	0.647	0.687	0.682	0.684	0.666
C ₇ (mol%)	0.03	0.03	0.03	0.03	0.04	0.07	0.07	—	0.03
Molecular weight C ₇	96.67	99.67	99.67	99.67	101.5	97.57	97.57	—	96.67
Water dewpoint (°F)	78.6	75.3	82.5	78.9	82.8	77.5	77.9	—	83.4
Hydrocarbon dewpoint (°F)	84.2	80.6	85.1	84.2	85.1	83.3	82.4	—	86

Table 7—Compositional analysis of the scenario case.

may require the introduction of dehydration and gas-drying pretreatment equipment.

The choice of a membrane system with similar characteristics is considered suitable in application to the CO₂-capture requirements of the scenario identified. The criteria for the suitability of the membrane-system type and configuration shall be based on the characteristics of the membrane material, module type, and flow arrangement.

A simplified process-flow configuration for a CO₂-removal system by use of the membrane-permeation technique is depicted in Figs. 5 and 6.

- Feed-gas coolers to cool the feed gas or maintain the inlet temperature at approximately 45°C to allow liquid condensate formation for efficient separation in the sour knock-out (KO) drum and coalescing filters
- Coalescing filters for removal of mist and liquid
- Nonregenerable adsorbent guard (carbon) bed filters for trace contaminants removal

- Particle filters for dust removal
- Preheaters to provide sufficient super heat to the gas

The preceding scheme is foreseen to be very adequate for light, stable-composition gases, but its main limitations are the nonregenerable nature of the adsorbent guard bed, which presents a risk when there is a sudden surge in HC content (C₇⁺) in the feed-gas stream than that initially estimated, which is capable of saturating the carbon bed in a lesser operating period, rendering it inefficient in performance, such that it can become functional only after replacement of the adsorbent.

Also, the gas preheater is the only equipment providing heating for effective control of the hydrocarbon dewpoint so as to provide protection for the membrane unit against hydrate formation and hydrocarbon-liquid dropout. Hence, malfunction of the heater system may require the entire membrane system to be taken offline, which can be avoided by sparing the heater system.

In the situation in which higher (or fluctuating) HC levels (C₇⁺) are expected, the enhanced pretreatment system can be used. The enhanced

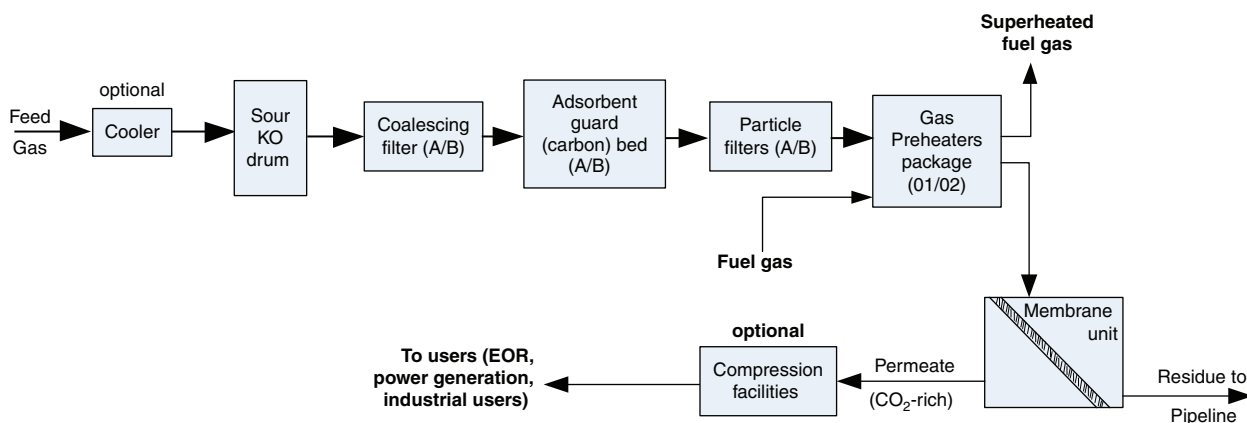


Fig. 5—Process-flow scheme of a CO₂-removal system that uses the membrane-permeation technique.

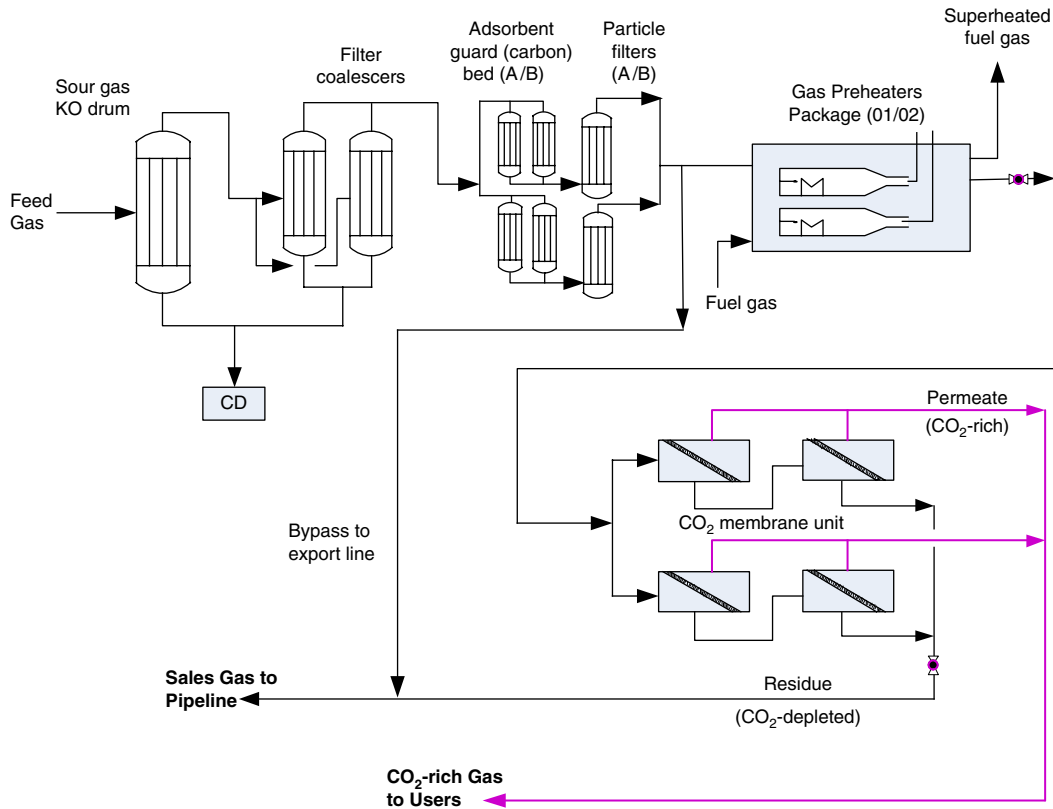


Fig. 6—Process-flow configuration of a CO₂-removal system by use of the membrane-permeation technique.

pretreatment by use of a regenerative system can be used to replace the nonregenerative adsorbent guard bed (although at a higher cost). The pretreatment system modification will be as illustrated in Fig. 7.

Cooling of the gas stream is first achieved in a feed-gas cooler (or a heat-recovery exchanger), and then passed through the KO drum and filter coalescers, which remove any condensates that may have formed. The regenerable adsorbent package receives the gas (free of liquid), where the HC ends and other contaminants are separated. The resultant gas passes through the particle filters and is heated in the preheaters package before being passed to the CO₂-removal membrane units. The regenerable adsorbent guard system is shown to have the additional benefit of being able to dehydrate

the gas of any water remaining in the feed alongside HCs and mercury that would normally be achieved by separate pieces of equipment, as well as being able to create room for heat recovery within the system.

Several studies have been conducted on membrane materials with respect to performances and suitability for separation of different gases. Among these, polymeric materials (which include rubbery or glassy polymers) have dominated industrial usage mostly because of the advantages they offer in terms of versatility and lower cost (Adewole et al. 2013, page 48; Zhang et al. 2013, page 84). A review of some of the polymeric materials and their performances is given in Table 8. From the table, the polyimide materials

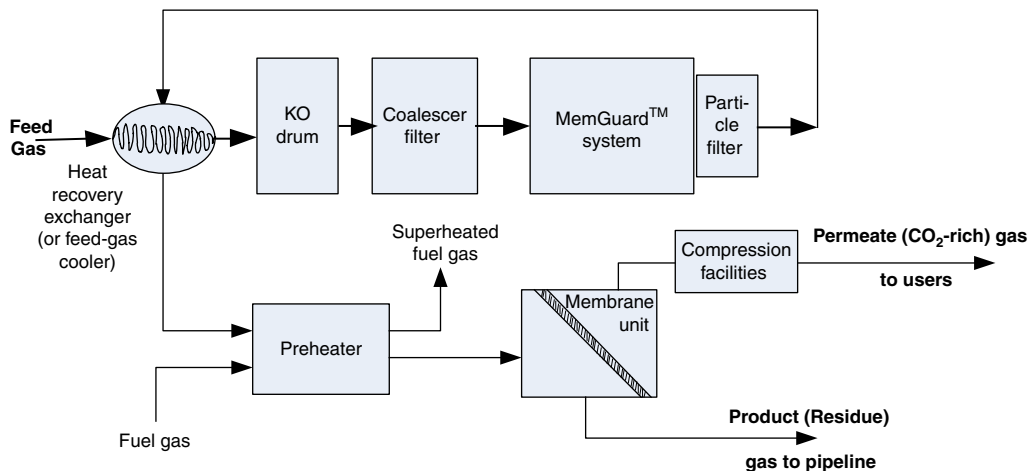


Fig. 7—Process-flow scheme of membrane-permeation system by use of the enhanced pretreatment system.

Membrane material	Cellulose acetate	Ethyl cellulose	Permasep (polyester)	Polyetherimide (fluorinated)	PDMS (silicone rubber)	Matrimid-5218	Polystyrene (PSF)	Polysulfone (PSF)
Membrane network	AN	AN	AN	DN	DN	DN	AN	AN
CO ₂ /CH ₄ selectivity ^(ref)	20 ⁽⁴⁾	—	—	33.5 ⁽³⁾	3.17 ⁽⁴⁾	34 ⁽⁶⁾	47.5 ⁽⁷⁾	33 ⁽⁵⁾
Reference	(3)	(1)	(2)	(3)	(1)	(6)	(1)	(5)

Permeation Rates of Gases Through the Polymer

	Barrers							GPU
CO ₂	2.3	47.5	0.31	45.8	2700	6.5	23.3	13.9
CH ₄	0.43	7.47	0.04	1.25	800	0.19	2.72	0.42
O ₂	—	11.2	—	11.5	500	—	7.47	—
N ₂	72.6	3.29	0.03	1.88	250	—	2.55	—
H ₂	20.1	49.2	1.65	—	550	—	56.0	—
H ₂ S	—	—	—	—	—	—	—	—
C ₂ H ₆	3.4	—	—	—	—	—	—	—
CO	—	—	0.03	—	—	—	—	—
He	—	35.7	—	—	300	—	40.8	—

PDMS = poly(dimethylsiloxane).

AN = asymmetric network.

DN = dense network.

GPU = gas-permeation units.

1 barrer = 1 GPU·cm.

1 GPU = 10⁻⁶ cm³ (STP)·(cm⁻²)·(sec⁻¹)·(cmHg⁻¹).

1 barrer = 10⁻⁶ cm³ (STP)·cm·(cm⁻²)·(sec⁻¹)·(cmHg⁻¹).

(1) Abdel-Aal et al. (2003)

(2) Hwang and Kammermeyer (1975)

(3) Luis et al. (2012)

(4) Zhang et al. (2013)

(5) Ismail and Lorna (2003)

(6) Scholes et al. (2012)

(7) Xu et al. (2001)

Table 8—Performance characteristics of some glassy-polymer materials in membrane systems for CO₂/CH₄ separation.

[for instance, polyetherimide (fluorinated) and Matrimid-5218], which are mostly used in the dense membrane network (such as hollow fiber), are shown to have better performance characteristics with respect to selectivity and permeability for CO₂/CH₄ separation compared with cellulose acetate. However, commercial application of polyimide in hollow-fiber CO₂-membrane systems (UBE Industries 2016; Ruffold et al. 2012, page 141) shows to have a limitation of feed-gas processing of not more than 100 MMscf/D. This is in contrast to commercial applications involving cellulose acetate in spiral-wound CO₂-membrane systems, as indicated in Table 3. The glassy polymers reviewed previously exhibit higher selectivities, but mostly lower permeabilities than the rubbery polymers (Adewole et al. 2013, page 48).

The versatility of the glassy polymers, especially polyimides and cellulose acetate, allows permeability and selectivity balance by management of plasticization effects, temperature control, and physical aging. Hence, commercial applications in natural-gas processing have had cellulose acetate and polyimide materials more widely selected for CO₂/CH₄ separation. There is, however, a competitive edge in membrane-application selection between cellulose acetate material and the polyimides (particularly those that are fluorinated) (Scholes et al. 2012, pages 16–19).

The Market Route to Captured CO₂

The use of CCS technologies dates back to the 1970s, when the attention and popularity paid to them was mainly for economic reasons, especially for EOR operations by oil and gas companies and not for concerns about the GHG effects and climate change.

One of the major concerns over the years about CCS (whether captured from the power plants flue gas or directly from oil and gas production) has been that the cost of capture is expensive and not economically feasible, but these concerns have gradually received abatements as other various concerns, such as the environment (GHG emissions and global warming) and gainful uses of CO₂ (EOR), come into play. These have been accelerated by intense research and development of CCS techniques and applications.

The capture (or removal) of CO₂ from natural gas, however, presents a more unique challenge compared with its capture from flare gas or other sources. While an operator of a power plant or an emitter of flare gas can choose to ignore the harmful effects of CO₂ when emitted to the atmosphere and adopt a do-nothing approach to its capture, especially if (for instance) the cost of capture is more than the environmental penalty (where it exists), the producer of natural gas may not easily do the same. This is because the presence of CO₂ (or H₂S) in the natural gas reduces the economic value of the product and is a potential threat to pipeline and other equipment conveying the natural gas with CO₂ content typically more than 2%. Therefore, for the producer of natural gas (with varying contents of CO₂ more than 2%), purification of the natural gas through removal of CO₂ and other impurities is seen as mandatory to meet pipeline specifications.

This selection process has significant capital and operating costs, which requires technical and commercial-feasibility studies to establish a selection process of the most appropriate treatment technique to implement. This is further influenced by the availability of disposal or usage routes for the removed contaminants, including reinjection of CO₂ for EOR.

In this study, three criteria shall be proposed. The aim is to ensure that an appropriate market route is developed for the captured CO₂ from a natural-gas production plant such that the gains/benefits of capture are further maximized instead of the captured CO₂ being flared, thereby contributing to emission of GHGs. The three criteria are accessibility, availability, and acceptability.

Accessibility

The aim of the accessibility criterion is to explore the opportunities within an oil-and-gas-producing company framework that will be required to make CO₂ accessible to the end user such that the cost is both affordable and sustainable. The sustainability index will be such that the eventual price of supplying (or making CO₂ accessible) is reflective of the full marginal costs of production and distribution. Such opportunities that can be explored include transportation and storage facilities.

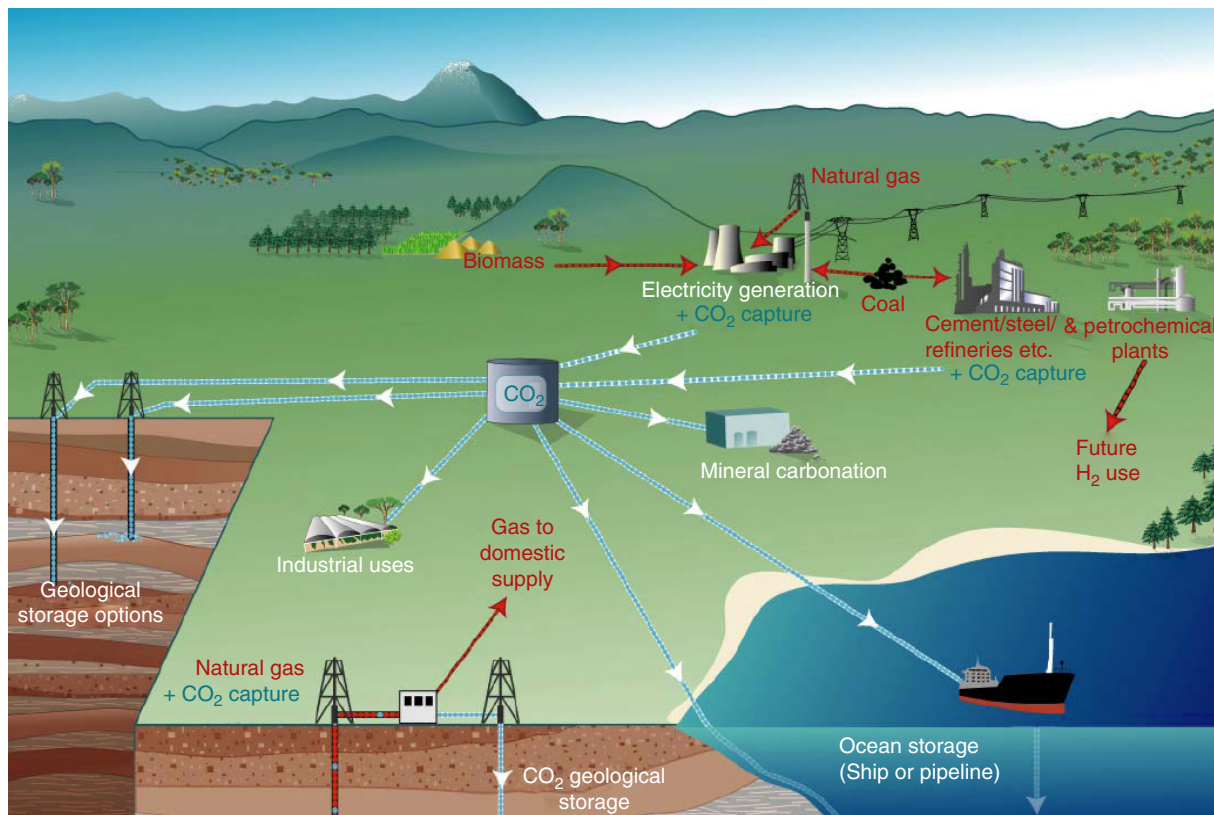


Fig. 8—CCU system (IPCC 2005).

CO₂ gas in its pure state has no color or odor and is nonflammable. Transportation of CO₂ can be achieved in a dense, solid, gas, or liquid phase with the dense-phase being the most-efficient state for transport. According to Doctor et al. (2005, page 184), pipeline transportation of CO₂ in a compressed dense phase is more cost-effective compared with low-pressure gas. Pipelines have been used effectively to transport large volumes of CO₂ for injection into depleted reservoirs for EOR (Global CCS Institute 2012, page 5; Cook 2012). Norway's Statoil has been transporting CO₂ (extracted from natural gas) through a 160-km pipeline for CO₂ injection into deep geological formations (Parliamentary Office of Science and Technology 2009, page 2).

Existing idle oil and gas pipeline networks may be used to transport CO₂. This is under consideration in the Niger Delta, requiring the addition of CO₂-compression facilities. Other alternative means of creating accessibility include the use of trucks to transport CO₂ to light users such as fertilizer-producing industries.

CO₂ captured from natural-gas feed by use of cellulose acetate membrane material is expected to be relatively pure compared with CO₂ captured from power-plant emissions, reducing compression and pipeline risks.

The accessibility criterion is therefore relevant in maximizing the economic gains through establishment of a transport framework, such as the construction of a (or use of an existing) pipeline network and/or storage facilities (such as CO₂-storage vessels) to service the localized CO₂ applications around the gas-production facility for which CO₂ is to be captured.

Availability

The availability criterion will seek to ensure that the produced CO₂ is made open and easily available to potential users. As already iden-

tified, the major users include the use of high-pressure CO₂ for EOR (which will be of significant value to oil and gas producers), powering gas-fired power plants for electricity and energy generation, and storage in geological formations (as a direct climate-change-mitigation method of usage). Other industrial uses for captured CO₂ include its use as a valuable industrial gas for chemical production (such as urea for fertilizer production, welding equipment, fire extinguishers, and several small-scale applications).

Captured CO₂ can also be used as a raw material in the production of some fuels such as gasoline, methanol, and carbon-based liquid. However, this method of usage does not provide the required CO₂ net emissions because fossil carbon still forms the root source of energy. For instance, hydrogen and CO₂ can be used as feedstocks for the production of methanol or gasoline fuel, which eventually results in CO₂ as a byproduct of emission.

Some of the major users shall be discussed briefly to access the availability index required to meet their needs.

The needs of most of the industrial processes are met through commercial production of CO₂ from other processes (such as anthropogenic sources). Other production sources, such as the fermentation of sugar, limekilns, and direct extraction from natural CO₂ wells, were discussed extensively in Mazzoti et al. (2005).

All the preceding are in addition to CO₂, which is also produced from the treatment of natural gas, as is widely discussed in this study. Fig. 8 illustrates some of the CO₂-capture sources and the major uses.

The ready availability of captured CO₂ combined with supply in an affordable and sustainable manner can ensure deliverability of CO₂ to potential users (such as industrial users) in comparison to deployment of separate CO₂-production equipment that could translate to more capital and operating costs for industrial consumers.

CO₂-storage (sequestration) in geological formations is one of the major users of captured CO₂, which can be greatly exploited

Location/Operator	CO ₂ Source	Size of CO ₂ Injected/Stored	Type of Storage
In-Salah, Algeria (operating since 2004)/BP	Gas processing (natural gas of approximately 5.5% CO ₂)	<ul style="list-style-type: none"> • 1.2 Mt/a • Injection cost is approximately USD 6/t CO₂ 	<ul style="list-style-type: none"> • A depleted gas reservoir located near the gas-processing plant (1.8 km depth) • No leakage has been reported so far
Barrow Island, Australia/Chevron-Exxonmobil-Shell-etc J.V.	Natural-gas processing (14% CO ₂)	3.3 Mt/a (start date of 2014)	Reinjection of the extracted CO ₂ from the CO ₂ -rich gas field into a sandstone reservoir (2.5 km) below Barrow Island
Abu Dhabi/Masdar and BP	Precombustion CO ₂ capture technology from a 400-MW power plant	0.8 Mt/a*	For EOR; CO ₂ feed stream from the steel plant to be compressed, dehydrated and pumped through 50 km of pipeline and injected in an onshore field for EOR
Alberta, Canada, near Zama City/PCOR, Apache Canada Ltd.	Gas processing (5–8% CO ₂ , 3–13% H ₂ S). Permeate output is 70% CO ₂ and 30% H ₂ S	0.067 Mt/a	For EOR in Zama Keg River oil field at 5 km depth

Mt/a = million tonnes per year.

*Start date of 2011 delayed because of issues with negotiating prices for the CO₂ and electricity produced at the H₂ plant

Table 9—CO₂-injection/-storage projects (MIT 2013).

as an economic and CO₂-mitigation option. This requires that captured CO₂ be readily available. Storage options for CO₂ use well-developed technologies that have been applied in the oil and gas industry and that have bright prospects for the future. A number of studies have discussed in depth the storage opportunities for captured CO₂, such as the Intergovernmental Panel on Climate Change (IPCC) special reports on CO₂. It has been proved to a larger extent that injection of CO₂ into deep geological formations at selected sites or wells is a long-term storage technique in which almost 99% or more of the injected CO₂ is retained for up to 1,000 years or more (Benson et al. 2005, page 197). Among the oil-recovery techniques used most by oil and gas companies, CO₂ miscible flooding is shown to be the fastest growing EOR technique, especially in the USA. With an average recovery factor estimated at 35% from CO₂ EOR (Jikich 2012, page 28), approximately 310,000 BOPD oil production, representing up to 5% of total USA oil, has been reported (Koottungal 2012, page 46).

Capture of CO₂ from natural gas for EOR is viewed as having the benefit of sequestering CO₂ in the oil-and-gas-producing formations, as well as being seen as a critical component of future GHG-management programs. In earnest, some of the major oil-and-gas-producing companies in Nigeria have applied oil-recovery techniques successfully for their wells, such as direct natural-gas reinjection and water reinjection. However, the availability of the captured CO₂ is expected to offer a better alternative to EOR in these companies, first as an economic resource and second as a contribution to climate-change-mitigation measures. A well-known example of a CO₂ EOR operation is found in the Sleipner field operated by Statoil in Norway, which captures CO₂ from natural gas (of approximately 9.5% CO₂) and injects approximately 1.0 million t of CO₂ annually through a 3-km-long well and stores it in a porous and permeable reservoir rock called the Utsira sand (British Geological Survey 2015). A survey of some other CO₂-injection/-storage projects, as published in the MIT map of projects (MIT 2013), is given in **Table 9**.

The recovered CO₂ is injected into the desired depleted reservoir, which pushes and displaces the water by introducing kinetic energy to the waterdrive, which in turn increases the bottomhole pressure thereby increasing the productivity index and mobility in oil or gas around the reservoir, with an increase in vertical sweep efficiency for the well flow. The final result is an increase in oil or gas production from the resultant well that has stopped flowing because of high water cut. This phenomenon is illustrated in **Fig. 9**.

For the industrial users of CO₂, it has been estimated that approximately 115 Mt/a of CO₂ is used in industries, with urea production (for fertilizers) accounting for more than 60% of that total (Mazzoti et al. 2005, page 33). This total industrial use, however,

forms approximately 0.5% of the total CO₂ emissions (put at 24 Gt/a of CO₂). Globally, use of captured CO₂ in industrial processes could only have a minimal effect on reduction of net CO₂ emissions. There exist urea-production industries in Nigeria that use great amounts of CO₂, such as Notore Chemical Industries Limited (formerly National Fertilizers Company of Nigeria, NAFCON), located at Onne near Port Harcourt Rivers State. Notore's production capacity has been estimated at 1000 t/d of ammonia and 1500 t/d of urea, with an estimated capability of producing up to 300 000 t/a of ammonia (NPK) and 500 000 t/a of urea (Notore 2012). According to the International Fertilizer Industry Association (IFA 2009), for every 1.0 tonne of urea produced, approximately 1.0 tonne of CO₂ is required for the production process. Urea is produced by the synthesis of ammonia through reaction of low-cost natural gas and CO₂ recovered from the off-gas of the ammonia-synthesizing process. For instance, in the scenario analyzed, feed gas of approximately 200 MMscf/D is capable of producing approximately 160 MMscf/D of residue gas and 38 MMscf/D of permeate (CO₂-rich gas). This is an equivalent of approximately 29 800 t/d of CO₂ (approximately 10.8 Mt/a of CO₂). Other fertilizer-production plants being planned in Nigeria include Dangote Petrochemical and Fertilizer Plant Olokola, Indorama Fertilizer Plant Eleme, Brass Fertilizer Company Brass, and Nagarjuna Fertilizer Plant Ogidigben (Eboh 2013). The existence of all these plants creates a potential sink for the captured CO₂ for which the technique is expected to produce the desired effect on climate change.

Acceptability

The aim of the acceptability criterion is to present the captured CO₂ as a clean, efficient, affordable, and reliable form of energy among the users and to place it in a comparative range with other clean-energy services, such as renewable-energy technologies. It will seek to promote its transfer to users. While it should be acknowledged that the technological process leading to capture of CO₂ from its source will always be more expensive than just emitting or venting to the atmosphere, its attractiveness among producers has increased considering the cost per tonne of CO₂ to be paid as a penalty in emission and the awareness of economic gains. However, current environmental regulations in Nigeria do not include a penalty cost for CO₂ emissions, but for gas flaring. While venting the captured CO₂ from natural-gas purification to the flare can be regarded as less expensive than additional investment in compression, storage, and/or transport to the end user, the CO₂-separation process is mandatory to achieve pipeline-gas specifications in which substantial investment has already been made. Therefore, the deployment of additional compression, transportation, and storage facilities could make it even more economical at a commercial level. Among the

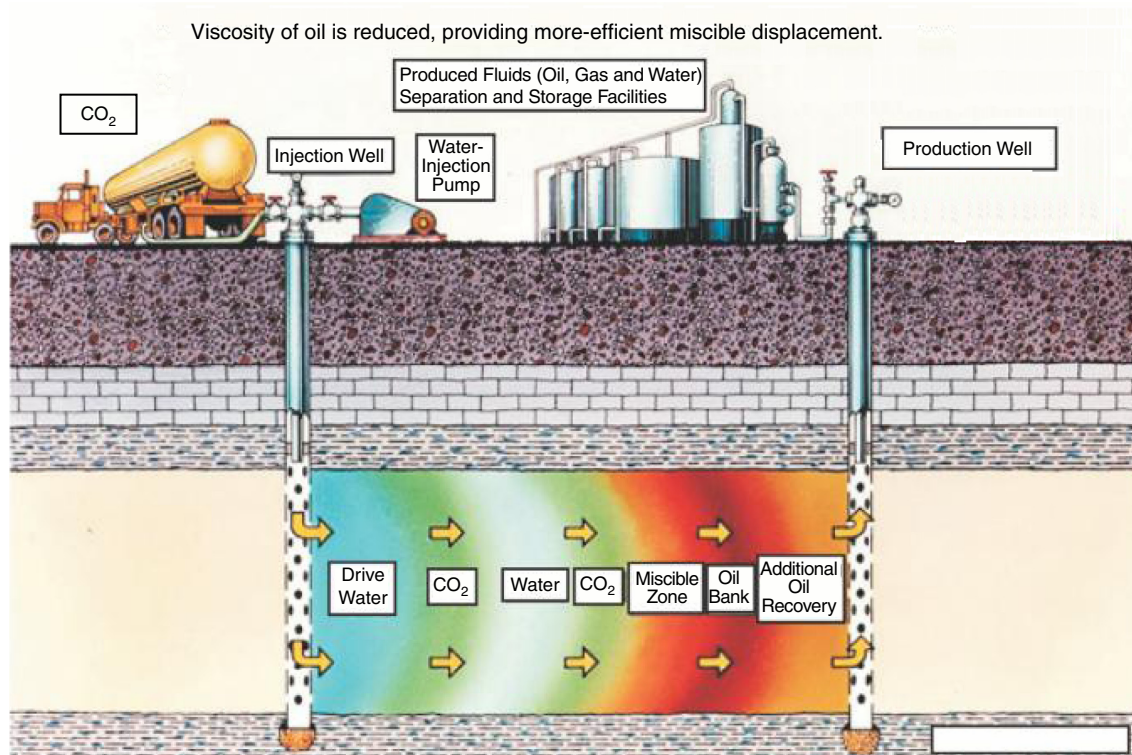


Fig. 9—CO₂-injection cycle for EOR (Ekmann 2011).

different CO₂-capture processes, capture from natural-gas processing has been shown to be the least expensive—from USD 5 and 25/t of CO₂ compared with USD 15 to 75/t of CO₂ captured from power plant or USD 25 to 115/t of CO₂ captured from other industrial sources (Thambimuthu et al. 2005). Estimated costs are shown in Table 10.

The acceptability criterion in the context of oil- and gas-production operations will therefore seek to make the comparative cost of captured CO₂ acceptable and affordable to its end usage. For instance, the use of captured CO₂ for EOR activities, as already discussed, is viewed as a very profitable business option of oil recovery compared with others, such as water or gas reinjection, or as a more-profitable option for a fertilizer company to purchase than to produce within its own industrial sources, as clearly depicted in Table 10.

Strengths, Weaknesses, Opportunities, and Threats (SWOT) Analysis. SWOT is a criterion used to structure and analyze the strengths, weaknesses, opportunities, and threats of a system. It shall be used in this study as a qualitative tool in the valuation of the CO₂ capture for environmental and economic gains objective. The strengths shall look into the durability and viability of implementation, the opportunities to unveil the chances and

favorable combination of circumstances to achieve successful implementation; the weaknesses to spotlight the flaws or weak points; and the threats to look into the menaces or sources of danger to implementation.

Strengths. The following are considered as strengths, but are not all-inclusive of the implementation of CO₂ capture, especially within Nigeria’s framework of emission mitigation and the gains within the confines of oil-and-gas-producing companies:

- Ability to produce natural gas to pipeline specifications.
- Commercializing the captured CO₂, instead of flaring directly, will result in a net reduction of carbon emissions, thereby increasing the sustainability index of the oil-and-gas-producing companies. This shall fulfill the investment by oil companies in strategic innovation in the enhancement of renewable energy and the development of innovative methods for environmental protection as part of the distinctive elements to a sustainable approach.
- Successful application of CO₂ capture in “CO₂ contented” natural-gas-production plants is capable of creating a competitive edge for oil and gas companies toward innovative solutions to CO₂-capture applications, which is fast becoming a global phenomenon on climate-change issues.

CCS Process	Cost Range
Capture from gas processing (or ammonia production)	USD 5–25/t of CO ₂ net captured
Capture from a power plant	USD 15–75/t of CO ₂ net captured
Capture from other industrial sources	USD 25–115/t of CO ₂ net captured
Transportation	USD 1–8/t of CO ₂ transported
Geological storage	USD 0.5–8/t of CO ₂ injected
Geological monitoring	USD 0.1–0.3/t of CO ₂ injected
Ocean storage	USD 50–30/t of CO ₂ injected
Mineral carbonation	USD 50–100/t of CO ₂ net mineralization

Table 10—CCS costs (IPCC 2005).

Natural-gas production (feed gas)	200 MMscf/D
Sales (residue) gas production	160 MMscf/D
Fraction of CO ₂ (6.5%) in feed gas at inlet of sour-gas KO drum (before capture)	13.0 MMscf/D (33 150 t/d of CO ₂)
Fraction of CO ₂ in residue gas (after capture)	1.688 MMscf/D (3344 t/d of CO ₂)
Captured CO ₂ (29% of off-gas)	11.3 MMscf/D (29 810 t/d of CO ₂)
CO ₂ savings (prevented from entry into atmosphere)	29 800 t/d of CO ₂ (10.8 Mt/a of CO ₂)

Table 11—CO₂ savings.

- The use of the existing legal framework/permit procedure in Nigeria for the transport of captured CO₂ to its users shall serve as a major strength.
- The transport of CO₂ gas is an established technology. This implies lesser considerations for fresh research in the field of CO₂ transport and leads to faster application.
- Efficient transport of large volumes of CO₂ in pipeline, ship, or truck, as well as storage of large volumes in a vessel as a result of high compressibility ratio and low density compared with similar gases such as natural gas.
- The use of CO₂ for EOR has the additional and added economic benefit of incremental oil production, which is capable of offsetting the costs of CO₂ capture, transport, and injection. Oil recovery is argued to be capable of being increased by as much as 10 to 15% through injection of captured CO₂ in EOR (IEA Greenhouse Gas R&D Programme 2001, page 14), as is already being implemented on a commercial scale in the USA, Canada, Turkey, and Trinidad and Tobago.
- The usage of existing data available from similar capture techniques, hydrocarbon surveys, and operation of field for CO₂ use in enhanced oil and gas recovery and abandoned hydrocarbon reservoirs.
- EOR is a well-known and established technology.
- CO₂ is not a poisonous or harmful gas.

Weaknesses. Some of the weaknesses of the CO₂ objective include

- High energy demand associated with the separation of CO₂ from natural gas through the tendency to achieve a higher purity of the CO₂ gas, usually leading to additional equipment, thereby increasing overall energy demand.
- Captured CO₂ can have other contaminant gases or impurities that are capable of affecting the CO₂ compressibility into volumes required for storage or transportation, thereby reducing capacities in which it can be stored or moved.
- Additional compression facilities are required to transport captured CO₂ through the pipeline to the intended destinations, which requires energy.
- Public acceptance and/or knowledge of CO₂ gas as a viable gas for alternative uses, such as fuel for power supply and even as an injection gas, is still very low.
- CO₂ gas is toxic to the cardiovascular system and upper respiratory tract at concentrations greater than 3%.

Opportunities. The following are some opportunities available to the CO₂-capture and -commercialization implementation:

- Use of existing transport infrastructure, such as flowlines to wells and pipelines that are no longer used optimally for transport and/or injection, capable of dramatically reducing the costs to a larger percentage and maximizing the economic gains.
- Use of existing pipeline routes and rights of way to make the permit procedure easier and faster.
- Improve the global industry image by creating opportunities for oil and gas companies to be seen and projected as “green.”
- No serious health and safety risks are associated with CO₂ processing—capture, storage, or transport. For instance, pipeline leakage of CO₂ and its products of degradation are not legally classified as toxic substances. CO₂ is nonhazardous on inhalation, is a nonirritant, and does not permeate the skin.

- Placement of CO₂-capture plants and storage sites (EOR) close to each other will positively affect the reduction in cost and environmental impact.
- Experience from similar CO₂-capture projects, such as in Eni Pakistan, Sleipner, and EOR operations, provides huge opportunities for faster implementation and deployment.
- New and growing market opportunities are available, especially in the areas of fertilizer production, agriculture (biomass), and automobiles (hydrogen economy).
- It will offer the Nigerian oil and gas industry flexibility in the way flare down targets are met, thereby contributing to meeting the climate-change targets of the CDM of which Nigeria is part.
- Presents a large opportunity for companies to play a direct role in reducing emissions by applying industry-specific knowledge and tools.
- CO₂ injection can replace the much-needed natural gas that is being injected for oil recovery in many of the Nigerian on-shore reservoirs.

Threats.

- There exists currently a very low public awareness, which requires education and outreach to all stakeholders.
- There is an absence of a regulatory framework (legal, permitting, licensing) for certain aspects of CO₂ capture, storage, and transportation.

CO₂ Savings and Contribution to CDM. As demonstrated in the subsection Acceptability, the use of the membrane process at the scenario presented is capable of producing approximately 38 MMscf/D of off-gas (CO₂-rich gas) on the basis of 160 MMscf/D of residue natural gas to be exported as sales gas. The compositional analysis of the scenario case is given in Table 7. Hence, the anticipated CO₂ savings and contribution to CDM through use of the membrane process is given in **Table 11**. By use of the AGA8-92DC detailed characterization equation for determining the mass density of natural gas, the mass density of the feed gas at the inlet of the sour-gas KO drum at an inlet temperature of 37.8°C and pressure of 95 barg is estimated to be 90.111 kg/m³.

Conclusion

From this case study, it can be inferred that the implementation of CCU is worth embarking on by oil- and gas-production companies in Nigeria. Given the high regard to sustainability issues, the implementation of CO₂-capture projects is viewed as having several gains and economic benefits. Some of these gains have been highlighted in the SWOT analysis and include company image, CO₂ EOR, industrial supply of CO₂, and emission control. If there is any topic in modern times that is much discussed and of concern to governments, analysts, professionals, and corporate planners, it is the issue of global warming, climate change, emission of GHGs, and the depletion of the ozone layer. This has led to evolving methods of transformation of the world economy from a hydrocarbon (fossil) based economy to one based on energy forms that are sustainable, such as the deployment of renewable-energy technologies and use of advanced clean technologies on conventional

energy sources. Even though dependency on fossils for provision of energy is expected to dominate the world economy for some time to come, the *World Energy Outlook 2007* (IEA 2007) outlined that only energy scenarios such as the use of clean-energy technologies can result in a 50 to 80% reduction in global CO₂ emissions up to 2050, and CCS has been identified as a major clean-energy technology that is specifically targeted at preventing CO₂ from reaching the atmosphere.

Some of the different techniques for CO₂ capture from natural gas were explored in the case study, of which the membrane technique was selected as the most-economical option for the case scenario as critically analyzed with other process techniques, including the absorption and adsorption processes. Given the operating parameters of the case study, the spiral-wound configuration, polymeric glassy material by use of cellulose acetate in a combined-series/parallel-flow-arrangement type of the membrane technique was considered more suitable to the needs of the gas-production facility. It is then expected that the realization of the CCU by operators with enormous CO₂-related emissions, especially natural gas produced with high CO₂ content, shall spur the undertaking and extension of the application of CCS to many of the power plants that are mostly gas-fired. The same techniques for capture of CO₂ from natural gas—namely, adsorption and membrane (Brunetti et al. 2010)—have been shown to also be applicable to CO₂ capture from flue gas with some slight modifications by use of the post-combustion capture method. CO₂ capture from the scenario case, for instance, is capable of yielding only approximately 29 800 t/d of CO₂ (10.8 Mt/a of CO₂) or approximately 0.045% CO₂ taken off the global emission scale. This, however, is small compared with the huge demand that shall be created in the CO₂ market by the main users alone, such as EOR and fertilizer production. This means that a vibrant and aggressive pursuance of the application of these clean-energy technologies for the lure of the economic gains and the much desired and expected mitigation measure of CO₂ emissions will create a sustainability path to the future of increased energy usage, especially from the fossil sources.

Nomenclature

- a_{ij} = selectivity or SF between components i and j
 D_i = diffusion coefficient
 D_i/D_j = ratio of the diffusion (selectivity) coefficients of the two gases, indicating the relative motion of individual molecules of the two components
 D_iK_i = membrane permeability measured in barrers, which is a measure of the membrane's ability to allow permeation by gas
 j_i = volume (molar) flux (cm³-STP) of component i
 K_i = gas sorption coefficient (cm³-STP of component i per cm³ of polymer per unit pressure), which is an indication of the number of molecules dissolved in the membrane material
 K_i/K_j = ratio of the sorption (selectivity) coefficients, indicating the relative concentration of components i and j in the membrane material
 l = membrane thickness
 L = length of the tube
 P_{ii} = partial pressure of component i on the permeate side
 P_{io} = partial pressure of component i on the feed side
 R_i = effective inner radius of the tube
 R_o = effective outer radius of the tube
 $\Delta P_i = P_{io} - P_{ii}$, partial-pressure differential through the membrane

Acknowledgments

We wish to thank the Nigerian Agip Oil Company (NAOC) for their permission to write this paper, and we acknowledge the various forms of support from our colleagues.

References

- Abdel-Aal, H. K., Aggour, M., and Fahim, M. A. 2003. *Petroleum and Gas Field Processing*. New York City: Marcel Dekker Inc.
- Adebowale, J. K., Ahmad, A. L., Ismail, S. et al. 2013. Current Challenges in Membrane Separation of CO₂ From Natural Gas: A Review. *International Journal of Greenhouse Gas Control* **17**: 46–65. <http://dx.doi.org/10.1016/j.ijggc.2013.04.012>.
- Baker, R. W. and Lokhandwala, K. 2008. Natural Gas Processing With Membranes: An Overview. *Ind. Eng. Chem. Res.* **47** (7): 2109–2121. <http://dx.doi.org/10.1021/ie071083w>.
- Benson, S., Cook, P., Anderson, J. et al. 2005. Underground Geological Storage. In *IPCC Special Report on Carbon Dioxide Capture and Storage*, prepared by Working Group III of the Intergovernmental Panel on Climate Change, eds. G. Borm, D. Hawkins, and A. Lee, Chapter 5, 195–276. New York City: Cambridge University Press.
- Bos, A., Pünt, I. G. M., Wessling, M. et al. 1999. CO₂-Induced Plasticization Phenomena in Glassy Polymers. *Journal of Membrane Science* **155** (1): 67–78. [http://dx.doi.org/10.1016/S0376-7388\(98\)00299-3](http://dx.doi.org/10.1016/S0376-7388(98)00299-3).
- British Geological Survey. 2015. CO₂ Storage – Sleipner Field beneath the North Sea. www.bgs.ac.uk/science/CO2/home.html (accessed 15 July 2013).
- Brunetti, A., Scura, F., Barbieri, G. et al. 2010. Membrane Technologies for CO₂ Separation. *Journal of Membrane Science* **359** (1–2): 115–125. <http://dx.doi.org/10.1016/j.memsci.2009.11.040>.
- Burr, B. and Lyddon, L. 2008. A Comparison of Physical Solvents for Acid Gas Removal. Technical Support Article, Bryan Research & Engineering, Inc, Bryan, Texas. <http://bre.com/portals/0/technicalarticles/A%20Comparison%20of%20Physical%20Solvents%20for%20Acid%20Gas%20Removal%20REVISED.pdf>.
- Cook, P. J. 2012. *Clean Energy, Climate and Carbon*. Victoria, Australia: CSIRO Publishing.
- Dindore, V. Y. 2003. *Gas Purification Using Membrane Gas Absorption Processes*. Doctorate thesis, University of Twente, The Netherlands.
- Doctor, R., Palmer, A., Coleman, D. et al. 2005. Transport of CO₂. In *IPCC Special Report on Carbon Dioxide Capture and Storage*, prepared by Working Group III of the Intergovernmental Panel on Climate Change, eds. R. Pichs-Madruga and S. Timashev, Chapter 4, 179–193. New York City: Cambridge University Press.
- Ebenezer, S. A. 2005. Optimization of Amine Base CO₂ Removal Process: Removal of Carbon Dioxide From Natural Gas for LNG Production. Semester Project Work, Institute of Petroleum Technology, Norwegian University of Science and Technology, Trondheim, Norway (December 2005).
- Eboh, M. 2013. Gas Flaring Reduced by 20% - FG. *Vanguard* (6 September 2013). <http://www.vanguardngr.com/2013/09/gas-flaring-reduced-by-20-fg/>.
- Ekman, J. 2011. Carbon Dioxide Capture, Utilization and Storage. Presented to the CCS Capacity Building Workshop, Carlestown, West Virginia, USA, 25 October.
- Freireich, E. and Tennyson, R. N. 1977. Increased Natural Gas Recovery From Physical Solvent Gas Treating Systems. In *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, Oklahoma, USA, March 7–9.
- Gaudernack, B. and Lynam, S. 1998. Hydrogen From Natural Gas Without Release of CO₂ to the Atmosphere. *International Journal of Hydrogen Energy* **23** (12): 1087–1093. [http://dx.doi.org/10.1016/S0360-3199\(98\)00004-4](http://dx.doi.org/10.1016/S0360-3199(98)00004-4).
- Global CCS Institute. 2012. Carbon Dioxide (CO₂) Distribution Infrastructure: The Opportunities and Challenges Confronting CO₂ Transport for the Purposes of Carbon Capture and Storage - An Observation Paper. Global CCS Institute, Canberra, Australia (August 2012).
- Hwang, S. and Kammermeyer, K. 1975. *Techniques of Chemistry, Volume VII: Membranes in Separations*. New York City: John Wiley and Sons.
- ICF International. 2006. Nigeria: Carbon Credit Development for Flare Reduction Projects. http://siteresources.worldbank.org/EXTGGFR/Resources/NigeriaGGFRGuidebook_ICF.pdf (June 2006).
- IEA Greenhouse Gas R&D Programme. 2001. Putting Carbon Back into the Ground. Technical Report, IEA Greenhouse Gas R&D Programme, Cheltenham, UK (February 2001).

- International Energy Agency (IEA). 2007. *World Energy Outlook 2007*. Paris: IEA.
- International Energy Agency (IEA). 2008. *Energy Technology Perspectives 2008, in support of the G8 Plan of Action: Scenarios & Strategies to 2050*, pages 47 and 69. Paris: IEA.
- International Energy Agency (IEA). 2010. *Energy Technology Perspectives 2010: Scenarios and Strategies to 2050*, page 51. Paris: IEA.
- International Energy Agency (IEA). 2012. *Key World Energy Statistics 2012*, page 10. Paris: IEA.
- International Fertilizer Industry Association (IFA). 2009. *Fertilizers, Climate Change and Enhancing Agricultural Productivity Sustainably*, pages 11, 28. Paris: IFA. <http://www.fertilizer.org/ItemDetail?iProductCode=9849Pd&Category=ENV&WebsiteKey=411e9724-4bda-422f-abfc-8152ed74f306> (23 March 2016).
- IPCC. 2005. Summary for Policymakers. In *IPCC Special Report on Carbon Dioxide Capture and Storage*, prepared by Working Group III of the Intergovernmental Panel on Climate Change, 1–6. New York City: Cambridge University Press.
- Ismail, A. F. and Lorna, W. 2003. Suppression of Plasticization in Polysulfone Membranes for Gas Separations by Heat-Treatment Technique. *Separation and Purification Technology* **30** (1): 37–46. [http://dx.doi.org/10.1016/S1383-5866\(02\)00097-7](http://dx.doi.org/10.1016/S1383-5866(02)00097-7).
- Jikich, S. 2012. CO₂ EOR: Nanotechnology for Mobility Control Studied. *J Pet Technol* **64** (7): 28–31. SPE-0712-0028-JPT. <http://dx.doi.org/10.2118/0712-0028-JPT>.
- Koch, D. R., Buchan, W. R., and Cnop, T. 2011. Proper Pretreatment Systems Reduce Membrane Replacement Element Costs and Improve Reliability. Technical Paper, Honeywell UOP, Antwerp, Belgium.
- Kohl, A. L. and Nielsen, R. B. 1997. *Gas Purification*, fifth edition. Houston: Gulf Publishing Company.
- Koottungal, L. 2012. 2012 Worldwide EOR Survey. *Oil and Gas Journal* **110** (4).
- Löwenstein, W. 2012. Evaluation of Selected DEG Energy Sector Projects in Asia. KfW DEG Summary Report, Institute of Development Research and Development Policy, Ruhr University Bochum, Germany (July 2012).
- Luis P., Van Gerven, T., and Van der Bruggen, B. 2012. Recent Developments in Membrane-Based Technologies for CO₂ Capture. *Progress in Energy and Combustion Science* **38** (3): 419–448. <http://dx.doi.org/10.1016/j.peccs.2012.01.004>.
- Mazzoti, M., Abanades, J. C., Allam, R. et al. 2005. Mineral Carbonation and Industrial Uses of Carbon Dioxide. In *IPCC Special Report on Carbon Dioxide Capture and Storage*, prepared by Working Group III of the Intergovernmental Panel on Climate Change, eds. B. Eliasson and R. T. M. Sutamihardja, Chapter 7, 319–337. New York City: Cambridge University Press.
- MIT. 2013. Carbon Dioxide Capture and Storage Projects. http://sequestration.mit.edu/tools/projects/map_projects.html (22 December 2015).
- Notore. 2012. Notore Set To Increase Fertiliser Production Through Joint Development With Mitsubishi Corporation. Editorial, Notore Chemicals Industries, Lagos, Nigeria (24 April 2012). <http://www.notore.com/index.php/article/read/42>.
- Olajire, A. A. 2010. CO₂ Capture and Separation Technologies for End-of-Pipe Applications—A Review. *Energy* **35** (6): 2610–2628. <http://dx.doi.org/10.1016/j.energy.2010.02.030>.
- Parliamentary Office of Science and Technology. 2009. CO₂ Capture, Transport and Storage. Postnote Number 335, Parliamentary Office of Science and Technology, London (June 2009) www.parliament.uk/documents/post/postpn335.pdf.
- Rackley, S. 2010. *Carbon Capture and Storage*. Burlington, Massachusetts: Butterworth-Heinemann.
- Rufford, T. E., Smart, S., Watson, G. C. Y. et al. 2012. The Removal of CO₂ and N₂ From Natural Gas: A Review of Conventional and Emerging Process Technologies. *Journal of Petroleum Science and Engineering* **94–95**: 123–154. <http://dx.doi.org/10.1016/j.petrol.2012.06.016>.
- Scholes, C. A., Kentish, S. E., and Stevens, G. W. 2008. Carbon Dioxide Separation Through Polymeric Membrane Systems for Flue Gas Applications. *Recent Patents on Chemical Engineering* **1** (1): 52–66.
- Scholes, C. A., Stevens, G. W., and Kentish, S. E. 2012. Membrane Gas Separation Applications in Natural Gas Processing. *Fuel* **96**: 15–28. <http://dx.doi.org/10.1016/j.fuel.2011.12.074>.
- Seader, J. D. and Henley, E. J. 2006. *Separation Process Principles*, second edition. Hoboken, New Jersey: John Wiley & Sons.
- Shimekit, B. and Mukhtar, H. 2012. Natural Gas Purification Technologies - Major Advances for CO₂ Separation and Future Directions, In *Advances in Natural Gas Technology*, ed. H. A. Al-Megren, Chapter 9, 235–270. InTech. <http://dx.doi.org/10.5772/38656>.
- Thambimuthu, K., Soltanieh, M., Abanades, J. C. et al. 2005. Capture of CO₂. In *IPCC Special Report on Carbon Dioxide Capture and Storage*, prepared by Working Group III of the Intergovernmental Panel on Climate Change, eds. Z. Abu-Ghararah and T. Yashima, Chapter 3, 105–178. New York City: Cambridge University Press.
- UBE Industries. 2016. Commercial Applications of Polyimides in Hollow Fibre CO₂ Separation Membrane. <https://www.ube.co.th/en/product-details.php?id=6> (accessed 23 March 2016).
- UNFCCC/CCNUCC. 2012. Project Design Document Form for CDM Project Activities (F-CDM-PDD), Version 04.1: Grid Connected Combined Cycle Power Plant Project in Qadirpur Utilizing Permeate Gas, Previously Flared. Regulatory Registration Form, UNFCCC/CCNUCC, Bonn, Germany (15 October 2012).
- Xu, Z.-K., Xiao, L., Wang, J. et al. 2001. Novel PMDA-ODA Polyimide/Polystyrene Nanocomposite Membranes for Carbon Dioxide Separation. In *Proc.*, National Conference on Carbon Sequestration, Washington, DC, p. 57.
- Zhang, Y., Sunarso, J., Liu, S. et al. 2013. Current Status and Development of Membranes for CO₂/CH₄ Separation: A Review. *International Journal of Greenhouse Gas Control* **12**: 84–107. <http://dx.doi.org/10.1016/j.ijggc.2012.10.009>.

Emmanuel O. Agiaye is a mechanical/piping engineer at NAOC. He has been with the company for more than 8 years, having previously worked for engineering companies in electric-power generation and in building construction for more than 3 years, with experience in upstream-facilities engineering, projects management, and project controls. Agiaye's current interests include facilities optimization, design strategy, asset evaluation, project execution, renewable-energy technologies, and CO₂-emissions reduction. He holds a BEng degree in mechanical engineering from the University of Benin, Nigeria, and an MSc degree in energy from Heriot-Watt University. Agiaye is a member of SPE, the Nigerian Society of Engineers, the Nigerian Institution of Mechanical Engineers, and the UK Institute of Mechanical Engineers. He is also a registered professional engineer of the Council for the Regulation of Engineering in Nigeria and an incorporated engineer in the UK.

Mohammed Othman is a senior completion, workover, and well-services supervisor with NAOC, where he has worked for more than 18 years. His research interest is in converting unwanted natural resources into proper usage for economic gain. Othman holds a BTech degree in industrial chemistry from the Abubakar Tafawa Balewa University, Nigeria. He is an SPE member, having served in different capacities as a board member and conference-committee chair, and having received numerous service awards from the SPE Nigerian Council. Othman is currently an adviser for the planning of the upcoming 2016 SPE Nigeria Annual International Conference and Exhibition in Lagos.