An overview of carbon capture technology
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CARBON CAPTURE FROM NATURAL GAS
Natural gas produced from gas and/or petroleum reservoirs could contain substantial amount of hydrogen sulfide and carbon dioxide, known as “acid gas.” The presence of small concentrations of H₂S (ppm levels) in natural gas results in a sour gas with a drastically-reduced market price and hampered wide utilization. Additionally, the presence of CO₂ in the natural gas could decrease its calorific value and increase its transportation cost. Therefore, natural gas desulfurization, or sweetening processes for treating natural gas, are an integral part of natural gas cleanup. After H₂S is captured chemically using a base solvent such as aqueous amines, the concentrated H₂S streams are sent to the Claus sulfur plants to produce elemental sulfur or can be used to produce sulfur oxides which are converted ultimately into sulfuric acid or used to produce gypsum [14].

The amines frequently used to capture H₂S for natural gas can also react and remove carbon dioxide. The carbon dioxide co-extracted in the desulfurization of natural gas can be emitted into the atmosphere after hydrogen sulfide is converted to sulfur or can be captured and sent to sequestration sites, depleted petroleum, and or/natural gas reservoirs or saline aquifers for disposal. The CO₂ captured from natural gas streams can also be used for enhanced oil recovery (EOR) to produce oil from petroleum reservoirs (see Fig. 1).

Figure 1. Geologic disposal options for acid gases. Source: Burruss and Brennan [2].

The CO₂ captured from natural gas is usually near atmospheric pressure and contains significant amounts of water so that its injection in a geologic formation requires multistage high-pressure compressors with intercooling. Based on the depth and conditions of the geologic formation, the injection is frequently carried out at about 150 bars. If the CO₂ to be sequestered still contains a small fraction of H₂S, this acid gas can be also injected in the geologic formation without major

Cite this article as: Palmer BR. An overview of carbon capture technology, Sustainable Technologies, Systems and Policies 2012 Carbon Capture and Storage Workshop:13
http://dx.doi.org/10.5339/stsp.2012.ccs.13
difficulties. The only problem would be that wet H₂S is highly corrosive to carbon steel so stainless steel facilities are required after the compression station. The compression plant is shown in Fig. 2.

![Figure 2. Compression of carbon dioxide for sequestration. Source: KBR.org 1 [10].](image)

The first industrial-scale carbon dioxide storage project was implemented at the Sleipner gas field in Norway. The produced natural gas contains about 9% CO₂. In this North Sea field, one million tons/year of liquefied carbon dioxide is injected into a saline aquifer in the Utsira sandstone formation as shown in Fig. 3. Injection depth is one kilometer. The sandstone formation has a storage capacity of about 600 billion tons of carbon dioxide. The project economics are very favorable, based on avoidance of the European carbon tax.

![Figure 3. Sequestration of carbon dioxide in the Utsira sandstone formation. Source: Energy-pedia.org [3].](image)

The Middle East has the potential to produce large amounts of acid gas as reservoirs of increasingly higher sulfur content must be tapped. This natural gas will be required to meet the considerable natural gas demands of the Middle East and the natural gas customers of this region. Acid–gas injection is being considered in the Middle East as a means to dispose of the tremendous amounts of CO₂ that will be produced in the future.

**CARBON CAPTURE FROM FLUE GAS (POST-COMBUSTION)**

The largest carbon dioxide source is combustion of coal for power generation. The flue gas produced from power generation facilities contains particulates and about 15% by volume carbon dioxide. A typical process for treating combustion products, including carbon dioxide removal, is shown in Fig. 4. The flue gas cleanup techniques involve (1) injection of ammonia followed by catalytic reaction to remove NOₓ (2) removal of particulates by electrostatic precipitation (3) removal of sulfur dioxide with calcium oxide, and (4) recovery of carbon dioxide capture by amine solvents.

The most common post-combustion carbon-capture process uses alkyl amines to chemically capture carbon dioxide from combustion gases [14]. Typical amines and concentrations for carbon dioxide removal are monoethanolamine (32%), diethanolamine (20–25%), methyl diethanolamine (30–55%) and diglycolamine (50%). In the capture process, the aqueous amine, which is a weak base, reacts with acidic CO₂, to form water-based aminated products. This is illustrated below for reaction with monoethanolamine [12,17]:

\[ 2RNH_2(aq) + CO_2(g) + H_2O(l) \rightarrow RNHCOO^-(aq) + RH^+_3(aq) \]  (1)
The aminated product is then stripped thermally to yield carbon dioxide at a high concentration and near atmospheric pressure.

Some gas streams contain both CO$_2$ and H$_2$S. This is the case in processing natural gas, for example. The sulfur-bearing H$_2$S is also acidic and is extracted by amines as indicated below,

\[
\text{RNH}_2(\text{aq}) + \text{H}_2\text{S}(\text{g}) \leftrightarrow \text{RNH}_3\text{HS}(\text{aq}).
\]

(2)

The amine extraction process is shown in more detail in Fig. 5. Extraction and stripping are operated counter currently. Extraction of hydrogen sulfide is equilibrium limited whereas carbon dioxide extraction is kinetically limited which could facilitate capturing each gas in different steps [16]. For sequestration by injection, carbon dioxide from the amine unit, which likely contains some hydrogen sulfide, is compressed as described above.

In 1976, Kerr-McGee Chemical (now North American Chemical) built an MEA amine unit for carbon dioxide capture at an electric generation utility at the Searles Valley, California, chemical plant. The plant ran for several decades, and the technology was licensed to the Shady Point Power Plant in Oklahoma in 1991 [1].
While acid–gas treatment and carbon dioxide capture with amines are similar, there are substantial differences in the two processes. The pressures in the extractors are substantially different. Desulfurization pressures in the range of 20–60 bars are typical \[4,16\]. Conversely, carbon dioxide capture from combustion gases operates near atmospheric pressure. Additionally the volume of gas from combustion processes is substantially greater than the amount of natural gas processed in amine units, and accordingly the equipment for combustion processing is substantially larger than the equipment required for natural gas processing.

**CARBON CAPTURE FROM FUEL GAS (PRE-COMBUSTION)**

These processes involve integrated gasification combined cycle (IGCC). In this process, coal is gasified in gasifiers under controlled conditions using steam and oxygen (or air) to produce raw synthesis gas (syngas) which consists mainly of (CO and H\(_2\)). The processes are advantageous to flue gas capture because the CO\(_2\) concentration is much greater and the pressure is elevated above atmospheric, greatly facilitating CO\(_2\) removal \[9\].

In IGCC, initially the raw syngas is cleaned from particulates and sulfur containing-compounds (H\(_2\)S, SO\(_x\)) and then is subjected to a water-gas-shift (WGS) reaction where CO reacts with water in the presence of catalysts in two stages in order to increase the hydrogen content of the syngas. Unfortunately, for every mole of H\(_2\) produced one mole of CO\(_2\) is produced in the WGS reaction as shown below:

\[
\text{CO}(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}_2(g) + \text{H}_2(g) \tag{3}
\]

At high temperatures, 350°C, iron oxide promoted with chromium oxide iron oxide promoted with chromium oxide is employed. As the temperature drops to 190–210°C, copper supported by a mixture of zinc oxide and aluminum oxide is employed \[18\].

Conventionally, acid gas is removed from the shifted syngas after cooling it to near ambient or sub-ambient temperature. This technology is well established. Korens et al. \[11\] lists 44 commercial-scale gasification units. A number of acid–gas treatment options are employed as described below.

Methyl diethanolamine (MDEA) has been used for the removal of acid gases from syngas for decades. It is still a strong contender as an acid–gas removal option because it is effective and there is a wide range of experience in application of this extractant. Additionally, it has been formulated with proprietary additives to increase sulfur selectivity over carbon dioxide.

The Selexol process employs a physical solvent for removal of acid gases. Selexol comprises mixed dimethylethers of polyetheleneglycol as the physical solvent and is a competitor to MDEA. Selexol removes hydrogen sulfide preferentially to carbon dioxide so these gases can be separated, if required. However, this may not be necessary for sequestration as acid gas can be injected directly. The Selexol solvent is stripped with steam or with inert gases to remove hydrogen sulfide and carbon dioxide.

One advantage of Selexol is that, since acid–gas extraction does not employ chemical reactions, the energy consumption is typically lower than the energy demand for amine processing. Accordingly, the Selexol process is a solid contender for IGCC carbon dioxide capture and sequestration. If desired two-stage removal of acid gas can be carried out, hydrogen sulfide is removed first followed by carbon dioxide. High concentration gases are produced in stripping, reducing subsequent sequestration costs. Reduction in the solvent temperature increases removal of hydrogen sulfide and carbon dioxide in Selexol acid–gas processing.

The Rectisol process employs refrigerated methanol as the physical solvent. This process is employed for production of high-purity syngas for chemical synthesis. Rectisol is considered to be the most costly process for treating acid gas. Accordingly, the Rectisol process probably is of limited application in carbon capture from power plants.

More recently use of fluorinated solvents has been examined because of the high solubility of CO\(_2\) in these solvents \[13,6\]. Additionally these solvents dissolve CO\(_2\) preferentially to N\(_2\), H\(_2\), CO and CH\(_4\). The use of an ionic liquid, a quaternary ammonium polyether, was also investigated for capture of CO\(_2\) \[7,8\]. This work paves the way for cleanup of syngas under warm conditions, allowing elimination of refrigeration in the sorption process.
Production of carbonyl sulfide, COS, can pose a problem in both IGCC and Claus sulfur recovery units, because this species does not react with amine solvents. Carbonyl sulfide removal can be effected by hydrolysis; the reaction is as follows:

$$\text{COS}_{(g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{CO}_{(g)} + \text{H}_2\text{S}_{(g)}.$$ 

This reaction is facilitated with an activated alumina-based catalyst and is normally designed to operate at 175 to 200°C. Hydrolysis thermodynamics become more favorable as the temperature is reduced so the operating temperature is a balance between the kinetic and thermodynamic considerations. Typically, the hydrolysis product gas is cooled using the sensible heat to generate steam before the acid gas removal stage(s) [5].

Most IGCC units use carbonyl sulfide hydrolysis prior to acid–gas removal. One exception is the Rectisol process. Carbonyl sulfide hydrolysis is required to obtain sufficient total sulfur removal when the MDEA and Selexol processes are employed. Conversely, very high extractions of hydrogen sulfide and carbonyl sulfide are possible with the Rectisol process.

The IGCC units employing oxygen as the oxidant is particularly suitable for nearly total carbon dioxide removal from the syngas for carbon dioxide sequestration. This application employs a carbon monoxide shift reactor followed by acid–gas absorption. In this instance, hydrogen sulfide can be removed in one acid–gas removal process (absorber and stripper), and carbon dioxide is removed in the subsequent acid gas removal step (absorber and stripper). The WGS may be carried out prior to acid–gas absorption with a catalyst that can tolerate sulfur. This process is illustrated in Fig. 6.

![Figure 6. Flow diagram of Selexol process for acid gas Removal from coal-derived synthesis gas. Source: Korens et al. [11].](image)

**CARBON CAPTURE FROM OXY-FUEL COMBUSTION**

This process involves combustion of coal in oxygen. The products of combustion are water and carbon dioxide. Early work by Argonne National laboratory is reported by Kumar et al. [20]. The adiabatic flame temperature in oxy-fuel combustion is very high so that the flame temperature is moderated by dilution of oxygen with the carbon dioxide produced in combustion. Carbon dioxide is cooled before utilization as the diluent. Water is removed from the gases produced in combustion by condensation, and the resulting carbon dioxide is nearly pure. This technique has a number of attributes; the product is nearly pure carbon dioxide which minimizes sequestration costs. Additionally it is possible that this process might be employed in existing power plants. The attributes are moderated by the high cost of producing high-purity oxygen [19].

One of the first demonstration plants is Callide-A Oxyfuel, which is a joint venture of several firms from Australia and Japan. The first phase is a 30 MW demonstration. The second phase will produce 150,000 tonnes/year of CO₂ for about four years. The injection of CO₂ into the Northern Denison Trough and sites in southeast Queensland also will be examined [15]. There is little experience in application of this technique so it is likely that the development costs will be substantial and the risk in building the first plants will be high.
ACKNOWLEDGEMENT
The author wishes to acknowledge the assistance of Professor Badie I. Morsi, Department of Chemical Engineering, University of Pittsburgh, in preparation of this manuscript.

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