Plains CO_2 Reduction (PCOR) Partnership
Practical, Environmentally Sound CO_2 Sequestration

CARBON SEPARATION AND CAPTURE

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EXECUTIVE SUMMARY

This report provides a qualitative summary of a large number of existing and emerging processes that could be used to separate CO_2 from combustion gases for the purpose of controlling carbon emissions. The largest sources of concern are fossil-fuel-fired electric generating plants. Cited studies comparing the application of commercial gas separation processes to these plants indicate very high cost and performance penalties for existing pulverized-coal (pc)-fired plants. Natural gas-fired combined-cycle plants are also severely impacted because of the sensitivity to reduced efficiency associated with high fuel cost. Much lower cost and performance penalties are indicated for coal-fired integrated gasification combined-cycle (IGCC) plants, where CO_2 capture can be integrated into the design. The time line for adoption of CO_2 capture depends critically on policy incentives to address the economic and technical risks. Coal-fired IGCC plants with provision for sequestration-ready CO_2 separation are on the near horizon to supply the growing CO_2 demand for enhanced oil recovery (EOR). Applications for new or existing pc-fired plants will require substantial improvements in technologies under development or very large policy incentives. The assessment presented in this report provides a snapshot of the rapidly changing developments that are in progress.

The separation of CO_2 from other species in mixed-gas streams has been practiced on the commercial scale for over 50 years. Most of these applications have been for natural gas sweetening operations, purification of reformer synthesis gas (syngas) to produce H_2 in refinery operations, and for ammonia production. High-purity sources of CO_2 are used in the food industry and as a consumable refrigerant. The largest use of CO_2 is for EOR. The growing interest in reducing CO_2 emissions, the emerging carbon trading markets, and the increasing demand for CO_2 for EOR all underscore the need for improved CO_2 capture technologies.

Commercial and still-developing concepts for CO_2 capture and separation can be grouped into five categories: absorption, cryogenic cooling, gas separation membranes, gas absorption membranes, and adsorption. These technologies can be applied to three broad categories of fuel-to-heat/power processes, including postcombustion (stack gas cleaning), precombustion (e.g., gasification or reforming), and oxygen combustion (in some CO_2 sequestration literature, this process is called oxyfuel combustion). Using oxygen rather than air for combustion eliminates the large quantity of N_2 diluent. Although most of the

development efforts in CO_2 capture have focused on power production, capture and separation processes would be applicable to industrial boilers and turbines, process heaters, kilns, cupolas, and other sources. The leading importance of power generation is clearly indicated by the distribution of sources shown in Tables ES-1 and ES-2.

The near-term options for separating CO_2 use either amine scrubbing solutions for postcombustion flue gas capture or physical solvents such as Selexol for precombustion IGCC systems. Oxygen combustion is under development at the pilot scale. All current commercial approaches to CO_2 capture result in significant energy and cost penalties. The energy penalty for a pc-fired power plant can approach 30% because of the large parasitic steam loads.

Gasification combined-cycle systems provide inherent efficiency and cost advantages to CO_2 capture through higher operating pressure and CO_2 concentrations. Some studies indicate that oxygen combustion may also be cost-effective. Performance and cost of CO_2 capture from lignite-fired power plants, cement production, and petroleum refining were estimated using the PCOR Partnership's spreadsheet estimation tool. The costs ranged from \$22/ton CO_2 for a coal-fired power plant retrofitted with an

Table ES-1. Top Six CO_2 Emission Sources*

Fossil Fuel Combustion	6185.1
Iron and Steel Production	60.0
Cement Manufacturing	47.3
Waste Combustion	20.7
Ammonia/Urea Production	19.5
Lime Manufacturing	13.6
Total CO_2	6374.0

* U.S. 2002 CO_2 emissions, million tons of CO_2 equivalent (from EPA data [2004]).

Table ES-2. Subsets of Fossil Fuel Combustion*

Electricity Generation	2469.3
Transportation	1944.9
Industrial	1053.6
Residential	411.3
Commercial	254.9
U.S. Territories	51.3

* U.S. 2002 CO_2 emissions, million tons of CO_2 equivalent (from EPA data [2004]).

amine scrubber to $51/ton for a petroleum refinery. While these estimates are substantially higher than the U.S. Department of Energy (DOE) goal of $10/ton, costs will drop as technologies improve and industry recognizes the potential for profit from the use of CO_2 in enhanced resource recovery operations.

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INTRODUCTION

As one of seven Regional Carbon Sequestration Partnerships (RCSPs), the Plains CO_2 Reduction (PCOR) Partnership is working to identify cost-effective CO_2 sequestration systems for the PCOR Partnership region and, in future efforts, to facilitate and manage the demonstration and deployment of these technologies. In Phase I of the project, the PCOR Partnership is characterizing the technical issues, enhancing the public's understanding of CO_2 sequestration, identifying the most promising opportunities for sequestration in the region, and developing an action plan for the demonstration of regional CO_2 sequestration opportunities.

This report describes technologies used to capture CO_2 from flue gas and process gas streams produced during the course of fuel combustion. Although typically pursued in the context of utility power generation, these technologies would also apply to industrial and municipal heat/power, process heaters, kilns, cupolas, and other sources. Information is also presented on new combustion processes and power cycles that facilitate more effective CO_2 capture. Limited public data are presented on the cost and performance of commercially offered power generation systems incorporating CO_2 separation and capture.

While each existing or future CO_2 source in the PCOR Partnership region will have many site- and process-specific performance criteria and cost issues, the objective of this report is to provide general information that can be used for early screening and decision making or modeling to examine "what if" issues. Site- and technology-specific decisions will require additional evaluation in later phases of the work.

CO_2 SEPARATION AND REMOVAL PROCESSES

Gas Absorption

Gas absorption processes are commonly used in commercial plants to remove CO_2 from mixed-gas streams over a wide range of pressures and CO_2 concentrations. Two types of solvents are typically used for CO_2 removal: physical solvents and chemically reactive solvents. Physical solvents dissolve CO_2, following Henry's law, but do not react with it. Chemically reactive solvents first dissolve CO_2 and then react with it. Physical solvents are more suitable for mixed-gas streams that are under high pressure. The elevated pressure increases CO_2 solubility, which, in turn, reduces the solvent circulation rate. Pressure does not affect the performance of chemically reactive solvents.

If the mixed-gas stream containing CO_2 is at elevated pressure, the physical solvent can be recovered by flashing off CO_2 at a lower pressure. Chemically reactive solvents require heat to separate the dissolved gas. Commercial experience has shown that the physical solvent process is more economical if the CO_2 partial pressure is above 200 psia. At low inlet CO_2 partial pressure, and where a very low outlet CO_2 concentration is required, chemically reactive solvent processes are more effective.

Hybrid solvents combine the best characteristics of both chemical and physical solvents and are usually composed of a number of complementary solvents. Developments are under way to develop tailor-made complementary solvents where the proportions are varied to suit the application.

Some of the more commonly used commercial gas absorption processes are listed in Table 1. The first four processes use solvents that physically absorb the CO_2 and are applied to mixed-gas streams under high pressure that contain a high concentration of CO_2. The solvent circulation rates for these processes are generally high. The three other processes use chemically reactive solvents. All of the chemical absorption processes can be used at atmospheric pressure, but in practice they are used for treating mixed-gas streams under substantial pressure such as for the removal of CO_2 from natural gas and synthesis gas.

Alkanolamines are a group of amines that are commonly used for acid gas removal (including CO_2). They include monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), diisopropanolamine (DIPA), and triethanolamine (TEA). Of these, MEA is the most alkaline; it has the highest dissociation constant and the highest pH in water solution. The others are progressively less alkaline in the order listed. Other properties that bear on the use of these amines follow in the same order as their alkalinities. The chemical reaction with CO_2 is fastest with MEA and decreases with the others. For these reasons, MEA-based processes are the most popular and are considered the best available control technology (BACT) for the removal of CO_2 from flue gas with low concentration and low partial pressure of CO_2.

Cryogenic Cooling

CO_2 can be separated from a mixed-gas stream by liquefaction when the CO_2 concentration is sufficient. CO_2 can be liquefied at any temperature between its triple point (–70°F) and its critical point (88°F) by compressing it to the corresponding liquefaction pressure and removing the heat of compression and condensation. There are two common commercial liquefaction processes. In the first process, the CO_2 is liquefied near the critical temperature, and water is used for cooling. This process requires compression of the CO_2 gas to about 1100 psia. A second liquefaction process operates at temperatures from 10° to 70°F and with a liquefaction pressure of about 250 to 350 psia. This process requires dehydration of the feed stream with an activated alumina or silica gel dryer and distillation of the condensate in a stripping column. The third cryogenic process cools the mixed-gas stream to a temperature sufficiently low to condense CO_2 out of the gas phase. This method is also used to remove vapors of organic compounds from vent gases and for other operations.

Gas Separation Membranes

Gas separation membranes use partial pressure as the driving force for separation and, consequently, will be most effective at high CO_2 concentrations and pressure. Differences in physical or chemical interaction between the components present in a gas mixture with the membrane material cause one component to permeate through the membrane faster than the other component. The gas component dissolves into the membrane material and diffuses through it to the other side. The membrane divides the feed gas stream into the permeate stream and the retentate stream. Ideally, the permeate stream would require little recompression for utilization.

The quality of the separation is determined by membrane selectivity and by two process parameters: 1) the ratio of the permeate flow to the feed flow and 2) the ratio of permeate pressure to the feed pressure. Depending upon the selectivity of the membrane, a high-purity CO_2 product may require a large number of stages, leading to increased recompression and capital costs. Membrane separation often competes with cryogenic separation and pressure swing adsorption when medium quantities of low-purity product gas are required. Membrane separation technology is currently better suited to treatment of mixed-gas streams fed from a high-pressure source, such as natural gas processing.

Table 1. Gas Absorption Processes Used for CO_2 Removal

No.	Process (and solvent)	Owner	Use
1	Sulfinol (MDEA and accelerator)	Shell Oil Company	Natural gas, refinery gases and synthesis gases
2	Selexol (a dimethyl ether of polyethylene glycol)	UOP	Natural gas, refinery gases, and synthesis gases
3	Rectisol (cold methanol)	Lurgi GmbH and Linde AG	Heavy oil partial oxidation process of Shell and Texaco; also Lurgi gasification
4	Purisol (N-methyl-2-pyrrolidone)	Lurgi GmbH	Natural gas, hydrogen, and synthesis gases
5	Catacarb (hot potassium carbonate and borate activator)	Eickmeyer & Associates, Kansas	Any mixed-gas stream
6	Benfield (hot potassium carbonate and ACT-1 corrosion inhibitor)	UOP	Synthesis gas, hydrogen, natural gas, town gas, and others
7	Amines (alkanolamines and hindered amines)	Both generic solvents and proprietary formulations with additives	Any mixed-gas stream

Gas Absorption Membranes

Gas absorption membranes are used as contacting devices between a gas flow and a liquid flow. The presence of an absorption liquid on one side of the membrane selectively removes certain components from a gas stream on the other side of the membrane. In effect, the absorption liquid increases the driving force across the membrane because the partial pressure of the absorbed gas on the liquid side is essentially zero. In contrast with gas separation membranes, it is not essential that the absorption membrane be selective as its purpose is solely to provide a contacting area without mixing gas and absorption liquid flow. The selectivity of the process is derived from the absorbing liquid.

Removal of flue gas components such as SO_2 or CO_2 is achieved through the use of porous hydrophobic membranes in combination with suitable absorption liquids, such as sulfite, carbonate, or amine solutions. For example, CO_2 is removed from flue gas with the aid of gas absorption membranes used in combination with MEA.

Gas Adsorption

Gas–solid adsorption systems that may be applicable to removal of CO_2 from mixed-gas streams employ adsorbent beds of alumina, zeolite, or activated carbon. Other solid materials used commercially in gas separation processes are alumina gel and silica gel, although processes using these gels are a hybrid of adsorption and absorption.

Four methods are used commercially for regeneration. Pressure-swing adsorption and regeneration (PSA) involves raising and lowering the pressure in the bed to preferentially capture and release the gases to be separated. Technologies requiring a vacuum for regeneration are called vacuum pressure-swing adsorption (VPSA) units. PSA and VPSA regeneration cycles are relatively short and are typically measured in seconds. Thermal- (or temperature-) swing adsorption (TSA) employs high-temperature regeneration gas to drive off trapped gases. TSA regeneration cycles are quite long (measured in hours) and require larger quantities of adsorbent than PSA systems. The third regeneration method employs a stream of fluid that does not contain any of the trapped gas to “wash” the bed. The fourth method uses a gas stream that contains a material that can displace the trapped gas from the bed and is essentially a chromatographic procedure.

Most commercial units use either PSA-type regeneration or a combined thermal swing/wash method that regenerates at reduced pressure, known as thermal swing. PSA technology is used for drying air, hydrogen purification in refineries, n-paraffin removal, and small- to medium-scale air fractionation. Depending on the feed gas and the species to be adsorbed, two vessels are filled with an adsorbent such as silica gel, molecular sieves, or molecular sieve carbon. One vessel serves as an adsorbing bed, with the feed entering at elevated pressure. When the bed is saturated, the feed is switched to the second vessel. Pressure in the first (spent) vessel is lowered to release the adsorbed species. The adsorbent in the vessel is regenerated, and the vessel is pressurized to make it ready for another cycle. The process is repeated in the second vessel. Similar to the absorption process, the adsorption can be primarily chemical or physical with physical adsorption being the less energy-intensive to reverse. These processes compete with cryogenic air separation units in applications requiring high-purity products, where the number of stages and the recycle flow rates increase to such an extent that the adsorption processes cannot successfully compete.

Combustion Modification Technologies

Substitution of oxygen for all or part of the combustion air has been proposed to produce a CO_2-rich flue gas requiring minimum separation for use or sequestration. Conventional air combustion processes in boilers or gas turbines produce flue gas that contains predominantly nitrogen (>80 vol %) and excess oxygen in addition to CO_2 and water. Separation technologies must separate CO_2 from these other components. If the air is replaced by oxygen, the nitrogen content of the flue gas approaches zero (assuming minimal air leakage into the system), and the flue gas contains predominantly CO_2 along with a small amount of excess oxygen and combustion water. The CO_2 can be recovered by compressing and cooling, followed by dehydration. The adiabatic flame temperature can be moderated by recirculating a part of the recovered CO_2.

While oxygen combustion with the recycle of flue gas has been studied conceptually, there are no field units. Commercial plant feasibility may be difficult to justify because of the auxiliary power consumption of the air separation unit needed to produce the oxygen.

APPLICATION OF CO_2 CAPTURE TECHNOLOGIES TO FUEL COMBUSTION

Postcombustion Removal

For removal of CO_2 from low-pressure (<2 psig), low-CO_2 concentration (<15 vol%) flue gases, MEA scrubbing is considered state-of-the-art for fossil fuel- fired system such as boilers and gas turbines. Several commercial facilities use MEA-based solvents to capture CO_2 from coal-, fuel oil-, and natural gas-derived flue gas streams for use in the food industry and, in the past, for enhanced oil recovery (EOR). These plants have had capacities in the range of 100 to 1100 tons/day, which is significantly less than the 5500 tons/day for a 500-MW coal-fired plant. Commercial providers of MEA technology include Fluor Daniel and ABB Lummus Global. A diagram of a system employing an MEA process for CO_2 capture is presented in Figure 1.

In gas turbine combined-cycle systems, flue gas from the heat recovery steam generator (HRSG) is cooled to about 110°F with circulating cooling water. Additional cooling is not required in systems employing flue gas desulfurization (FGD). The flue gas is partially compressed to 17.5 psia by a centrifugal blower to overcome the gas-path pressure drop. The flue gas enters the absorber base and flows upward countercurrent to the lean MEA solution. CO_2 is removed from the flue gas in the packed-bed absorber column through direct contact with MEA. The CO_2-depleted flue gas is exhausted to the atmosphere. The CO_2-rich solution is heated in a heat exchanger and sent to the stripper unit where low-pressure steam from the steam turbine crossover provides the thermal energy to liberate the CO_2. The CO_2 vapor is condensed, cooled, and sent to a multistaged compressor where the CO_2 is compressed to a pressure of over 1200 psia. The CO_2-laden stream is dehydrated using glycol or molecular sieve processes. After drying, the CO_2 is ready for transport and sequestration.

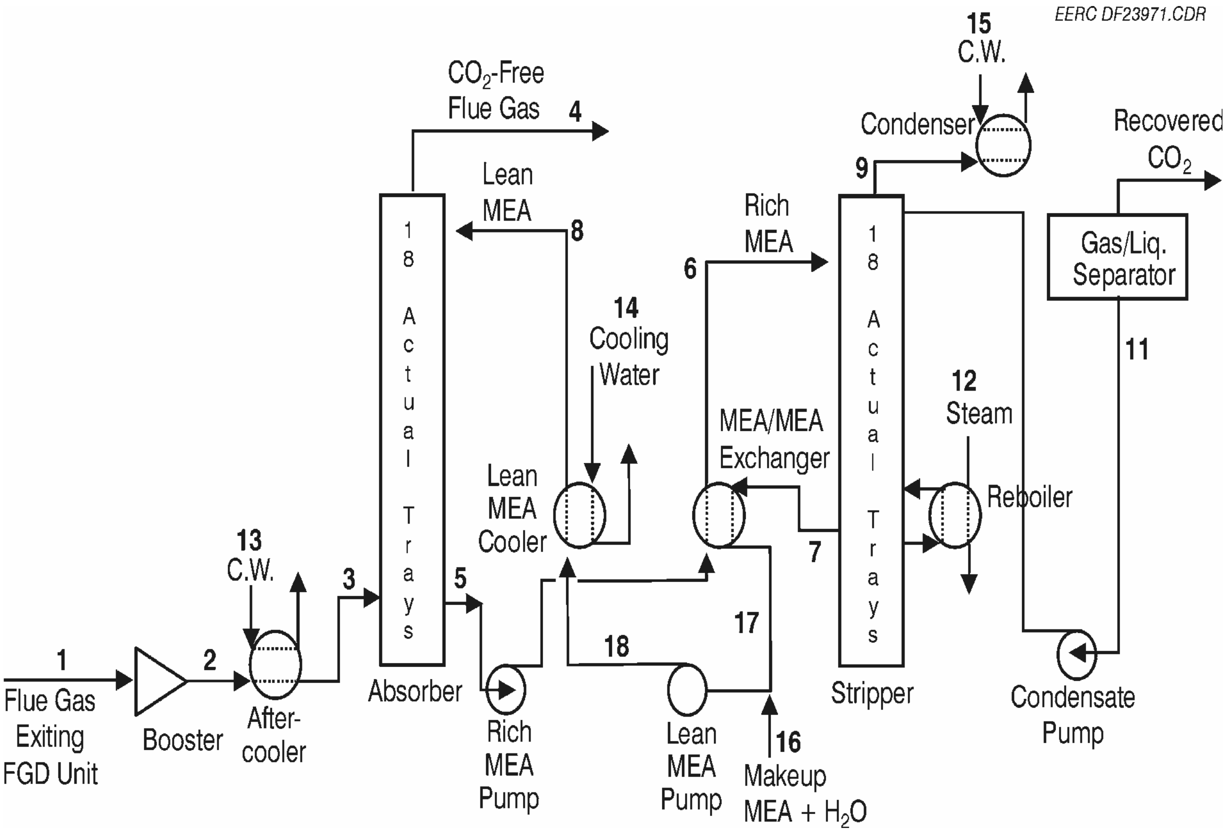

Figure 1. Process flow diagram of CO_2 removal by MEA absorber/stripper.

The MEA process can achieve recoveries of 85% to 95%, with CO_2 purities over 99 vol%. However, the MEA process also requires a significant amount of power to operate pumps and blowers for gas and solvent circulation. The largest parasitic load to the power cycle is associated with the steam used for solvent regeneration. Energy consumption as steam can be as high as 3.6 to 4.5 10^6/ton CO_2 recovered. Additional issues with the process are equipment corrosion; solvent degradation caused by the presence of dissolved O_2 and other impurities; or reaction with SO_2, SO_3, and NO_x to produce nonregenerable, heat-stable salts. This requires SO_2 levels below 10 ppm, NO_2 levels below 20 ppm, and NO_x below 400 ppm. Solvent degradation and loss also occur during regeneration.

Recent advances in chemical solvents have included the commercial introduction of the KS-family of hindered amines by Mitsubishi Heavy Industries (MHI). Their molecular structure is tailored to enhance reactivity toward a specific gas component, in this instance CO_2. Benefits relative to MEA include higher absorption capacity (only 1 mol of hindered amine is required to react with 1 mol CO_2 compared with 2 mol MEA), 90% less solvent degradation, 20% lower regeneration energy, 15% less power, 40% lower solvent recirculation rates due to higher net absorption capacity, lower regeneration temperature, less corrosion in the presence of dissolved oxygen, and lower chemical additive cost.

Other advanced liquid sorbent systems being developed include:

- Potassium carbonate/piperazine complex (University of Texas at Austin, which may permit the use of waste heat because the regeneration temperature is lower (131° vs. 248°F).
- Aqua (Aqueous) Ammonia Process (Powerspan, National Energy Technology Laboratory [NETL]), which has the ability to also capture SO_2, NO_x, HCl, and HF and to produce potentially marketable by-products.
- PSR solvents (University of Regina, Saskatchewan), which are proprietary designer solvents formulated for optimized separation of CO_2 from any gas stream.

These chemical solvent systems are being developed to improve the cost-effectiveness of CO_2 capture through higher CO_2 absorption capacity, faster CO_2 absorption rates (to achieve lower solvent circulation rates and smaller equipment), reduced solvent degradation, less corrosiveness, and lower regeneration energy requirements. Development efforts for these technologies range from bench to pilot scale.

Dry, regenerable, solid sorbents are also being developed for postcombustion CO_2 capture in both low- and elevated-temperature flue gas. With these sorbents, essentially pure CO_2 (>99%) is recovered owing to selective absorption of CO_2. Dry regenerable solid sorbent systems under development include:

- Alkali carbonate system (Research Triangle Institute [RTI]).
- Amine-enriched sorbents (NETL).

The first process requires a multiple reactor system, with absorption occurring in one reactor and transfer of the loaded sorbent to a second reactor for regeneration and release of CO_2. The second process involves cyclic use of multiple beds, similar to PSA/TSA. Because these are dry systems, there is no need to heat and cool large amounts of water, as required in an MEA system, which leads to lower regeneration energy requirements. Another advantage is the higher contact area for CO_2 absorption. Development efforts for these technologies are currently at the bench scale.

Membrane systems being developed for the separation of CO_2 from flue gas include:

- Molecular gate membrane (Research Institute of Innovative Technology for the Earth [RITE]), a cardo-polyimide membrane that is selective to CO_2 permeation.

- Kvaerner hybrid membrane absorption system (Kvaerner Process Systems), a gas–liquid membrane contactor that replaces a traditional absorber. CO_2 diffuses through a microporous, hydrophobic solid membrane into liquid flow. The solvent, rather than the membrane, provides the selectivity. Compared to a conventional absorber, it weighs 70% less and has a 65% smaller footprint.

Precombustion Removal

Precombustion removal principally refers to near-complete capture of CO_2 before fuel combustion and would be implemented in conjunction with gasification (of coal, coke, waste, residual oil) or steam/partial oxidation reforming (of natural gas) to produce syngas containing CO and H_2. Subsequent shift conversion produces CO_2 from CO to allow maximum recovery of carbon (as CO_2) while producing H_2-rich syngas. The H_2-containing syngas (with N_2 added for temperature control) can be combusted in gas turbines, boilers, or furnaces.

Typical CO_2 concentrations before capture are 25 to 40 vol% at pressures of 363 to 725 psia. The high partial pressure of CO_2, relative to that in flue gas, enables easier separation through solvent scrubbing. In refineries and ammonia-production facilities, where H_2-rich syngas is produced by gas reforming, H_2 recovery (by acid gas removal) is performed using chemical solvents (e.g., Benfield or MDEA [methyldiethanolamine]). PSA is also used, but the CO_2-rich stream may have significant residual fuel value, making it an attractive stream for in-plant use.

The MDEA and Rectisol processes continue to be used for deep sulfur removal in IGCC applications; bulk CO_2 removal is also achieved. The Rectisol process removes CO_2 and H_2S in methanol at -94°F, which requires large amounts of gas cooling and reheating. With respect to potential future requirements for high (>90%) CO_2 recovery during gasification, the double-stage Selexol process combining desulfurization and CO_2 separation is favored. The double-stage or double-absorber Selexol unit preferentially removes H_2S in one product stream and then removes CO_2 as a second product stream. The synthesis gas enters the first absorber unit at approximately 686 psia and 105°F. In this absorber, H_2S is removed from the fuel gas stream by "loading" the lean Selexol solvent with CO_2. The CO_2 -saturated solvent preferentially removes H_2S. The rich solution is regenerated in a stripper by heating. The stripper acid gas stream, consisting of 33% H_2S, 59% CO_2, and water, is then sent to a Claus sulfur removal unit (U.S Department of Energy, 2002).

Following processing in the Claus unit, cleaned fuel gas from the first absorber is cooled and routed to the second absorber unit. In this absorber, the fuel gas is contacted with lean solvent. The solvent removes approximately 97% of the CO_2 from the fuel gas stream. The fuel gas from this second absorber is warmed and humidified in the fuel gas saturator, reheated and expanded, and then sent to the burner of the combustion turbine. CO_2 is flashed from the rich solution and is then ready for compression and dehydration to pipeline-ready conditions.

Although very effective for CO_2 removal, current solvent absorption methods produce system efficiency losses principally because of the need to cool the raw gas to near or below ambient temperature. To improve overall power generation efficiency, new CO_2 separation approaches are being developed for both gasification and reforming applications. Most of these technologies are based on selective membrane systems.

New systems under development include:

- Sorption-enhanced water–gas shift process (Air Products), in which a water–gas shift catalyst is combined with CO_2-selective hydrotalcite adsorbent. Multiple adiabatic fixed beds are used for cyclic reaction/adsorption and regeneration.
- CO_2 selective membrane (Media and Process Technology, University of Southern California), a membrane reactor that combines water–gas shift with CO_2 removal. It employs a tubular ceramic membrane, permeable only to CO_2, inside a water–gas shift reactor.
- Membrane water–gas shift reactor (Eltron Research/SOFCo/Chevron Texaco) is a catalytic membrane reactor (CMR) that utilizes oxygen transport membrane technology to facilitate in situ partial oxidation reforming. Syngas passes to a dense metal alloy membrane reactor to facilitate selective permeation of H_2 and enhanced shift. H_2 permeabilities are one order of magnitude higher than palladium and two orders of magnitude less expensive. Sweet syngas is required, however.
- Hydrogen membrane reformer (Norsk Hydro, SINTEF, and UiO) is a two-reactor process that combines reforming, water–gas shift reaction, and H_2 separation. It utilizes a dense, mixed conducting membrane (MCM). Since the transport process is based on ion diffusion, the selectivity of the membrane is infinite as long as the membrane is gas impervious (barring any defects).
- Palladium membrane reactor (NETL). This reactor system combines a palladium-based membrane with the water–gas shift reaction. The high temperature (1652°F) and pressure of operation and the catalytic effect of the membrane eliminate the need for a separate water–gas shift catalyst. A sulfur-tolerant membrane is possible.
- Hybrid alumina/organosilane membrane (NETL). In this system, organic molecules are grafted onto a substrate surface to attain higher selectivity toward CO_2 permeation.
- Electrical swing adsorption (Oak Ridge National Laboratory) uses carbon-bonded activated carbon fiber as adsorption material. Adsorbed gas is removed by a low-energy electric current.
- Thermally optimized polymer membrane (Los Alamos National Laboratory, Idaho National Engineering & Environmental Laboratory, Pall Corporation, University of Colorado, Shell Oil Company), in which polymer-based membranes exhibit high selectivity because of size-based exclusion and solubility variances of molecules within the polymer matrix. Polymer membranes have been commercially successful for a number of industrial applications. The intent of

additional research is to increase the temperature of application.

- Inorganic nanoporous membrane (ORNL) with pore sizes of less than 1 nm. Composite membranes made of a ~2-μm membrane (e.g., alumina) layer on a ~450-μm porous support structure can allow operation at temperatures up to 1852°F.

- Warm gas sodium-based solid sorbents (NETL) have been developed for PSA/TSA application for removal of IGCC syngas streams. They rely on chemical reaction for CO_2 capture. Regeneration temperatures are currently too high at 1292°F.

Other advanced processes and/or unconventional systems are being developed with the intent of improving efficiencies and lowering the cost to capture and purify CO_2. These include:

- Regenerative carbonate process (Alstom Power), which utilizes a recirculating stream of lime (CaO) to capture CO_2 during combustion. Calcium carbonate is regenerated in a calciner to liberate pure CO_2. In this process, there is no thermodynamic efficiency loss for CO_2 capture.

- Chemical looping gasification (Alstom Power). The intent of this process is to produce a nearly pure CO_2 stream and a medium-Btu gas (>90% H_2) after CO_2 separation. The high energy and cost penalty associated with O_2 separation is avoided (it is similar in concept to chemical-looping combustion). It uses two separate chemical loops, one for oxygen transfer and one for CO_2 capture.

- ZEC technology (ZECA Corporation), hydrogasification of carbon-based fuel to H_2 with CO_2 capture in a carbonate cycle. It would achieve permanent sequestration of CO_2 through mineral carbonization. The ultimate embodiment of the process is the high-efficiency (70% to 75%) conversion of H_2 fuel gas to electricity through application of a coal-compatible fuel cell (CCFC).

- Unmixed fuel processor (UFP) (GE Global Research [GEGR]) is a gasification process developed to convert coal, steam, and air into hydrogen; sequestration-ready CO_2; and a low-quality, high-temperature air stream used for power production in a gas turbine. Regenerable oxygen transfer material is used to provide oxygen for the process; no external air separation unit (ASU) is required.

- CO_2 hydrate (SIMTECHE, Nexant, Los Alamos National Laboratory) is a below-ambient-temperature, high-pressure, aqueous-based process that captures CO_2 from syngas through the formation of CO_2 hydrates. H_2 acts as an inert and is not retained in the hydrate crystal. The CO_2 is recovered from the hydrate slurry by heating and reducing pressure.

Oxygen Combustion

Oxygen combustion is used in industry for the treatment of nonferrous scrap and could be applicable to process heaters, large industrial and utility boilers, and gas turbines. Air is replaced with an enriched or nearly pure oxygen stream produced from an ASU. A tempering medium such as recycled flue gas or water is added to control system temperatures and heat release/transfer. A CO_2-rich stream is produced, with the intended sequestration application dictating the level of upgrading.

For enhanced coalbed methane recovery (ECBM) or saline aquifer sequestration, only condensation of moisture may be required as some constituents (e.g., N_2) can be present, and a supercritical, dense-phase fluid is not required. Under this scenario, zero emissions would be possible. Where supercritical fluid is required, non-condensable contaminants such as N_2, NO_x, O_2, and Ar can be removed by flashing in a gas–liquid separator. The levels of noncondensable impurities and thermodynamics limit recovery of CO_2 and affect the purity of the sequestration stream.

Oxygen combustion has several advantages. The volume of flue gas reaching downstream systems is one-third to one-fifth that of conventional coal boilers. Recycle of flue gas is limited to 50% in current gas turbines, so flue gas volumes to the HRSG would be reduced by half. The process produces a flue gas stream containing more than 80 vol% CO_2, depending upon the fuel composition, purity of oxygen from air separation, and air leakage into the boiler.

Impurities such as SO_2, NO_x, particulate, and Hg become concentrated in the flue gas, thus reducing capital and operating costs for contaminant removal. NO_x may be low enough to eliminate further control, and capital and operating cost savings (for control systems) may offset air separation capital and operating costs.

Retrofit applications would be designed to maintain the same steam outlet conditions. The higher heat capacity of the gas should potentially facilitate greater heat absorption. Higher heat absorption would result in higher boiler efficiency, but this would be offset by higher auxiliary power load for fan power to the recycle gas for temperature control.

Issues with oxygen combustion center principally around the high cost for air separation, which is currently attainable at very large scale only by cryogenic distillation. Relative to coal gasification, combustion requires up to three times the amount of oxygen because all of the carbon is converted to CO_2. The air separation unit capacity (and parasitic power load) likewise will be commensurately larger. Other issues include expected lower flue gas exit temperature (that may increase the risk of low-temperature corrosion from condensation of sulfuric acid), burner operation, flame stability, levels of unburned carbon, flame luminosity and length, and changes in slagging/fouling characteristics under the different atmosphere.

Development efforts involving conventional pulverized coal testing with oxygen combustion are at the scale of several hundred kW and less. Developers and testing organizations include CANMET, Mitsui Babcock, American Air Liquide, Babcock & Wilcox, Foster Wheeler North America, and the Energy & Environmental Research Center.

Oxygen firing in circulating fluid-bed boilers may have an advantage over pc firing in that a significant degree of temperature control can be achieved by recirculating solids. Lower flue gas recycle would reduce parasitic power load for fans. In addition, higher O_2 concentrations may be possible, resulting in a smaller boiler island size and reduced capital cost. Development issues center around continuous solids recirculation. Currently, testing is at the large pilot scale with development efforts being conducted by Alstom Power, ABB Lummus Global, Praxair, and Parsons Energy.

As previously mentioned, the high cost of oxygen separation is a major issue with oxygen combustion. State-of-the-art cryogenic distillation air separation has little room for improvement or cost reduction. Current development activities are centered on ion transport membranes. These are complex crystalline structures with oxygen ion vacancies onto which oxygen adsorbs and decomposes into ions. The ions are transported through the membrane by sequential occupation of oxygen ion vacancies with the ion transport balanced by the counterflow of electrons. Oxygen partial pressure provides the driving force, which requires high-pressure air at temperatures above 1292°F. Barring the presence of defects, the membrane is selective to oxygen transport only.

The ion transport membranes can theoretically integrate high-temperature oxygen separation from air with the combustion process, leading to a significant reduction in parasitic power as well as lower cost for O_2 production. Development issues include materials of construction, integration with or into the boiler, control of wall temperature (as a consequence of combustion reaction), and carbon formation. Developers and systems include Praxair and Alstom Power (oxygen transport membrane [OTM]), and air products (ion transport membrane [ITM]).

Concepts being developed that utilize ion transport membranes for oxygen separation include:

- Advanced zero emission power (AZEP) process (Alstom Power, Norsk Hydro), which is utilized with conventional gas turbines. Air from the compressor is supplied to a new MCM reactor. The reactor combines O_2 separation, combustion, and heat transfer. Preliminary evaluations show a 2% loss in plant efficiency for separation vs. a 10% loss with flue gas CO_2 separation.

- Integration into a fired boiler (Praxair) in which an OTM is incorporated directly into the boiler. It can be utilized with gaseous or liquid fuel.

- Utilization with circulating fluidized-bed (CFB) or circulating moving-bed (CMB) boiler (Alstom Power). In this case, the OTM stands alone but is thermally integrated with the boiler. It requires a high-temperature air source and is heated by in-bed heat exchange of CFB or CMB.

Other advanced processes and/or unconventional cycles are being developed with the intent of improving efficiencies and lowering the cost to capture and purify CO_2. These include:

- CO_2 hybrid process (Foster Wheeler North America). This process combines oxygen-blown partial gasification with oxygen combustion of syngas in a gas turbine. The gas turbine exhaust provides sensible heat and oxygen for char combustion to produce steam for partial gasification. Flue gas from the char combustion contains all of the CO_2 from the process; recovery is accomplished by compression and flash of noncondensables.

- Chemical looping combustion or sorbent energy transfer system (TDA Research, Alstom Power, Chalmers University). In this technology, separation of CO_2 occurs during combustion, and no energy is expended for CO_2 separation. There is no direct contact of fuel with air, and no air separation unit is required. An oxygen carrier transfers oxygen from the combustion air to the fuel. The net chemical reaction and heat release is equivalent to that of conventional combustion. The process is currently applicable only to gaseous or liquid fuels unless the solid fuel is first gasified in O_2.

- Water cycle (Clean Energy Systems) is based on a high-temperature/pressure aerospace-derived gas generator operating at 1500 psi and 3000°F. The fuel is fired stoichiometrically with oxygen, and water is injected to control temperature and protect gas generator components. The working medium is a high-pressure, high-temperature steam–CO_2 mixture comprising 90% steam and 10% CO_2.

- Graz cycle (Institute for Thermal Turbomachinery and Machine Dynamics). As with the water cycle, it uses a 25:75 steam–CO_2 mixture as the working fluid. It combines the gas turbine cycle with the steam cycle to improve efficiency. Gaseous fuel is reacted with stoichiometric oxygen in the combustor at 580 psi, with steam (as opposed to water) injected for temperature control.

- MATIANT cycle (Institute of Mechanical Engineering, University of Liege [Belgium]) combines a Brayton-like cycle (in which CO_2 serves as the principal working fluid) with a steam cycle.

IMPACT OF CO_2 CAPTURE ON SYSTEM EFFICIENCY

Göttlicher (2004) has summarized CO_2 removal systems for fossil fuel-fired power plants and divided them into the following five groups:

- Process Group I comprises processes with CO shift or steam reforming prior to CO_2 removal. The resulting hydrogen-rich fuel gas can then be combusted with air after H_2/CO_2 separation.

- Process Group II covers processes where fuel is combusted in an atmosphere of oxygen mixed with recycled CO_2 or steam.

- Process Group III includes all kinds of fossil fuel-fired power generation systems in which CO_2 is removed from the flue gas after combustion at the exhaust end of the plant.

- Process Group IV includes the Hydrocarb processes whereby carbon is separated from the fuel prior to combustion.

- Process Group V deals with CO_2 separation in fuel cells suitable for the use of fossil fuel-derived gases.

Göttlicher (2004) states that CO_2 separation processes applied to a fossil fuel-fired power plant result in additional parasitic energy consumption and reduction of power output. Assuming a pipeline pressure of 1595 psia, the energy requirement for liquefaction by intercooled 5-stage compression starting from 14.5 psia amounts to about 0.06 kWh/lb CO_2. For 90% CO_2 removal, the CO_2 liquefaction reduces the efficiency of a Pittsburgh No. 8 coal-fired power plant by 3.1 percentage points, while the efficiency of natural gas-fired power plants is reduced by 2.0 percentage points. These reductions in efficiency depend on the carbon content and heating value of the fuel and the extent of CO_2 removal. The following figures on efficiency reduction are based on the assumption that the CO_2 removed is at 14.5 psia.

Process Group I

In Process Group I, the efficiency reduction due to CO_2 removal is predominantly caused by:

- Energy destruction because of steam reforming or gasification and CO shift results in an overall efficiency reduction of 2.5 to 5 percentage points.

- Energy demand of the gas separation process (i.e., regeneration, compression) reduces efficiency by about 1 percentage point.

- Volume displacement of the separated carbon dioxide produces an efficiency reduction of about 1 percentage point.

The efficiency reductions for Process Group I range from 4 to 7.4 percentage points for an IGCC with CO shift (in which 80% to 90% of the CO_2 is removed) and around 14.5 percentage points for a natural gas-fired combined cycle with steam reforming, CO shift, and absorption by MDEA (resulting in CO_2 removal below 60%).

Process Group II

Efficiency reductions because of O_2/CO_2 firing (as cited in the literature and as calculated by the authors) range from 4.8 to 8.5 percentage points for IGCC power plants and about 6 percentage points for natural gas-fired plants.

Process Group III

In this process scheme, most of the concepts apply flue gas scrubbing with amine-based chemical sorbent. Such removal processes consume up to two-thirds of the steam during solvent regeneration. Efficiency figures cited in the literature are in the range of 8 to 11 percentage points when 80% to 90% of the CO_2 is removed from coal-powered plants or 5.5 to 11 percentage points when removed from gas turbine combined-cycle (GTCC) plants.

Process Group IV

These processes separate carbon from the fuel prior to combustion. This option is a reasonable approach only for fuels containing a high proportion of hydrogen. For example, in the Hydrocarb process, a fuel mixture consisting of biomass and natural gas or oil undergoes hydropyrolysis to form a methane-rich fuel gas, which then goes to a methane cleavage reactor where H_2 and carbon are produced. The carbon is separated from the H_2 stream. The specific CO_2 emissions of the fuel that is produced by this process group are lower than the CO_2 emissions from the feedstocks. Conversion efficiencies (on an HHV basis) for various mixtures of biomass and coal, oil, or natural gas range from 3.5% (for hydrogen production from biomass only) to 71.6% (for synthesis gas production from biomass and methane). Comparison of this process with other CO_2 removal options discussed earlier requires multiplication of the conversion efficiency by a cycle or plant efficiency (i.e., for reciprocating engines, steam and gas turbine cycles, etc.).

Process Group V

Phosphoric acid fuel cells (PAFC), molten carbonate fuel cells (MCFC), and solid oxide fuel cells (SOFC) can be operated with fossil fuel-derived gases. The efficiency of power plants with PAFC is below the efficiencies of other combined cycles. MCFC or SOFC combined cycles are expected to achieve higher efficiencies. In all three cases, extra energy demand in the range of 0.02 to 0.05 kWh/lb CO_2 is required for the necessary separation of residual fuel, and the CO_2 removal rate is probably limited to around 80% with specific CO_2 emissions of 0.33 to 0.37 lb of CO_2 per kWh.

COST OF CO_2 CAPTURE IN REPRESENTATIVE COMMERCIAL POWER GENERATION SYSTEMS

Capital and operating cost data for CO_2 capture were calculated for three commercial power generation technologies (U.S. Department of Energy [DOE], 2002, 2004). The case numbers have been taken from studies performed by DOE, EPRI, and Parsons. The three systems include:

- Case 1B – natural gas turbine combined cycle (GTCC).

- Case 3E – coal gasification combined cycle (IGCC).
- Case 7A – supercritical steam pulverized coal-fired (SCPC).

Table 2 presents the major performance metrics for the three cases with CO_2 removal. For comparison, the net plant efficiencies for 1B, 3E, and 7A without CO_2 removal are 53.6%, 43.1%, and 40.5%, respectively.

Gas Turbine Combined Cycle

Case 1B is a GTCC plant using a single-train General Electric H-class gas turbine with CO_2 removal using an amine process. Net generation is 311 MWe at a higher heating value (HHV) efficiency of 43.3%. The power plant design includes removal of 90% of the CO_2 from the HRSG flue gas. An aqueous solution of inhibited (oxygen-tolerant) MEA is used to remove the CO_2, which is then concentrated, dried, and compressed to a supercritical condition suited for pipeline transport.

Table 3 presents the costs estimated for the GTCC power plant with and without CO_2 removal. The table shows that the cost of CO_2 removal and compression is roughly $85 million. The cost of CO_2 removal and compression can be estimated as the difference between the plant with removal (Case 1B) and the plant without (Case 1D), or $447/kW. This exercise shows that CO_2 removal makes up about 35% of the total plant cost.

Integrated Gasification Combined Cycle

The IGCC example in the DOE report uses advanced technology for both the gasifier (high-pressure E-Gas™ technology) and gas turbine (General Electric H-class advanced turbine system [ATS] machine) featuring the gas turbine and steam turbine on a single shaft and generator. The gasification case with CO_2 removal is designated 3E in the report and in Table 4.

Estimation of the cost for CO_2 removal is somewhat more complex for the gasification plant because some of the gas cleaning would be needed whether or not CO_2 is a required product. Additionally, equipment costs other than those required for water–gas shift equipment may be necessary.

Table 2. Summary of Power System Performance with CO_2 Removal

Major Performance Metrics	DOE/EPRI/Parsons Cases		
	1B, GTCC	3E, IGCC	7A, SCPC
Gross Plant Power, kWe	343,107	474,275	402,254
Auxiliary Power Load, kWe	32,290	87,490	72,730
Net Plant Power, kWe	310,817	386,785	329,294
Net Plant HHV Efficiency, %	43.3	35.4	28.9
Net Heat Rate, Btu/kWh HHV	7879	9638	11,816
CO_2 Removed, ton/day	3105	8158	8525

Table 3. GTCC Plant with and Without CO_2 Removal

Bare Erected Cost	Case 1B (with removal) Cost, $K	Case 1D (without removal) Cost, $K	Difference 1B – 1D, $K
CO_2 Removal and Compression	85,024	0	85,024
Combustion Turbine and Accessories	52,608	52,608	0
HRSG, Ducting and Stack	20,737	20,844	–107
Steam T-G Plant, including cooling water system	16,936	36,342	–19,406
Accessory Electric Plant	19,948	13,551	6397
Balance of Plant	35,076	28,954	6122
Subtotal	230,329	152,299	78,030
Engineering Services and Fee	13,820	9138	4682
Process Contingency	11,262	5172	6090
Project Contingency	37,555	24,141	13,414
Total Plant Cost (TPC)	292,965	190,749	102,216
TPC, $/kW	943	496	447

The DOE report also describes an IGCC system, Case 3B, in which CO_2 is not recovered. For Case 3B, the plant uses a proprietary amine solvent in a traditional absorber/stripper arrangement to remove H_2S from the fuel gas stream, after which elemental sulfur is recovered in a Claus plant.

Costs reported for the CO_2 removal (Case 3E) gasification plant are presented in Table 4. The costs associated with CO_2 removal, capture, and compression has been estimated by determining the difference between the cases with and without CO_2 removal. The estimated unit cost of $399/kW is less than the $447/kW that was estimated for the natural gas combined-cycle case, indicating that the gasification process may be more amenable to the chemical steps needed to modify the power generation design for CO_2 recovery and sequestration. Owing to reduced fuel cost, the gasification process may also be less expensive to operate with CO_2 capture. This is shown in Table 5, which presents the estimated first-year operating costs for the natural gas combined-cycle and IGCC plants.

Supercritical PC

The DOE Case 7A is a coal-fired, supercritical steam plant with CO_2 removal and recovery. The coal-fired boiler is staged for low NO_x formation and is also equipped with a selective catalytic reformer and a wet limestone forced-oxidation FGD to limit SO_2 emissions. A once-through steam generator powers a double-reheat supercritical steam turbine with a power output of 402 MWe. The steam turbine conditions are 3500 psig/1050°F throttle with 1050°F at both reheats. Net plant power, after consideration of the auxiliary power load, is 329 MWe. The plant operates with an estimated HHV efficiency

Table 4. IGCC Plant with and Without CO_2 Removal

Bare Erected Cost	Case 3E (with removal) Cost, $K	Case 3B (without removal) Cost, $K	Difference 3E – 3B, $K
Gasifier, ASU, and Accessories	128,621	130,308	–1687
Gas Cleanup and Piping	73,607	26,496	47,111
CO_2 Compression	42,662	0	42,662
Combustion Turbine and Accessories	62,161	61,863	298
HRSG, Ducting, and Stack	20,429	20,684	–255
Steam T-G Plant, including cooling water system	33,436	36,618	–3182
Accessory Electric Plant	27,855	23,066	4789
Balance of Plant	80,209	77,260	2949
Subtotal	468,980	376,295	92,685
Engineering Services and Fee	28,139	22,578	5561
Process Contingency	17,647	16,267	1380
Project Contingency	69,347	56,340	13,007
TPC	584,112	471,480	112,633
TPC, $/kW	1510	1111	399

of 28.9% at a corresponding heat rate of 11,816 Btu/kWh. Flue gas from the FGD system goes to an inhibited MEA absorber–stripper system where 90% of the CO_2 is removed.

The costs reported for the supercritical PC cases with and without CO_2 removal (i.e., 7A and 7C, respectively) are presented in Table 6. Large increases in both total plant costs and unit cost per kW are indicated.

Comparison of GTCC, IGCC, and SCPC

A summary of plant efficiency, power output, plant cost, and cost of electricity is presented in Table 7 for the three power systems with CO_2 capture. Results are also presented for the baseline plants for comparison. Costs are based on a 90% CO_2 capture level, coal costs of $1.24/million Btu natural gas costs of $2.70/million Btu, and a capacity factor of 80%. The results presented in Table 7 show that each power generation system is impacted by the addition of CO_2 capture technologies. Plant power output reductions vary from approximately 9% for IGCC to as high as almost 30% for supercritical PC. The impact on IGCC is the least because the high pressure of operation and high relative CO_2 concentration allows CO_2 to be captured using the more efficient physical solvent.

A more recent study by the CO_2 Capture Project (CCP) shows a trend toward reduced costs and improved performance. In a paper presented at the 2004 Carbon Sequestration Conference (U.S. Department of Energy, 2004), results were reported for conceptual design work performed to reduce the performance and cost penalties imposed by CO_2 capture on GTCC power generation. The work evaluated a base case using technology and designs associated with today's use of amine capture systems, largely in the context of petroleum refineries. The study

Table 5. Operating Costs of GTCC and IGCC with CO_2 Removal

First-Year Cost	Case 1B, GTCC, $K	Case 3E, IGCC, $K
Operating Labor	2064	5503
Maintenance	5846	11,828
Administrative and Support Labor	1100	2559
Consumables	5014	1927
By-Product Credits	NA*	–972
Fuel	37,649	26,321
TPC	51,673	47,166

* Not applicable

Table 6. Supercritical Steam Plant Cost Data with and Without CO_2 Removal

Bare Erected Cost	Case 7A (with removal) Cost, $K	Case 7C (without removal) Cost, $K	Difference 7A – 7C, $K
PC Boiler and Accessories	108,950	109,560	–610
Flue Gas Cleanup	59,410	61,490	–2080
CO_2 Removal and Compression	111,770	NA	111,770
Ducting and Stack	18,010	20,540	–2530
Steam T-G Plant, including cooling-water system	79,380	92,470	–13,090
Accessory Electric Plant	31,340	24,150	7190
Balance of Plant	121,570	125,840	–4270
Subtotal	530,430	434,050	96,380
Engineering Services and Fee	31,830	26,040	5790
Process Contingency	6020	NA	6020
Project Contingency	84,140	67,990	16,150
TPC	652,420	528,080	124,340
TPC, $/kW	1981	1143	838

Table 7. Plant Impact and Avoided CO_2 Costs

	Natural Gas Combined Cycle		Gasification Combined Cycle		Supercritical PC	
	1D Without Capture	1B with Capture	3B Without Capture	3E with Capture	7C Without Capture	7A with Capture
Net Plant Output, MW	384	311	425	387	462	329
Energy Penalty, %		19.0		8.9		28.8
Net Plant Efficiency, %	53.6	43.3	43.1	35.4	40.5	28.9
Plant Cost, $/kW	$496	$943	$1111	$1510	$1143	$1980
Cost of Electricity (COE), ¢/kWh	3.07	4.88	4.10	5.36	4.48	7.39
Incremental COE, ¢/kWh		1.81		1.26		2.91
Avoided CO_2 Cost, $/ton		$54.79		$17.69		$39.55

then evaluated degrees of design integration and simplification (the “low-cost” and “low-cost integrated” cases). The results are given in Table 8. The “best integrated technology” design assumes improvements in amine performance in addition to the equipment and design cost reductions included in the low-cost and low-cost integrated cases. The reduction of avoided cost from about $54 to $26/ton is significant and, while still higher than DOE’s goal of $10/ton, indicates a positive trend.

CASE STUDY OF THE ENGINEERING FEASIBILITY AND ECONOMICS OF CO_2 CAPTURE ON AN EXISTING COAL-FIRED POWER PLANT

Alstom Power Inc., ABB Lummus Global Inc., and American Electric Power assessed the retrofit of CO_2 capture technologies for Unit No. 5 of the AEP Conesville Power Plant (Alstom Power, 2001). Alstom Power examined three retrofit concepts termed A, B, and C and defined as follows:

A. Conventional coal combustion in air, followed by CO_2 separation with a commercial MEA-based absorption and stripping process.

B. Coal combustion in oxygen with flue gas recycle for temperature control (oxycombustion).

C. Coal combustion in air with oxygen removal and CO_2 separation using a mixture of MEA and MDEA.

Each concept was compared to the base case, i.e., the existing plant operating without CO_2 capture. The study concluded that:

- There are no major technical barriers to prevent application of the concepts.
- Gas cleaning and compression are relatively simple.
- Energy penalties for capture and compression are high for all of the concepts. Net plant output is reduced from the base case by 59% (for Concept C) to 77% (for Concept A).

- Specific costs are high, ranging from \$800 to \$1800/kW with replacement power included and from \$1000 to \$2200/kW when replacement power is not included.

- The incremental cost of electricity ranges from 3.4 to 8.4 cents/kWh and the avoided CO_2 cost ranges from \$42 to \$98/ton of CO_2.

- The CO_2 capture ranged from 91% to 96% of the amount generated.

- The oxycombustion concept is the best alternative of the three based on incremental cost of electricity and mitigation cost evaluation criteria.

The processes used in the three concepts are basically the same as described earlier for oxycombustion and amine capture technologies. Important aspects specific to the three concepts that were studied include:

- For Concept A, solvent regeneration requires approximately 4.7 million Btu/ton CO_2. In the Alstom study, steam from the intermediate pressure turbine served as the source of the thermal energy.

- A conventional cryogenic ASU provides the oxygen for combustion in Concept B.

- In Concept C, the oxygen in the flue gas would poison the sorbents, requiring conversion to CO_2 by burning natural gas in a De-Oxy catalyst process. The CO_2 could then be removed with the mixture of MEA and MDEA. Solvent regeneration requires about 3.4 million Btu/ton CO_2 or 72% of that required in Concept A.

Table 9 presents major plant performance estimates for the three concepts. Net plant output was significantly reduced as a result of the CO_2 capture systems, which can be easily seen in the table. Therefore, each concept was also analyzed with replacement power making up the difference. It was assumed that replacement power would be supplied by a natural gas-fired turbine combined-cycle (GTCC) operation with an efficiency of 57.1% on a lower heating value (LHV) basis. CO_2 would not be captured during the production of replacement power.

Net plant efficiencies are reduced from 35% (HHV basis) for the base case to 20.5% for Concept A, 22.5% for Concept B, and 22.4% for Concept C (all calculated without replacement power). The efficiency of the oxycombustion concept is similar to the other concepts despite its much larger auxiliary power requirement because the other concepts consume large amounts of steam, thus penalizing their efficiencies.

The reported costs for the three concepts are shown in Table 10. The specific costs (\$/kW) are based on the lower net output in cases without replacement power. The replacement power is assumed to be GTCC without CO_2 capture capabilities (as described in the previous paragraph), which is priced at \$450 per kW installed.

Annual operating and maintenance (O&M) costs for the base case are about \$16/kW of fixed O&M and about \$0.0045/kWh for variable O&M. The variable costs are solely for FGD lime and for ash and sludge disposal. Incremental costs for Concepts A, B, and C were calculated to range from about 0.4 to 0.6 cents/kWh for fixed costs and about 0.9 to 2.3 cents/kWh for variable O&M.

The report also performed a sensitivity analysis in which 66 CO_2 capture cases were compared. All of the cases indicated that the cost of electricity would

Table 9. Conesville Station Performance Data (without replacement power unless otherwise noted)

Performance Item	Base Case No Capture	Concept A MEA	Concept B Oxycombustion	Concept C MEA and MDEA
Coal Energy Input, million Btu/h	4229	4229	4140	4229
Natural Gas Energy Input, million Btu/h	0	18	11	886
Total Energy Input, million Btu/h	4229	4247	4151	5114
Total T-G Output, kW	463,478	331,422	463,056	431,290
Total Auxiliary Power, kW	29,700	76,007	189,709	95,317
Net Plant Output, kW	433,778	255,414	273,347	335,973
Net Plant Efficiency, %, HHV	35.0	20.5	22.5	22.4
Net Plant Efficiency with Replacement Power, % HHV	NA	27.3	28.4	25.7
Net Plant Heat Rate, Btu/kWh, HHV	9749	16,626	15,188	15,223

Table 10. Concept Costs for the Conesville Station CO_2 Capture Retrofit

Concept	Units	Without Replacement Power	With Replacement Power
A. MEA Scrubbing	$ millions	409	489
	$ per kW	1602	1128
B. Oxygen Combustion	$ millions	285	357
	$ per kW	1042	823
C. MEA – MDEA Scrubbing	$ millions	738	782
	$ per kW	2197	1803

significantly increase as a result of CO_2 capture but that the oxygen combustion technology, Concept B, would result in the lowest incremental cost of electricity (12%to 19% lower than Concept A and 47% to 51% lower than Concept C) of the concepts studied for CO_2 capture over 90%. Similar results were obtained when mitigation costs were compared. If less CO_2 could be captured, Concept A would probably be the best alternative.

ESTIMATION OF CAPTURE COSTS FOR IMPORTANT CO_2 SOURCES IN THE PCOR PARTNERSHIP REGION

A spreadsheet tool was prepared to support the PCOR Partnership's evaluation of options for CO_2 sequestration. The objective of the spreadsheet is to calculate performance and cost estimates for various CO_2 separation and capture scenarios for three important CO_2 sources in the PCOR Partnership region: power generation, petroleum refining, and cement production. An effort was made to provide consistent estimates across all of the options; therefore, the results are best used for screening and comparison. Because performance and cost for many components within the systems are variable, plant-, site-, or technology-specific evaluations would require additional process design and engineering for each specific case. Costs and other impacts of replacement power are not currently considered in the spreadsheet tool. All of the spreadsheets calculate costs for the production of the CO_2 stream at the appropriate pressure for pipeline transport and sequestration. The spreadsheet was developed using the guidelines prescribed in the "Carbon Capture and Sequestration Systems Analysis Guidelines" prepared by NETL and dated April 2005.

Power Generation

Coal-fired power generation is the largest stationary source of CO_2 in the PCOR Partnership region. The spreadsheet tool can be used to calculate the CO_2 capture cost for six different subcritical pc units firing either lignite, bituminous or subbituminous coal:

- Plants without CO_2 removal with SO_2 and NO_x control.
- Plants without CO_2 removal or SO_2 or NO_x control.
- Retrofit plants with amine system CO_2 removal.
- New plants with amine system CO_2 removal.
- Retrofit plants with oxygen combustion systems.
- New plants with oxygen combustion systems.

The spreadsheet can also be used to calculate the cost of CO_2 removal in IGCC and GTCC plants.

Several subcritical pulverized lignite-fired units are located in west-central North Dakota, so plant performance and CO_2 capture costs were estimated for retrofit plants with 1) an amine system and 2) an oxygen combustion system. The results, presented in Table 11, indicate that both capture methods are similar in net thermal efficiency. The cost to produce electricity for the oxygen combustion system is roughly 30% higher than the amine plant. The table presents both capture and avoided cost for power plants. The capture cost is the actual cost of removing the CO_2 from the flue gas and is calculated by subtracting the cost of electricity of the reference case without CO_2 removal from the cost of electricity for the case with CO_2 removal and converting this differential cost of electricity to an annual cost and then dividing by the tons of CO_2 removed per year. In the case of power plants, in which some of the power produced is used

Table 11. Estimates for CO_2 Capture in Typical PCOR Partnership Lignite-Fired Power Plants

	Subcritical PC Plant Without CO_2 Removal	Retrofit Plant, amine process	Retrofit Plant, oxygen combustion
Net Thermal Efficiency, %	33.0	23.5	21.2
Cost of Electricity, ¢/kWh	2.0	2.5	3.3
CO_2 Capture Cost, $/ton CO_2	NA	23.2	31.6
Avoided Cost, $/ton CO_2	NA	35.0	54.7

to capture the CO_2, it is usually considered more appropriate to express the costs of CO_2 avoided, sometimes referred to as the mitigation cost. This is calculated by comparing a plant with removal to a reference plant without removal by dividing the differential cost of electricity by the difference between the quantity of CO_2 emitted by the plant without removal and the quantity of the CO_2 emitted by the plant with CO_2 removal (Haines et al., 2004).

The costs of producing electricity are in the range of those calculated for the Conesville Station retrofit case study. Avoided CO_2 costs calculated by the spreadsheet are slightly lower than the range calculated for the case study.

Other Industries

Spreadsheets were also developed for two of the PCOR Partnership region's largest stationary CO_2 sources: petroleum refining and cement production. To construct the spreadsheets, data from power generation studies were combined with data from the industry and CO_2 production and capture via amine systems. These performance and cost estimates are considered to be order-of-magnitude approximations.

The spreadsheets were used to estimate CO_2 removal costs of $50.77/ton and $45.54/ton for typical PCOR Partnership petroleum refining and cement production operations, respectively.

CONCLUSIONS

Several conclusions can be drawn about the cost and effectiveness of technologies that can be used to capture CO_2 from large industrial sources:

- A wide range of CO_2 separation and removal processes are either available or under development.

- The concentrations of SO_2, SO_3, and NO_x in flue gas limit the techniques that can be applied to the capture of CO_2 from fossil fuel-fired power plants, the largest source of CO_2 emissions in the United States.

- When applied to fossil fuel-fired power plants, CO_2 separation processes reduce power output through an increase in energy consumption. Efficiency reductions can range from 2% to roughly 11%, depending upon the fuel, the plant configuration, and the type of capture system.

- Calculated avoided CO_2 costs currently range from roughly $18 to $55/ton. Improvements in both design integration/simplification and sorbents are reducing these costs.

- Oxygen combustion technology was found to be the best alternative for CO_2 capture for a bituminous coal-fired power plant. The PCOR Partnership cost and efficiency estimations for lignite-fired power plants reached similar conclusions.

- The spreadsheet tool developed for use by the PCOR Partnership to screen scenarios and estimate cost and performance of source/capture technology pairs appears to produce results that agree reasonably well with other studies and models.

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