Carbon Dioxide Capture Technology for the Coal-Powered Electricity Industry:

A Systematic Prioritization of Research Needs

by

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Bachelor of Science, Chemical Engineering
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Submitted to the Engineering Systems Division
in Partial Fulfillment of the Requirements for the Degree of

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Abstract

Coal is widely relied upon as a fuel for electric power generation, and pressure is increasing to limit emissions of the CO_2 produced during its combustion because of concerns over climate change. In order to continue the use of coal without emitting CO_2, low cost technologies must be developed for capturing CO_2 from power plants. Current CO_2 capture technology is expensive, both in terms of capital and operating cost, so research and development efforts will be heavily relied upon to improve the economic profile of the technologies. With scarce resources available for R&D, and a number or different technologies competing for these funds, efforts must be prudently prioritized in order for successful advancements to be realized.

This thesis assesses the state-of-the-art CO_2 capture technologies available today, as well as the leading technology options for improvement. It also examines types of R&D, government and industry roles in R&D efforts, and methods and tools for managing these efforts. From these analyses, qualitative conclusions about how to prioritize CO_2 capture technology R&D efforts to ensure advancement are offered.

There are three technological pathways for CO_2 capture – post-combustion, oxy-fired, and pre-combustion capture - and several technology options for improvement in each pathway. There are currently no clear winners, and there is much uncertainty in which technologies have the most potential to reduce the cost of capture. Government and industry interests should both be involved in advancing R&D, but should play different roles depending on the type of research and the maturity of the technology. Portfolios of potential technologies in various stages of development should maintained by both government and industry researchers and developers, and they should use a variety of portfolio management tools to aid in decision-making. This approach will ensure that the best technologies are advanced and CO_2 capture technologies will be capable of helping meet future challenges.

Thesis Supervisor: Howard Herzog
Title: Principle Research Engineer, Laboratory for Energy and the Environment

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List of Acronyms

ASU	Air Separation Unit
CO_2	Carbon Dioxide
COE	Cost of Electricity (in $/kWh$_e$)
DOD	Department of Defense
DOE	Department of Energy
ECV	Expected Cash Value
EOR	Enhanced Oil Recovery
ESP	Electrostatic Precipitator
FGD	Flue Gas Desulferizer
GAO	General Accounting Office (U.S.)
HHV	High Heating Value
HRSG	Heat Recovery Steam Generator
IECM	Integrated Environmental Control Model
IGCC	Integrated Gasification Combined Cycle
ITM	Ionic Transport Membrane
kW_e	Kilowatts Electric Power
kWh_e	Kilowatt-Hour Electric Power
MCFC	Molten Carbonate Fuel Cell
MEA	Monoethanolamine
MW_e	Megawatts Electric Power
MW_{th}	Megawatts Thermal Energy
NASA	National Aeronautics and Space Administration
NH_3	Ammonia
NO_x	Nitrogen Oxides
PC	Pulverized Coal
SCR	Selective Catalytic Reducer
SO_2	Sulfur Dioxide
SOFC	Solid Oxide Fuel Cell
TPC	Total Plant Cost (in \$/kW_e)
TRL	Technology Readiness Level
WGS	Water Gas Shift

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Biographical Note

Salem Esber holds a BS in chemical engineering, cum laude, from Ohio University (2002). He worked for nearly two years as an engineer for the Ohio Environmental Protection Agency, and has had summer research experiences with the International Institute for Applied Systems Analysis and the Department of Chemical Engineering at the University of South Carolina, and a summer internship with Pacific Environmental Services, Inc.

Salem was born in Canton, OH, on February 5, 1979, and grew up in Oxford, OH, where he graduated from Talawanda High School (1997). He enjoys fishing, outdoor recreation, athletics, and travel.

1.0 Introduction

1.1 Background & Motivation

The demand for energy in the U.S., and across the globe, has been steadily increasing in recent years, and is projected to continue to increase for years to come. Much of this demand is met through the production of electric power from inexpensive coal in combustion systems, which emit large quantities of carbon dioxide to the atmosphere in the process. Simultaneously, concerns over the effects of global climate change, which is strongly a factor of atmospheric CO_2 concentrations, are also increasing. In order to manage the conflict between increasing demand for affordable electric power and increasing concerns over climate change, strategies for supplying low-carbon power are being pursued.

In the event that serious CO_2 emission limitations are adopted, technological solutions will be needed to avoid CO_2 emissions while the use of coal is continued. The separation of CO_2 from post-combustion flue gas or, alternately, from fuel prior to combustion, can be achieved with existing technology, but not without high capital and operational costs. This thesis assesses the state-of-the-art technologies and potential options for improvement in CO_2 capture processes for the coal-fuelled electric power industry, and recommends a path forward for advancing research and development for those technologies.

1.2 Thesis Objectives & Approach

The primary question this thesis seeks to answer is,

> **"How should research and development efforts in CO_2 capture technologies for the coal-fuelled electric power industry be prioritized and advanced?"**

This question implicitly asks a number of other important questions; what should the roles of government and private industry be, what decision making tools and structures can be used to ensure a rigorous and effective process, what should be done in the short term versus the long term, how should risks and rewards be balanced, and, ultimately, which technologies should be chosen and who should decide what these are?

To answer the overarching question, it is important to have a strong understanding of what the technology options are and what their limits appear to be. There are a number of potential technological approaches and pathways for capturing CO_2, and a broad and scattered literature base describing them. It is difficult for decision-makers to gain a complete awareness of all the options, let alone gain enough understanding of each to decide where to allocate scarce research and development resources. To help in overcoming this difficulty, this thesis presents a comprehensive review of technology options for CO_2 capture for the coal power generation industry, and allows interested individuals to gain an understanding of the status of CO_2 capture technology and the potential pathways forward.

In addition to a technology assessment, this thesis also examines issues in managing research and development efforts, and discusses policies which can be undertaken to help focus these efforts and ensure that CO_2 capture technology is advanced. It will look at potential steps that can be taken in the near term that will provide options for long-term solutions.

Supplying the energy to facilitate wealth and prosperity, while simultaneously alleviating the risks of climate change, is a challenge that requires advances in both technology and policy. Technology options must be well understood, and they require prudent policy decisions in order to advance. Based on conclusions drawn from the technology assessment and the research and development review, this provides suggestions for a systematic approach for analyzing options and formulating decisions in research and development efforts in CO_2 capture technology.

2.0 Post-Combustion Technology

Post-combustion CO_2 capture refers to the capture of CO_2 from the flue gas stream of a conventional pulverized coal (PC) power plant. Conventional coal plants are based on a simple concept – they use the heat from burning raw coal to make steam, which drives turbines to generate electric power. Several process variations are possible, but nearly all coal-powered plants operating in the U.S., and in the world, are conventional subcritical or supercritical PC plants.

2.1 Overview

2.1.1 Pulverized Coal Power Plant without CO_2 Capture

In order to understand how post-combustion capture works, and to appreciate the technological challenges, it is important to first understand how a PC power plant works (see Figure 1). In a typical plant, raw coal is milled to the consistency of talcum powder, and fed pneumatically to the boiler in a stream of pre-heated combustion air (Deutch & Moniz, 2006). The coal particles are rapidly heated as they enter the combustion chamber, which pyrolitically decomposes the organic structure within the coal into combustible gases, gaseous tars, and a carbonaceous char particle that includes the ash materials. The gases and carbon combust in the coal flame at temperatures between 2100 and 2700 °F, giving off heat and producing CO_2 and water vapor, and leaving behind an ash residue. Also in the combustion chamber, SO_2 and NO_x are formed by oxidation of sulfurous and nitrogenous compounds present in the coal. NO_x is also produced through a thermal formation process in which oxygen atoms present in the flame gases react with N_2 from the combustion air (Williams, *et al.*, 2000).

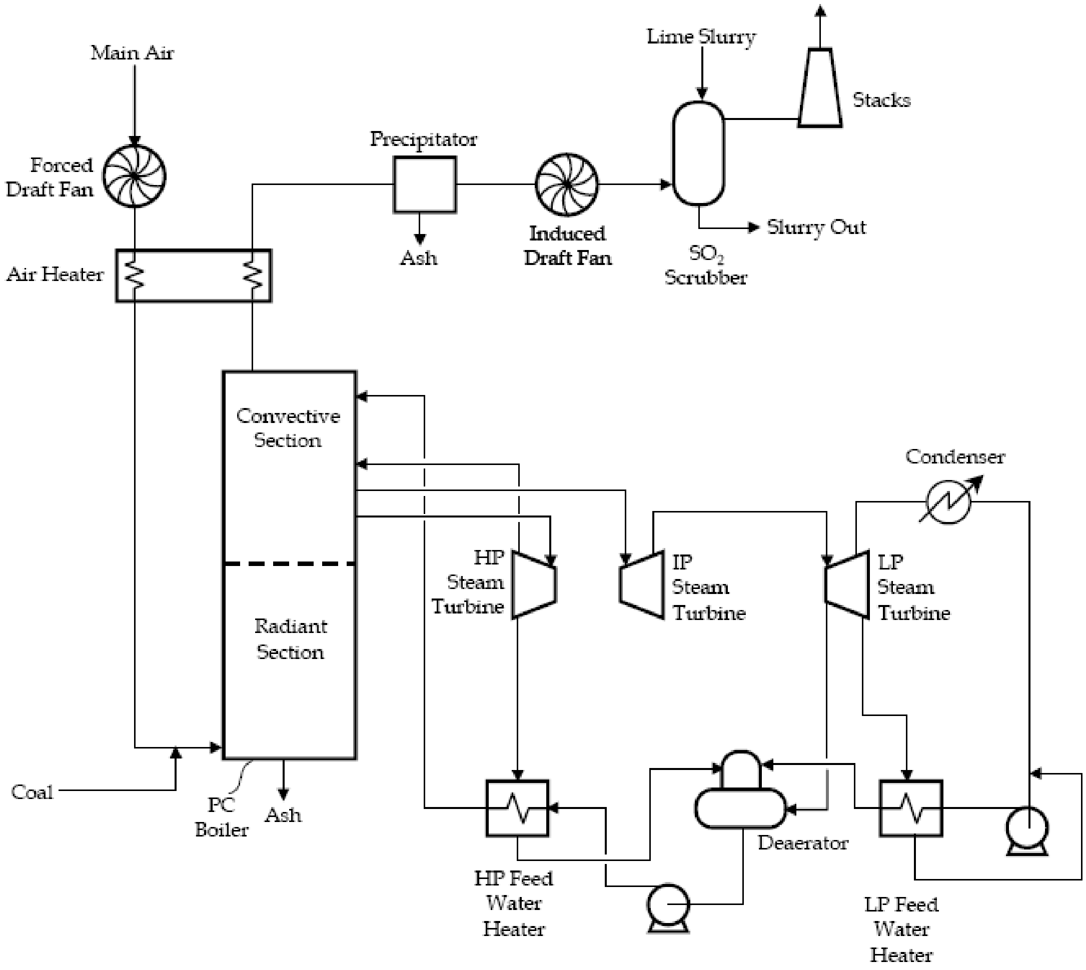

Figure 1. Pulverised Coal Power Plant without CO_2 Capture (Adapted from U.S. DOE NETL, 2002)

Heat from the combustion process is transferred to pressurized water through tubes that line the boiler wall, generating high pressure steam for the steam cycle (to be described below). The flue gas leaves the convective section of the combustion chamber at around 600 °F, and passes through the air heater after which its temperature is reduced to about 300 °F (U.S. DOE, NETL, 2002). At this point, the flue gas is made up primarily of N_2, H_2O, and CO_2.

In modern plants, the flue gas is then treated to meet environmental restrictions before release to the atmosphere. Some plants have a selective catalytic reducer (SCR) following the air heater, although it is not pictured in Figure 1. The SCR uses ammonia or urea to reduce NO_x to N_2, although in-boiler controls are often used in lieu of these expensive systems. The flue gas then typically passes through an electrostatic precipitator (ESP) to remove boiler fly-ash, then through an induced draft fan which forces the gases through the system, and maintains a slight negative pressure in the boiler. Finally, a flue gas desulfurizer unit (FGD) is sometimes used to remove SO_2 when high sulfur coals are burned (U.S. DOE, NETL, 2002). The treated flue gas is then ejected to the atmosphere.

The steam cycle is where the energy in the steam is converted to useable electric power. Subcritical PC plants typically have one steam reheat cycle (as shown in Figure 1), although some have a double reheat system. The high pressure steam reaches pressures around 2400 psi and temperatures of 1000 °F before being passed through the high pressure turbine. The outlet from this turbine is reheated, then passed through an intermediate pressure turbine, then either reheated again or passed directly to the low pressure turbine. The low pressure turbine outlet is condensed and pumped through a series of heat exchangers, de-aerated, and sent back to the boiler to generate high pressure steam (U.S. DOE, NETL, 2002). All of the turbines are coupled to generators, which produce electricity. PC plants with subcritical steam systems typically have plant thermal efficiencies in the 34-38% range, on a higher heating value (HHV) basis[1] (Deutch & Moniz, 2006).

The steam cycle can be designed to operate at higher temperatures and pressures to improve the efficiency of the plant. Current supercritical steam cycles operate at around 3530 psi and 1050 °F, with an overall plant thermal efficiency of around 38-40%. There are some "ultra-supercritical" plants in operation at 3850 psi and 1100 °F, and materials advancements could allow pressures of 5300-5600 psi and temperatures of 1290-1330 °F, reaching efficiencies of 42-45% for bituminous coal (Deutch & Moniz, 2006). For plants with supercritical and ultra-supercritical steam systems, the flue gas processing

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[1] Thermal efficiency is defined as the percent ratio of electric output to energy fed to the system. For example, a 500 MW plant that is fed 4.88×10^9 Btu/hr would be 35.0% efficient by the following calculation:

$$\frac{500MW}{4.88x10^9\,Btu/hr} * \left(\frac{1000kW}{1MW}\right) * \left(\frac{3414Btu}{kW \cdot hr}\right) * 100\% = 35.0\%$$

portion of the plant downstream of the boiler remains essentially the same, as does the flue gas composition. Upgrading an existing subcritical system to supercritical or ultra-supercritical is not a trivial matter, however, and effectively means that the majority of the plant would need to be rebuilt.

It is important to note that improvements in efficiency offered by supercritical and ultra-supercritical systems are equivalent to a reduction in CO_2 emissions. As efficiency is improved, more electricity is generated from the same amount of coal input and, likewise, the same amount of by-product (including CO_2) output. If CO_2 capture is considered, the fact that there is less CO_2 produced per kWh_e of electricity generated (at higher efficiencies) means that there is less capture cost per kWh_e.

2.1.2 Pulverized Coal Power Plant with CO_2 Capture

Post combustion CO_2 capture technology concepts can vary greatly, but the common characteristic is that the capture process takes place following combustion and steam generation. Flue gas properties can be highly variable, depending on the properties of the coal and the configuration of the boiler, but generally fall within the ranges shown in the "Raw" flue gas column in Table 1 prior to flue gas cleaning.

In today's state of the art PC power plants, electro-static precipitators (ESPs), flue gas desulfurizers (FGDs), and often selective catalytic reducers (SCRs) are employed to remove particulate matter, sulfur dioxide (SO_2), and nitrogen oxides (NO_x), respectively. The ESP, FGD, and SCR change the composition of the flue gas in important ways. Table 1 shows typical flue gas properties for a PC power plant that employs these technologies, but does not have a CO_2 capture system.

Flue Gas Analysis		
	Raw	**Treated**
Temperature (°F)	300	129 - 143
Pressure (psi)	14.4	14.4
Flow rate (ton/hr)*	2700 - 3200	2800 - 3400
N_2 (%)	67 - 74	62 - 67
H_20 Vapor (%)	8 - 15	16 - 22
CO_2 (%)	11 - 12	~11
O_2 (%)	5 - 6	~5
Ar (%)	0.8 - 0.9	0.7 - 0.8
SO_2 (ppm)	400 - 2300	3 - 15
NO_x (ppm)	20 - 25	2 - 5
HCl (ppm)	30 - 110	3 - 10

*On a 500 MW_e plant basis.

Table 1. Typical Raw and Treated Flue Gas Properties (IECM, 2005).

The post-combustion capture of CO_2 is analogous to the capture of other air pollutants; it is the addition of another set of process equipment at some point in the flue gas processing train. Generally, CO_2 capture processes are designed to follow the ESP, FGD, and SCR, and these units may require re-optimization or reconfiguration. Acid gases such as SO_2 and NO_x can poison solvents in capture processes, and particulate matter can also degrade solvents and damage process equipment, so a relatively clean flue gas stream may be needed for CO_2 separation.

The challenge is to remove a significant portion of the CO_2 from the flue gas stream, at the lowest possible cost. The primary separation is that of CO_2 and N_2. For the purposes of this thesis, it will be assumed that the removed CO_2 stream will be prepared for pipeline transportation and geologic storage, which means it must be pressurized higher than the critical pressure of CO_2, usually to 100 atm or greater. The CO_2 must be nearly free from non-condensable gases such as N_2 and O_2, so that single phase flow can be achieved, and must be dehydrated to avoid corrosion problems.

The relatively low concentration of CO_2 in the flue gas makes the separation difficult, and actually eliminates some capture technologies from reasonable consideration. A higher concentration of CO_2 provides a higher driving force for separation processes. This fact explains why separation from the flue gas stream of a coal-fired plant is more attractive than separation from a gas-fired plant or directly from air, where CO_2 concentrations are lower. In addition, it is very significant that the flue gas from a coal boiler leaves the system at atmospheric pressure, and hence has a low CO_2 partial pressure. Separations which are driven by a high CO_2 partial pressure differential, such as most membrane separation systems, can essentially be dismissed because of the prohibitive cost of pressurizing such a large volume of gas.

Post-combustion CO_2 separation is a major challenge because such a large volume of flue gas is generated. For example, a typical 500 MW_e subcritical PC power plant burning Illinois #6 coal with a HHV efficiency of 35% emits approximately 2.7 million kg/hr of flue gas, of which 463,000 kg/hr is CO_2 (Deutch & Moniz, 2006). To put this in perspective, the same plant produces approximately 12,700 kg/hr of SO_2 and 1,900 kg/hr of NO_x (most of which is captured in the air pollution control devices). Controlling CO_2 is a considerably larger task than previous flue gas pollution control efforts. It requires large process units, large quantities of process energy, and can require large quantities of additional process feedstock.

SO_2 and NO_x can be serious concerns for CO_2 capture systems, even in low concentrations. Levels of SO_2 in the flue gas are a direct function of the sulfur content in the coal, so higher sulfur coal types are more problematic for capture systems than low sulfur coals. NO_x levels are a function of nitrogen levels in coal, but more a function of burner design and flame conditions. SO_2 and NO_x can foul solvents in chemical absorption systems and SO_2 can cause corrosion. Most chemical absorption systems require that SO_2 and NO_x concentrations be less than 10 ppmv and 20 ppmv, respectively (IEA, 2004). These levels are lower than is currently required, but are attainable with current technology. Existing plants with FGDs would require a modification to achieve these levels, but new plants could be designed to do this at relatively little additional cost. Low NO_x burners and an SCR could be used to meet the NO_x requirements (FLUOR, 2004). For other types of post-combustion capture systems, SO_2 and NO_x requirements may be different, but the presence of these compounds may still complicate matters.

The oxygen in the flue gas is also a concern for solvent systems, and must be taken into consideration. It rapidly degrades amine solvents, and an inhibitor must be added to the solvent in order for it to survive in the presence of O_2 (Roberts, *et al.*, 2005).

2.2 Current Technology/State of the Art

2.2.1 Technology Overview

Post-combustion separation is currently employed in about a dozen facilities worldwide to produce CO_2 for commercial sale, and the technology used is a chemical absorption system using monoethanaoloamine (MEA) as the absorbent (Herzog & Golomb, 2004). In a PC power plant, the amine system is added to the process following the FGD, just before the flue gases go to the stack, as shown in Figure 2. The balance of the plant essentially remains the same, although some modifications to the steam cycle are necessary to accommodate the heat requirements in the amine plant. The FGD may also need improvement to further reduce SO_2, which otherwise fouls the solvent in the amine plant.

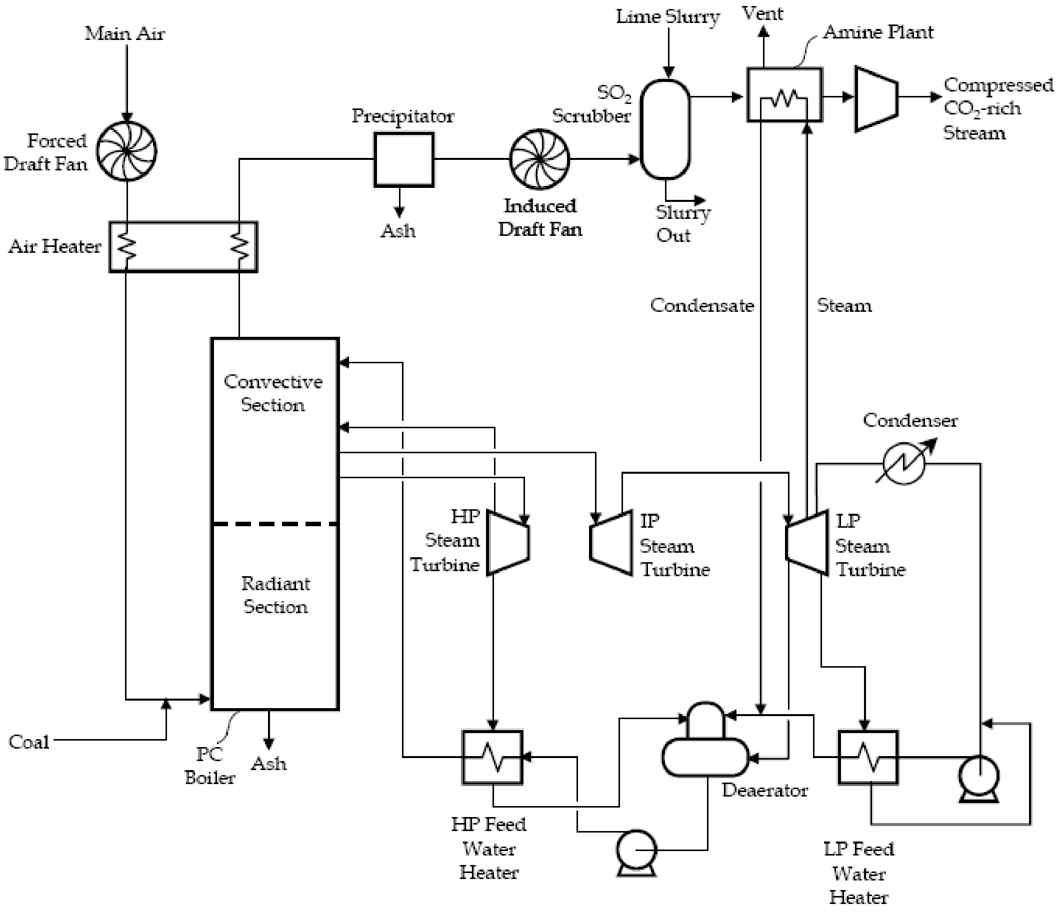

Figure 2. Pulverized Coal Power Plant with Amine Scrubbing for CO_2 Capture (Adapted from U.S. DOE NETL, 2002)

In a chemical absorption plant, the flue gas is contacted with the MEA in a packed absorption tower (see Figure 3). The CO_2 and MEA react to form a protonated amine and a bicarbonate anion in solution by the following reaction:

$$C_2H_4OHNH_2 + H_2O + CO_2 \leftrightarrow C_2H_4OHNH_3^+ + HCO_3^- \qquad (1)$$

The remaining flue gases are washed to remove any residual MEA, and exhausted to the atmosphere. After filtration and a heat recovery step, the CO_2-enriched solvent is passed through a regeneration unit in which counter-current steam drives the reaction to the left, producing a stream of H_2O and CO_2. The H_2O is condensed out, leaving a stream of CO_2 that is over 99% pure and prepared for compression. The CO_2-lean solvent is cooled and recycled to the absorption tower (Herzog & Golomb, 2004).

In addition to the MEA absorbent, Mitsubishi Heavy Industries, Ltd., and Kansai Power Co. have developed a proprietary blend of hindered amines that is used in a similar system (Iijima, *et al.*, 2004). The hindered amine solution is said to have a 67% higher CO_2 absorption capacity, and a 20% lower heat of regeneration (Iijima, *et al.*, 2004). This allows for smaller solvent flows and associated pumping costs, and smaller diameter absorbers and strippers. The lower heat of absorption means that less steam is required for regeneration and the energy penalty is lower. The solvent is also resistant to degradation by oxidation, such that make-up requirements are one-fifth of those of MEA and corrosion problems present by the degradation products are not such an issue (Iijima, *et al.*, 2004).

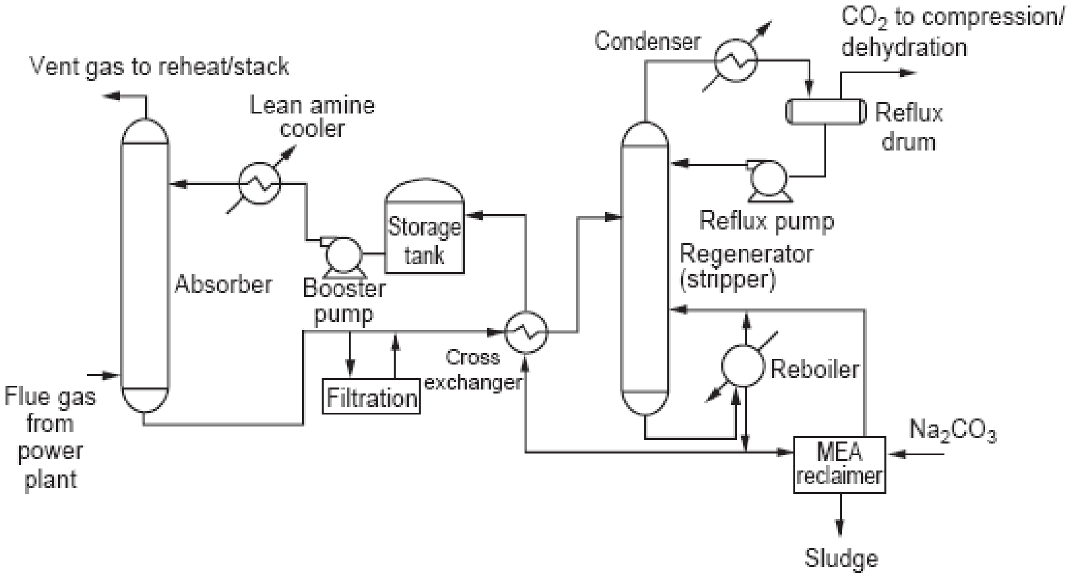

Figure 3. Amine Chemical Absorption Process (Adapted from Herzog & Golomb, 2004)

Regardless of solvent choice, the solvent cooling, heating, and pumping processes and the compression of the purified CO_2 all require energy, and reduce the overall efficiency of the plant. The absorption column and regeneration unit are both expensive capital investments. If this technology is to be implemented on new PC plant builds, these costs must be lowered. Improvements are possible in the heating and cooling processes if better heat integration techniques are developed. Pumping costs and the capital cost of the units can be reduced if solvent improvements are made which reduce the amount of solvent required. The amount of energy required to compress the CO_2 from atmospheric pressure (at which the system operates) to a one-phase liquid for pipeline transportation and storage could also be improved with advanced compressor designs.

2.2.2 CO_2 Capture Cost

One thing is certain about CO_2 capture – it increases both the total plant cost (TPC) and the cost of electricity (COE). Deutch and Moniz performed a study in which TPC and COE were estimated for pulverized coal plants with subcritical, supercritical, and ultra-supercritical steam systems, both with and without capture. Their estimates were formulated based on an analysis of recent design studies, with input from experts in industry, and are summarized in Figure 4. The results show that adding an amine chemical absorption system increases TPC by 54-74% and increases COE by 57-69%, (Deutch & Moniz, 2006). The increase in TPC and COE is more pronounced for less efficient subcritical systems than for the higher efficiency super and ultra-supercritical systems.

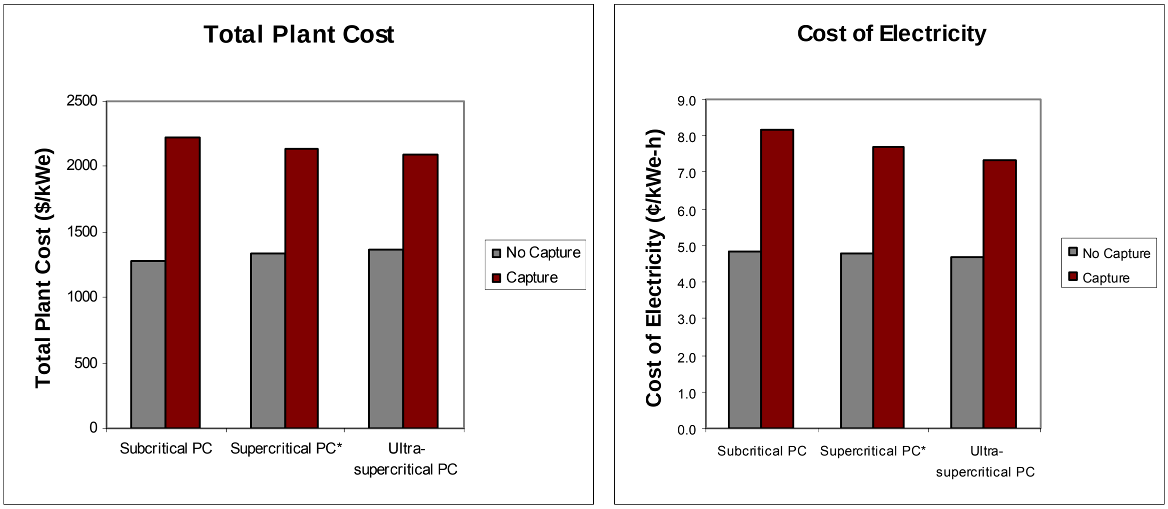

Figure 4. Total Plant Cost and Cost of Electricity for PC Plants with and without Capture (Adapted from Deutch & Moniz, 2006)

2.2.3 *Plant Efficiency Losses*

Capturing and compressing CO_2 is the most expensive part of the capture, transport, and storage process. The costs can be expressed in terms of overall plant efficiency losses, which translate into lost electricity production, and lost revenue. For a subcritical PC system, the losses can be categorized into CO_2 recovery heat, CO_2 recovery power, and compression energy. The CO_2 recovery heat is the steam that is used to heat the CO_2-enriched amine in the regeneration unit. The CO_2 recovery power is the additional power required to drive the flue gas fan and the sorbent pump which moves the amine solvent through the recovery system. The CO_2 compression energy is the energy required to compress the CO_2 to conditions for transport and storage.

Figure 5 shows what typical losses are for a subcritical plant and how these lower the overall efficiency of the plant. For supercritical and ultra-supercritical systems, the same losses would be experienced in terms of category and quantity, although the losses are simply subtracted from a higher original efficiency. For example, an ultra-supercritical plant with an efficiency of 43.3% loses 9.2 efficiency points[2] to have an efficiency of 34.1% with capture, just as the subcritical plant dropped 9.2 points from 34.3% to 25.1% (Deutch & Moniz, 2006).

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[2] It is important to make the distinction between "efficiency points" and percentage losses in efficiency. A loss in efficiency points is a decrease in efficiency where one point loss is equal to one percentage point loss in the overall efficiency. A percentage loss in efficiency is a decrease in overall efficiency as a percentage of the original efficiency. For example, a drop in efficiency from 40% to 30% would be a 10 point efficiency loss, and a 25% loss in efficiency.

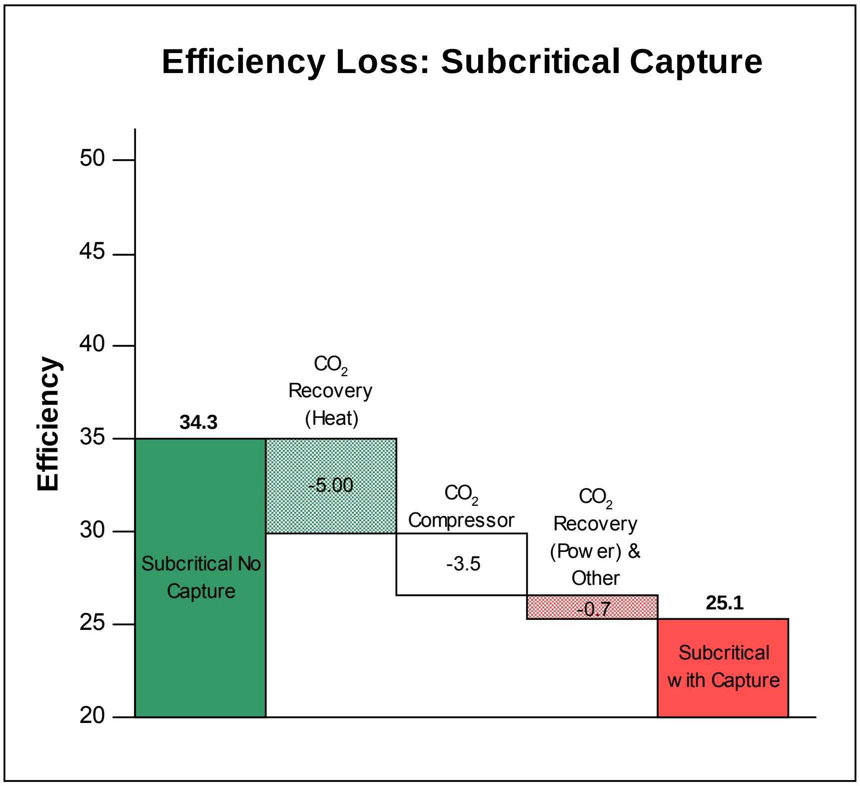

Figure 5. Efficiency Losses by Category for a Subcritical PC Plant with Capture (Adapted from Deutch & Moniz, 2006)

2.2.4 Reliability and Operability Issues

Reliability is highly valued in the electric power industry, both from the perspective of the supplier and the consumer. Consumers demand a power system which provides a steady stream of consistent quality power, with few or no interruptions or fluctuations in voltage. Producers require high availability in order to keep costs low and to recoup investments. The generation, transmission, and distribution of power is a complicated matter, and any factors which limit the reliability or availability of plants are highly undesirable.

Pulverized coal plants without CO_2 capture currently have very strong and well-tested reliability records. The reliability of amine capture systems has not been tested on such a wide scale, nor has it been performed on the size of gas streams as those found at large power plants (Roberts, *et al.*, 2005). It is not a very complicated chemical process, however, and high availability of the capture portion of the plant is expected.

One important characteristic of post-combustion capture systems is that they are installed downstream of the steam generation system and are completely separate from the power block, where the electricity is generated. The implication of this feature is that if the capture system encounters difficulty, the portion of the plant that produces power will be largely unaffected. The plant can continue operation while the CO_2 is vented to the atmosphere, until the capture system can be brought back online. In essence, a plant with post-combustion capture should be no less reliable than a similarly designed plant without capture. This is different from such systems as IGCC, which may have to be completely shut down if the capture equipment experiences failure or must undergo maintenance.

2.3 Research Areas/Potential New Technologies

The high cost of capture using amine systems has prompted research into alternative post-combustion CO_2 capture options and novel improvements to existing technologies. Efforts are focused on bringing down the capital cost or energy penalty of certain parts of the process. For example, much work is currently underway to lower the heat required for regeneration of CO_2 solvents, because it is such a strong component of the energy penalty of capture, as shown in Figure 5.

2.3.1 Advanced Solvents

A variety of solvents could be used in the absorption/regeneration process, and each has its advantages and disadvantages. The key physical factors in solvent selection are heat of absorption/regeneration, CO_2 absorption rate, CO_2 absorption capacity, resistance to degradation and impurities, corrosion, and volatility (Cullinane, *et al.,* 2002, Rochelle, 2005). A solvent with a low heat of absorption requires less energy during regeneration, which can lead to significant savings. A solvent with a high absorption rate minimizes absorber size and pressure drop across the absorber and associated pumping costs. A high absorption capacity allows more efficient operation and can reduce solvent volume requirements and equipment size. Solvents with high resistance to degradation reduce solvent make-up costs, and can reduce gas clean-up costs in the stages prior to the absorption system. (Cullinane, *et al.,* 2002). Corrosive solvents are undesirable because they can shorten process equipment lifetime. Solvent volatility can be an important issue because a volatile solvent can escape with the flue gases and may exceed environmental limits.

These factors must be optimized as solvent research goes forward, and must be balanced when determining which solvent is the most appropriate to use in a plant design. Regeneration energy, however, is by far the most important factor in affecting cost because of its strong impact on overall plant efficiency, as noted in Section 2.2.3.

MEA has been the most commonly chosen solvent so far, and has often been enhanced with additives to improve its performance. Improvements must still be made, however, for post-combustion solvent absorption/regeneration processes to be a competitive option for CO_2 capture. It is useful to compare novel or advanced absorbents to MEA because it is in use today. Table 2 shows how a number of alternative solvents compare with MEA, and the following sections give further explanation (Note: hindered amines were discussed in Section 2.2.1).

Performance of Alternative Solvents Relative to MEA						
	Heat of Regenerat-ion	**CO_2 Absorption Rate**	**CO_2 Absorption Capacity**	**Resistance to Degradation/ Impurities**	**Corrosion**	**Volatility**
Sterically Hindered Amines	+	?	+	+	+	?
Aqueous NH_3	+ ?	-	+	+	+	-
K_2CO_3/PZ	+	+	=	?	?	=
Amino-acid Salts	+	+	+	=	?	+
Alkali-metals	?	+	+	+	?	+
Other Amines	=	=	=	=	=	=
Performance Characteristics Key: + Better, - Worse, = Similar, ? Indeterminate						

Table 2. A Comparison of Alternative Solvents to MEA

Aqueous Ammonia

There has recently been discussion of using aqueous ammonia as a solvent rather than MEA, in a similar absorption/regeneration process. Ciferno, *et al.* and Resnick, *et al.* have published papers that discuss the benefits of using ammonia as a solvent, including a high CO_2 loading capacity, low equipment corrosion risk, low absorbent degradation, and a low energy requirement for absorbent regeneration (Ciferno, *et al.*, 2005, Resnick, *et al.*, 2004). They also highlight the potential for selling the ammonium sulfate and ammonium nitrate by-products as an additional source of revenue which would help recoup some of the cost of capture.

Both authors claim that there is a significant increase in CO_2 loading capacity when comparing aqueous NH_3 to MEA, although they disagree on just how much. Resnick, *et al.*, estimate NH_3 solutions to have three times the capacity as MEA, while Ciferno, *et al.*, estimate the increase to be about 25% (Ciferno, *et al.*, 2005, Resnick, *et al.*, 2004). This would allow for smaller solvent flows, and hence smaller equipment and pumping costs.

Ciferno, *et al.*, claim that using NH_3 could lead to a reduction in steam requirements of up to 67%, and Resnick, *et al.*, claim that steam use could be reduced by 49-64% from an MEA system (Ciferno, *et al.*, 2005, Resnick, *et al.*, 2004). Because the regeneration steam is one of the principal costs in a chemical absorption system, this is a significant savings opportunity. Additionally, the combination of lower solvent degradation and a cost of NH_3 that is about 6-10 times less than MEA leads to significantly lower solvent make-up cost. The bulk of NH_3 that is degraded would be in the form of ammonium sulfate or ammonium nitrate, both of which are saleable fertilizers[3].

There are significant problems with using ammonia as a solvent, however, as identified by Rochelle (Rochelle, 2005). The volatility of ammonia is a major obstacle, because it has a tendency to exit the absorber column to the atmosphere with the flue gas. Rochelle estimates that the NH_3 concentration in flue gas could be as high as 3%, much greater than environmentally acceptable levels of less than 10 ppm (Rochelle, 2005). Steps such as cooling the exit gas or adding a water or acid wash could reduce these levels, but would introduce additional costs and complications that would negate many of the advantages of using ammonia, and there seems to be no apparent practical method to avoid this problem (Rochelle, 2005).

Rochelle also believes that the estimates of Ciferno, *et al.*, and Resnick, *et al.*, of reductions in regeneration steam are optimistic, and the steam requirements would be similar, if not higher, than those for MEA (Rochelle, 2005). Additionally, he argues that the rate of absorption for the NH_3 process would be much slower than MEA, which may require the absorber to be three times the height of an MEA absorber and add a major increase to the capital cost of the system (Rochelle). .

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[3] The market for ammonium sulphate and ammonium nitrate fertilizers is small compared to the amount of these substances that would be produced if ammonia solvent systems were widespread. It is possible that a major CO_2 capture effort would result in such an increase in supply of these fertilizers that prices would be depressed significantly, reducing the benefit of selling the by-products.

Some key questions that remain are:

1. Can the volatility problem be reasonably solved?
2. Are CO_2 capacity improvements significant?
3. Are steam regeneration improvements significant?
4. Do the other advantages outweigh the disadvantages of the slow reaction rate?

Piperazine/Potassium Carbonate Solution

Researchers have been investigating the possibility of using an aqueous piperazine/potassium carbonate (K_2CO_3/PZ) solution as a replacement for MEA in a chemical absorption system (Cullinane, *et al*., 2002). The proposed system works in the same manner and has the same configuration as the process shown in Figure 3, except that the solvent is a 5m K^+/2.5m PZ solution rather than an MEA solution.

The research has shown that a piperazine/potassium carbonate solution is better than an MEA solution in terms of heat of absorption and rate of absorption, and roughly equal to MEA in CO_2 capacity (Cullinane, *et al*., 2002). This solution has a lower heat of regeneration than the MEA solution translating to a 25 to 49% decrease in regeneration energy (Cullinane, *et al*., 2002). The piperazine/potassium carbonate solution also has a rate of absorption that is 1 to 5 times faster than MEA, allowing for a smaller absorption column (Cullinane, *et al*., 2002). The piperazine/potassium carbonate solution has been shown to have a low volatility, reducing the environmental emissions problem that ammonia faces. The cost of PZ (\$2.20/lb) is a little higher than MEA (\$0.76/lb) however, which may offset some savings (Cullinane, *et al*., 2002).

Some key questions that remain are:

1. Is solvent degradation significant?
2. Is corrosion a problem?

Amino-acid Salts

Some work has been done to investigate the advantages of using amino-acid salts such as potassium glycinate, potassium taurate, and potassium sarcosine (Feron & ten Asbroek, 2004). Some salts were found to absorb CO_2 faster than MEA, some could potentially reduce regeneration energy significantly, some have good resistance to degradation, and all have low volatilities (Feron & ten Asbroek, 2004). One distinct advantage that some amino-acid salts have is that they have a particularly high CO_2 capacity, which could allow for considerably smaller equipment sizes. A complicating factor is that a precipitate forms during absorption, which requires that equipment be able to handle slurries.

These solvents could be especially useful where small equipment size is necessary, such as space-limited sites. Some key questions that remain are:

1. What effects will the precipitate have on process design?
2. Is corrosion a problem?

Alkali Metal-based Sorbents

Alkali metal-based sorbents are another option for capture. These slurries of $NaHCO_3$, Na_2CO_3, or K_2CO_3 can absorb CO_2 in a spray dryer or fast transport reactor, and can be regenerated in a bubbling fluidized bed (Eom, *et al.*, 2005). They have shown high CO_2 capacity, high resistance to degradation, and fast reaction times. It is not clear if there is any advantage in the energy requirements of regeneration, although there are claims that regeneration requires less heat than the MEA process (Coker, *et al.*, 2005). More work is required to determine the potential for this technology to be competitive, and some key questions remain:

1. Is there any reason to pursue these sorbents absent a heat of regeneration advantage?
2. Is corrosion an issue?
3. Will volatility or airborne salt dust be an issue?

Other Amines

The use of other amines, such as diethanolamine (DEA), methyldiethanolamine (MDEA), 2-(butylamino)ethanol (BEA), N-methyldiethanolamine (NMDEA), 2-(methylamino)ethanol (MMEA), 2-(ethylamino)ethanol (EMEA) and 2-(2-aminoethyl-amino)ethanol (AEEA) have been considered as an alternative to pure MEA solutions (Hoff, *et al.*, 2004, Bozzuto, *et al.*, 2001). Blending of these amines and the addition of compounds such as piperazine can also affect performance, and there are certainly other amines that were not listed. MDEA and AEEA have shown improvements over MEA in terms of lowered heat of regeneration and somewhat higher capacity in the case of AEEA, but these are not revolutionary improvements (Hoff, *et al.*, 2004, Bozzuto, *et al.*, 2001). Most other amines have shown poorer performance than MEA, and great advances should not be expected (Hoff, *et al.*, 2004).

2.3.2 Process Integration

There is the potential to significantly reduce parasitic energy losses if heat integration and novel flow-sheeting methods are used in typical amine absorption systems (Roberts, *et al.*, 2004). Most current designs include stripping steam that is bled from the steam turbine power generation system, which is the most important process integration.

Another improvement that has been suggested is to use the heat generated when compressing the purified CO_2 stream in the stripper reboiler (Fisher, *et al.*, 2005). This improvement saves up to 4.6% of CO_2 removal costs, although it causes a slight increase in capital costs (Fisher, *et al.*, 2005). The stripping column could also be operated at variable pressures, with compressors between each step in the column. In this way, partial CO_2 compression actually takes place in the regeneration column, and can save 8.4% of capture costs (Fisher, *et al.*, 2005). The two improvements added to the regeneration system simultaneously could result in a total capture cost reduction of 9.8%, and an overall cost of electricity savings of 5.2% (Fisher, *et al.*, 2005). These are significant improvements that could be made today, with relatively little additional research and development.

There are probably many other opportunities for cost saving through higher levels of process integration. A major research thrust should be to further reduce the costs of amine absorption systems by taking advantage of potential savings through deeper integration of the capture plant with the rest of the power plant.

2.3.3 Cryogenic Processes

A recent study by a team from Alstom Power and Ecole des Mines de Paris investigated a cryogenic separation technique that takes advantage of the CO_2 sublimation temperature (frosting temperature) to make the CO_2/N_2 separation (Clodic, *et al.*, 2005). In this approach, flue gases are cooled by a refrigerant in a heat exchanger to below the frosting temperature of CO_2, around -120 °C, such that solid CO_2 builds up on the heat exchanger tubes (see Figure 6). After sufficient solids build-up, the heat exchanger is heated, evaporating a pure stream of CO_2 for compression and transportation. Two heat exchanger/evaporators are used in a swing configuration, with one frosting and the other defrosting. Cold energy in the defrosting exchanger is recovered and used in the frosting exchanger, improving the energy efficiency of the process.

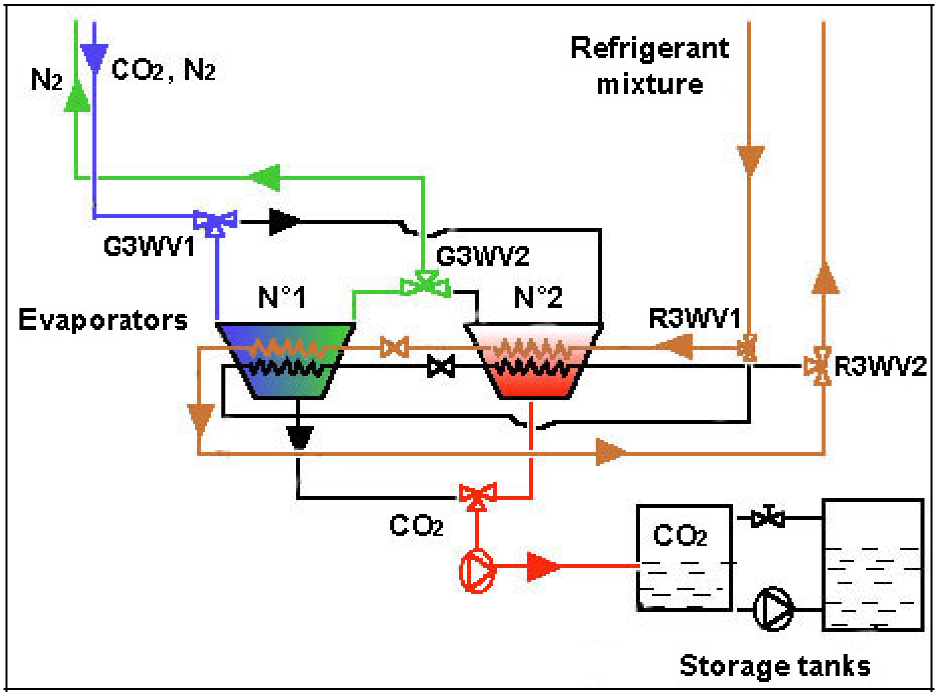

Figure 6. Alstom/Ecole des Mines de Paris Anti-Sublimation Process (Adapted from Clodic, *et al.*, 2005)

The authors have built a mock-up model to demonstrate feasibility and estimate efficiency. At 90% CO_2 capture, the anti-sublimation process was estimated to have an energy penalty of only 3.8 - 7.3 percentage points, which is considerably better than any other processes so far developed (Clodic, *et al.*, 2005). They also cite the possibility that other pollutants could also be captured in such a system, which may eliminate the need for other costly pollution control equipment, such as FGDs.

Key questions surrounding this concept are:

1. How does this concept compare to the MEA process on an economic basis?
2. Do the anti-sublimation/sublimation and heat transfer processes happen fast enough such that equipment size is reasonable?
3. Can this technology scale up to handle the flue gas from a power plant?

It should be noted that other cryogenic processes, such as low temperature distillations and an adaptation of the Ryan-Holmes process used by the natural gas industry have been discussed, but are generally found to be impractical.

2.3.4 Other Technologies

Stimulus-Responsive Separation Aids and Structured Fluids

There is some interest in separation processes that are based on stimulus-responsive separation aids and structured fluids. Stimulus responsive separation aids rely on small changes in process operations to effect large changes in capacity (Herzog, 2002). An example of such a system is the carbon fiber composite molecular sieve that is being developed at Oak Ridge National Laboratory. This is a monolithic electrically conductive carbon adsorbent composed of carbon fibers bound by a phenolic resin, and it operates by adsorbing CO_2 when gases are flowed through it, then desorbing it when a current is passed through the sieve (Judkins & Burchell, 2001).

A structured fluid is a separation aid that self-assembles reversibly to first capture then release CO_2 (Herzog, 2002). An example of a structured fluid (which, incidentally, is also a stimulus responsive separation aid) is a liquid crystal system which could capture CO_2 then release it when an electric current is passed through (Herzog, 2002). These processes are only in the beginning stages of research, but have the potential to dramatically reduce the energy required to make a CO_2 separation.

Lithium Zirconate Temperature Swing Adsorption Wheel

A mechanism has been proposed for removing CO_2 by adsorption on a solid lithium zirconate surface in a novel concept that allows for a continuous process (see Figure 7). In this technique, CO_2 is adsorbed to Li_2ZrO_3 which coats a rotating wheel by passing flue gas across the rotor at temperatures in the range of 450-600 °C (Alstom, 2006). After the adsorbed CO_2 is moved 180° around the track of the rotor, it is removed by a hot sweep gas. The CO_2 is then cooled and compressed, and the CO_2-depleted flue gas is cooled and vented to the atmosphere (Alstom, 2006). This process is similar to chemical absorption because it is limited by the heat of regeneration of the adsorbent.

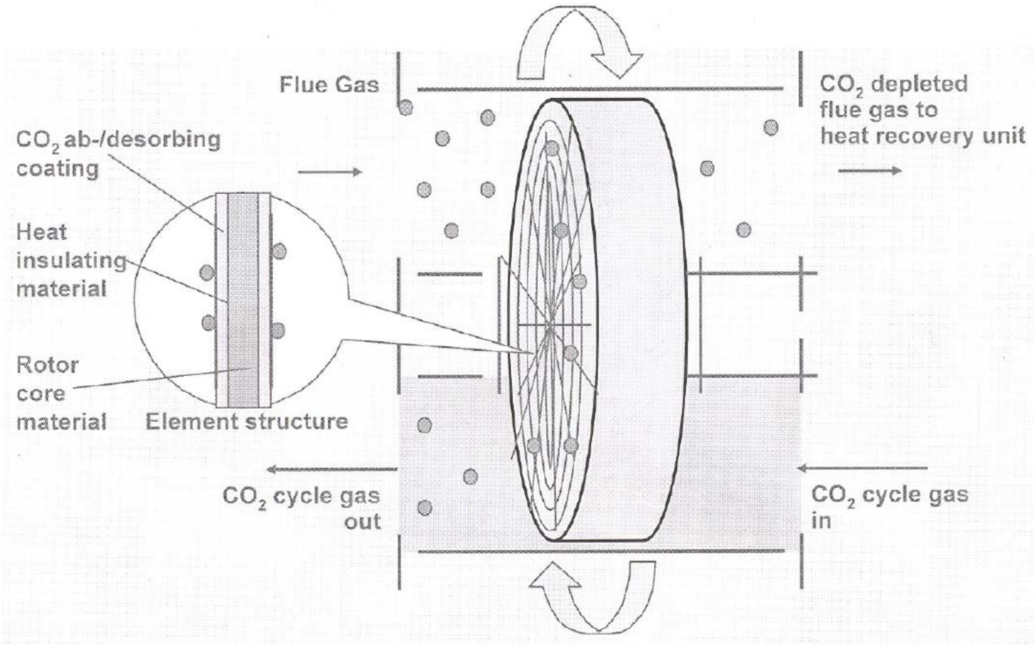

Figure 7. Lithium Zirconium Wheel Diagram (Adapted from Alstom, 2006)

Molten Carbonate Membranes

Some consideration has been given to other novel separation techniques. One such approach is to use molten carbonate to transport carbon in the form of carbonate ions across a membrane (Granite & O'Brien, 2005). The advantage to using molten carbonate is that it is nearly 100% selective for CO_2, it has a relatively high conductivity, and could potentially have a low parasitic power requirement (Granite & O'Brien, 2005). However, it is very corrosive, is poisoned by SO_2, can degrade if temperatures are too high, and requires huge stacks to scale up to match the requirements of a power plant (Granite & O'Brien, 2005).

Solid electrolyte membranes

Solid electrolyte membranes could do the same job as molten carbonate and avoid some of the corrosion and degradation problems, but there are still major difficulties with the membrane technology (Granite & O'Brien, 2005). Much work is required to make molten carbonate or solid electrolyte membranes a reality.

Membrane contactors

Membrane contactors are another technology which can improve CO_2 capture processes, and can be used in place of absorber and stripper columns in the amine chemical absorption process (Herzog, 2002). The advantage to membrane contactors is that they can increase the surface area for the absorption and stripping process, allowing for much smaller equipment sizes (Herzog, 2002). This savings is partially offset by the cost of the membrane, however. This type of capture system is best suited for situations in which space is limited.

2.4 Chapter Conclusions

Post-combustion capture of flue gas CO_2 is a viable option for CO_2 control. The current state-of-the-art systems use MEA chemical absorption/regeneration systems to achieve capture, although with high additional capital costs and a high energy penalty. MEA capture increases TPC by 54-74% and COE by 57-69%, depending on which type of steam system is employed. The bulk of the energy is lost in regenerating the solvent and compressing the CO_2 for transport and storage.

There are a number of technological solutions under development now in attempts to reduce the cost of capture for post-combustion systems. Several alternative solvents have been investigated, each having their advantages and disadvantages, but none seems to be clearly superior to MEA. Deeper integrations of a chemical absorption system into the overall plant could yield some significant gains without requiring revolutionary innovations. Some novel concepts, such as the cryogenic CO_2 frosting process, stimulus-responsive separation aids and structured fluids, the lithium zirconate wheel, and some membrane processes have also been investigated and may have some advantages, including reducing heat of regeneration requirements.

What is clear is that there is a lot of uncertainty about which processes could lead to real improvements, and which really have no real prospects for reducing the cost of capture. When reviewing the literature, it is difficult to compare processes or technologies that have been studied by different groups because they each have different bases for analysis, and they often inject optimism into their analyses. Technologies should be carefully and objectively analyzed, and efforts should be made to reduce uncertainty and bias.

3.0 Oxy-fired Technology

Oxy-fired coal combustion technology has been discussed as a solution for bringing down the cost of capturing CO_2. Some small-scale demonstrations of oxy-firing have been done, and some pilot scale plants are planned, but oxy-fired coal power plants have not otherwise been deployed at a large scale. Using oxy-fired technology can offer improvements over capturing CO_2 from post-combustion flue gases, but absent capture, there is currently no incentive to use oxy-firing for the coal power production.

3.1 Overview

In a typical oxy-fired PC design, the plant is very similar to a conventional PC power plant, as described in Section 2.1.1. The feed system, boiler, steam system, and ESP are essentially the same, but a portion of the flue gas is recycled following the ESP, and a cryogenic air separation unit (ASU) is used to provide 95% pure oxygen to the boiler (see Figure 8).

In this system, the primary separation is N_2 and O_2 prior to combustion, so that the flue gas is made up primarily of CO_2 and water vapor (U.S. DOE, NETL, 2002). The purification of CO_2 and preparation for transport and storage is thus made much easier and less expensive than for an air-fired system. The flue gas recycle step is necessary to control flame temperature and stability and to ensure proper heat flux in the boiler (Buhre, *et al.*, 2005). Most oxy-fired designs are designed with a supercritical steam cycles, at around 3530 psi and 1050 °F, with an overall plant thermal efficiency of around 30% (Deutch & Moniz, 2006).

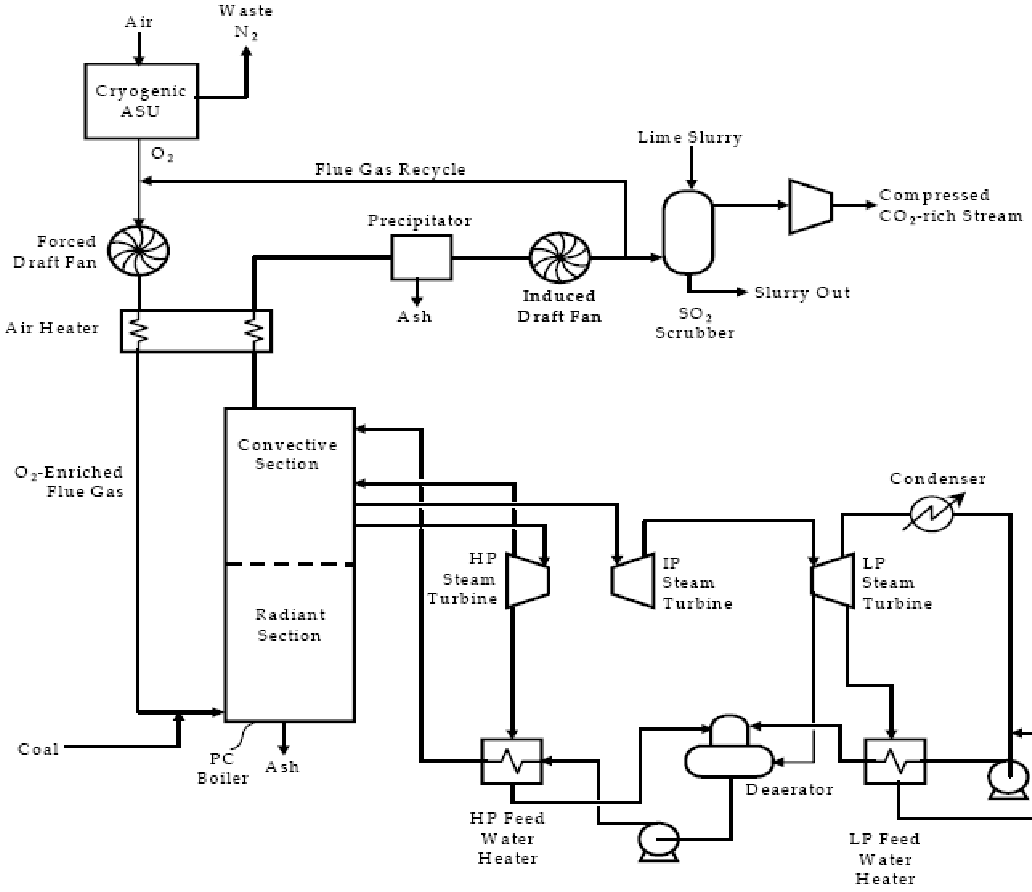

Figure 8. Oxy-fired Pulverized Coal Power Plant with CO_2 Capture (Adapted from U.S. DOE NETL, 2002)

There are several features that differentiate oxy-fired systems from conventional PC power plants. The O_2 content of the gas feed to the boiler is higher, typically around 30%, compared to the 21% O_2 gas (air) which is fed to a conventional boiler (Buhre, *et al.*, 2005). The high CO_2/H_2O gas in the furnace has a higher gas emissivity, which allows the same radiative heat transfer with a smaller volume of boiler gases than a PC system (Buhre, *et al.*, 2005). The flue gas volume prior to CO_2 purification and compression is decreased by about 80%, although it is a higher density gas and has higher concentrations of contaminants on a per volume or per mass basis (Buhre, *et al.*, 2005).

The technology needed for an oxy-fired system is available today; it does not require any major breakthroughs to build and operate one. Pilot-scale operations have been built, but none at any larger scale have been developed because incentives to capture the CO_2 are not in place, and there is no reason to use this technology except for CO_2 capture (Deutch & Moniz, 2006). The Babcock and Wilcox Company has reported flame stability, 65% NO_x reductions, and CO_2 concentrations of 85% in the flue gas (with 5% air infiltration) in a pilot-scale study (The Babcock and Wilcox Company, 2006). Boiler operation showed no negative impact, unburned combustibles were lower or the same, and furnace exit gas temperatures, convective pass heat absorption, and boiler exit gas temperature were similar to an air-fired case in this study (The Babcock and Wilcox Company, 2006).

A demonstration plant is planned for Hamilton, Ohio, where a 24 MW_e coal-fired power plant will be retrofitted with oxygen feed and flue gas recycle (The Babcock and Wilcox Company, 2006). It will undergo performance testing and should offer some insight into how the retrofit and operation of an oxy-fired system at a larger scale will work. Vattenfall, a Swedish company that owns power plants in Germany, has plans to build a 30 MW_{th} lignite burning oxy-fired boiler in Germany by 2008 (Ing & Häge, 2005). This boiler will built from the ground up and will be designed for oxy-fired combustion. It will test the entire process, from coal feed to CO_2 compression and liquefaction, with complete interconnection of the combustion and gas processing chain (except it will not have full steam cycle). The plant will demonstrate interaction of components and the basic procedural principles, and will prepare Vatenfall to complete their plans to build a 300-600 MW_{th} demonstration plant by 2015 and a 1000 MW_{th} or greater full commercial plant by 2020 (Ing & Häge, 2005).

3.2 Current Technology/State of the Art

3.2.1 Technology Overview

There are three distinctive features of an oxy-fired system: 1) the cryogenic air separation unit, 2) the flue gas recycle system, and 3) and the CO_2 purification and compression system. These systems must be well understood in order to identify potential problems and areas for improvement.

Cryogenic Air Separation Unit

Cryogenic oxygen production is a mature technology, and only minor improvements can be expected in reducing the cost or energy demands of the cryogenic ASU process (Simmonds, *et al.*, 2005). It is currently the only large-scale technology for oxygen production from air, and will probably be the air-separation technology utilized in the first generation of oxy-fired power plants (Jordal, *et al.*, 2005). Most oxy-fired systems assume 95% pure oxygen from the ASU (the remainder being primarily argon), although this could be adjusted up to purities greater than 99%, or down (Jordal, *et al.*, 2005). Higher purity oxygen is more expensive both in terms of capital and operating cost, however, and it generally offers little additional benefit to use oxygen more pure than 95%. The cryogenic ASU consumes roughly 20% of the plant gross power output when used in an oxy-fired system (Jordal, *et al.*, 2005). Supplanting cryogenic ASU with a less expensive and less energy-intensive air separation technology would be a major development in reducing the cost of CO_2 capture, and some leading options will be discussed later.

Flue Gas Recycle

As mentioned previously, flue gas recycle is necessary to control flame temperature and stability, to control heat flux properties in the boiler, and to maintain boiler temperatures below the ash melting point. There are two different types of flue gas recycle, external recycle and internal recycle. In external recycle, the flue gas stream is split after particulate removal, and ductwork is used to deliver a portion of the flue gas back to the boiler. The current state-of-the-art for oxy-fired combustion systems is to use external flue gas recycle. Typically, 60-70% of the flue gas is recycled (Deutch & Moniz, 2006, Buhre, *et al.*, 2005). In internal recycle processes, which are used in the glass and steel industry, high momentum oxygen jets induce a recycle flow within the boiler (Buhre, *et al.*, 2005). Internal recycle will be discussed in Section 3.3.3.

CO_2 Purification and Compression

Requirements for purified CO_2 stream conditions may vary depending on the target use for the CO_2 (storage, EOR, other) and on legal, regulatory, and environmental issues

(Jordal *et al.*, 2005). For example, if it is acceptable to co-sequester CO_2, SO_2, and NO_x from both a technical and regulatory standpoint, then some expensive processing steps, such as FGD, can be eliminated. Generally, it is accepted that the CO_2 stream must be greater than 95% pure, essentially free from non-condensable gases such as N_2, Argon, and O_2, free from water (to reduce corrosion and avoid formation of hydrates), free from particulate matter, and pressurized to about 110 atm (Jordal *et al.*, 2005, Mancuso, *et al.*, 2005).

Figure 9 shows a possible design for a CO_2 purification and compression plant that could be integrated into an oxy-fired power plant (Mancuso, *et al.*, 2005). In this scheme, flue gas at 80 °C (stream 1) is first directly contacted with cool water in a scrubber tank, where the majority of the moisture in the flue gases are condensed out and any remaining particulate matter is also removed (Mancuso, *et al.*, 2005). A portion of the flue gas is then recycled, and the remainder goes through a compression and cooling process before being further dried in a desiccant drying system. In the cold box, there is a two stage flash tank system which separates the non-condensable gases, which are then passed through an expander turbine to recover some useful energy, and then vented. The purified flue gas is compressed to 110 atm and cooled to ambient conditions for pipeline transport and storage.

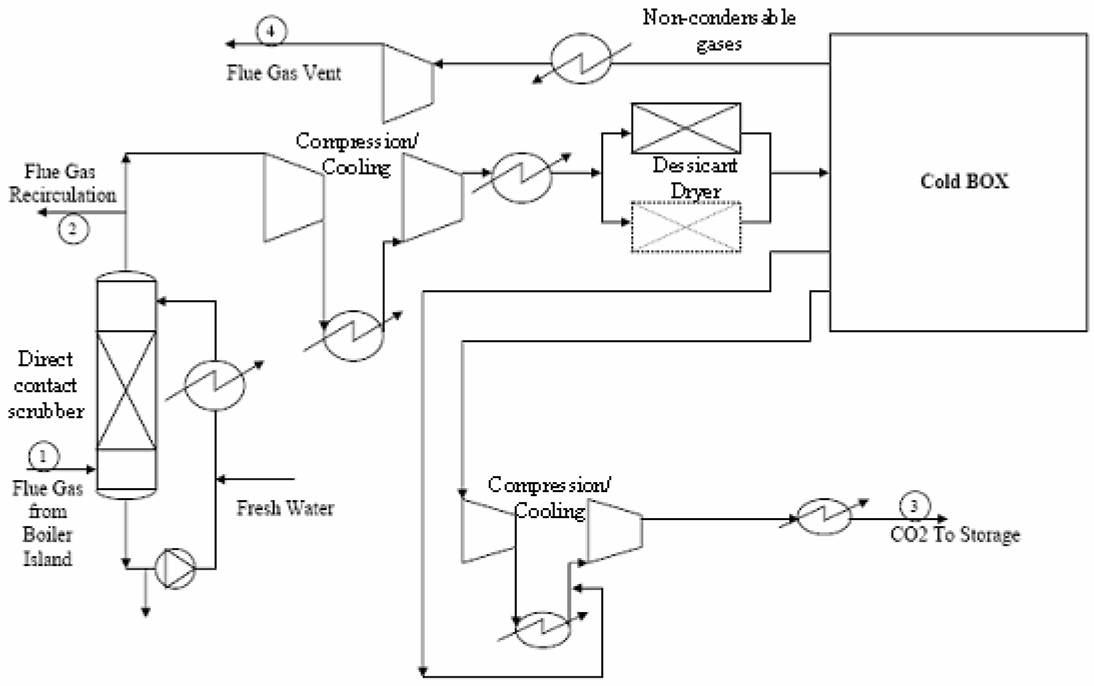

Figure 9. CO_2 Purification and Compression Plant (Adapted from Mancuso, *et al.*, 2005)

This is just one design for a purification and compression system. Other designs are possible, and steps can be taken in other parts of the power plant that would make purification simpler. For example, firing the boiler with as little excess O_2 as possible and designing and building a boiler that allows very little leakage air in reduces the presence of non-condensable gas, reducing purification requirements (Jordal *et al.*, 2005).

3.2.2 CO_2 Capture Cost

As with post-combustion systems, adding CO_2 capture increases both the TPC and the COE over a no-capture plant. Recent estimates of TPC and COE for a supercritical plant both with and without oxy-firing and CO_2 capture are summarized in Figure 10 (Deutch & Moniz, 2006). These results show that using oxy-firing with CO_2 capture increases TPC by 43% and increases COE by 46% over a no-capture plant, and these numbers are consistent with other estimates and from small-scale industrial experiences (Deutch & Moniz, 2006). These TPC and COE projections are lower for an oxy-fired system than for PC plants with today's commercial amine capture systems.

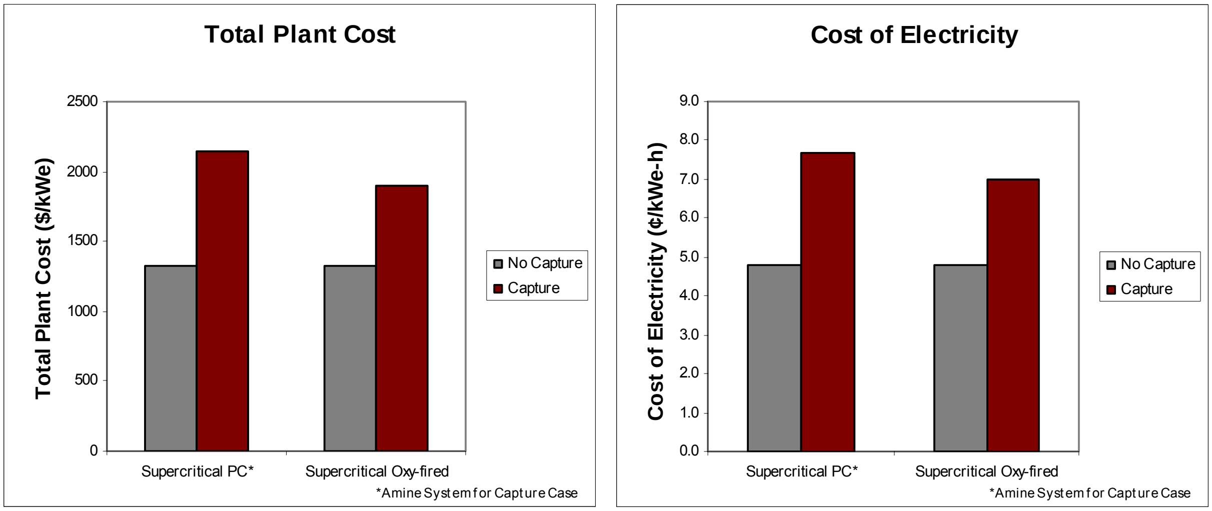

Figure 10. Total Plant Cost and Cost of Electricity for Supercritical PC Plants without Capture and with Oxy-Firing (Adapted from Deutch & Moniz, 2006)

3.2.3 Plant Efficiency Losses

As in the amine capture systems, there is significant energy consumption for an oxy-fired plant with capture, which results in overall losses in plant efficiency (Deutch & Moniz, 2006). For an oxy-fired PC system, the primary losses can be categorized into ASU energy, compression energy, and other losses. There is actually a slight gain in efficiency due to improvements in boiler efficiency and reduced energy usage in the FGD, but this is more than offset by the losses. A large amount of energy is required in the ASU to make the primary separation of N_2 from O_2. The CO_2 compression energy is the energy required to compress the CO_2 to conditions for transport and storage, and the other losses can be mainly attributed to the energy requirements of the CO_2 purification system and the flue gas fan. Figure 11 shows what typical losses are for a supercritical oxy-fired plant and how these lower the overall efficiency of the plant relative to a supercritical plant without oxy-firing and capture.

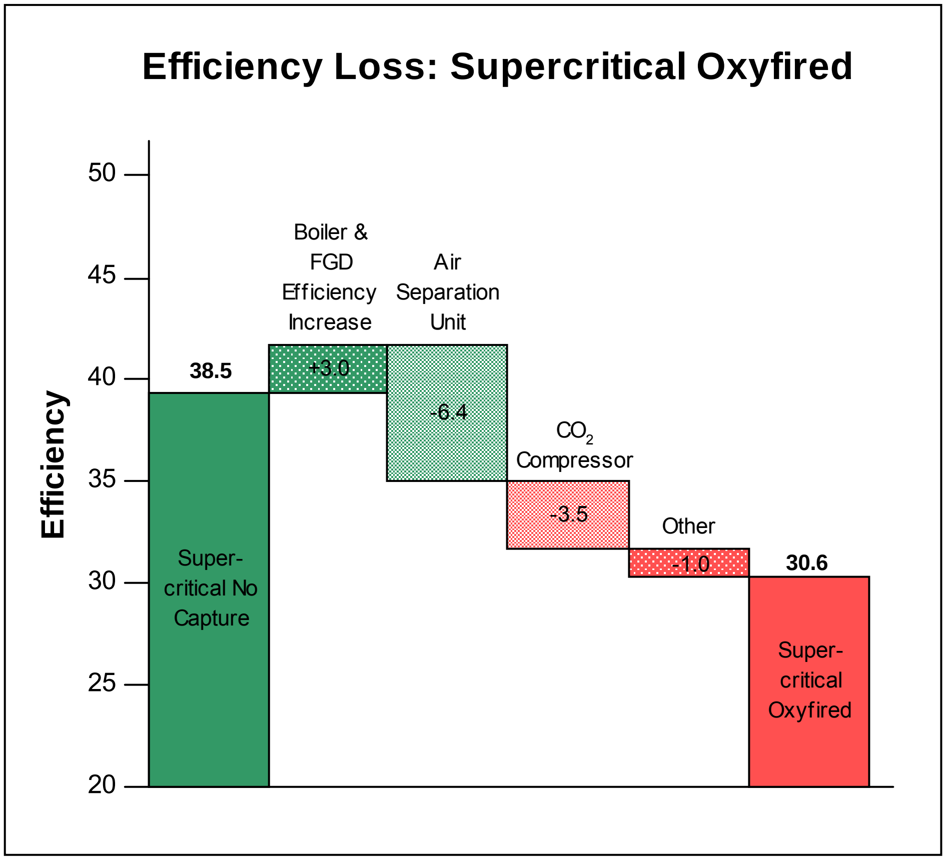

Figure 11. Efficiency Losses by Category for an Oxy-fired Supercritical PC Plant with Capture (Adapted from Deutch & Moniz, 2006)

3.2.4 Reliability and Operability Issues

Pulverized coal plants without CO_2 capture currently have very strong and well-tested reliability and operability records. Oxygen-fired boilers and burners have extensive operating histories in the steel and glass industries, and have very good reliability and operability characteristics. Several laboratory and pilot studies have been performed and show that, although there are some differences in performance, reliability and operability should not be compromised if oxy-firing is applied (Buhre, *et al.*, 2005).

One of the key differences between air fired and oxygen fired systems is that the mixture of gases in the boiler have different heat transfer and heat capacity characteristics (Buhre, *et al.*, 2005). This affects how heat is transferred from the boiler into the steam system and how stable the flame is. If the properties are substantially different, boiler or fuel feed system redesign may be necessary to achieve performance comparable to an air fired system. Results of lab and pilot-scale tests show that boiler performance actually improves with oxy-firing because of better heat transfer characteristics, although flame stability is compromised in some cases (Buhre, *et al.*, 2005). Some authors have concluded that higher oxygen concentrations must be maintained in the boiler to sustain a stable flame, and this is a problem that can be managed (Buhre, *et al.*, 2005).

There is some concern that the higher heat flux to the boiler walls and increased fouling and SO_3 deposition could lead to more corrosion in the boiler, and this issue should be further investigated (Jordal, *et al.*, 2005). Another concern is that the gas-phase concentrations of volatile metals such as mercury, selenium, and possibly arsenic may be slightly higher in an oxy-fired system, although one advantage is that the formation of submicron ash particles may be slightly reduced. (Buhre, *et al.*, 2005). Evidence shows that oxy-fired plants have lower NO_x emissions, and may possibly even have lower SO_x emissions (Buhre, *et al.*, 2005).

A reliability and operability advantage with post-combustion capture systems is that the entire plant does not need to shut down if there is a problem with the CO_2 capture equipment, as discussed in Section 2.2.4. For an oxy-fired plant, the situation is a little different. If the plant is configured such that the flue gas is cleaned of SO_2 prior to the CO_2 purification and compression steps, then the plant can continue operation if the purification and compression system encounters difficulty, with CO_2 vented to the atmosphere. Reliability and operability and would not be compromised for such a configuration. However, if SO_2 is co-captured with the CO_2, and the CO_2 equipment goes down, SO_2 concentrations in the flue gas would be too high to vent the stream to the atmosphere. If the plant is to continue operation, there must be a system in place to control SO_2.

3.3 Research Areas/Potential New Technologies

Figure 11 shows that the largest consumer of energy in an oxy-firing system is the ASU, and the CO_2 compression energy is also a major consumer of energy. Efforts are underway to improve the compression process, but novel ideas for less energy-intensive air separation processes to replace the cryogenic ASU are the primary focus for improvements in oxy-fired plants. Effective process integration, particularly with heat loads, can also make oxy-fired power plants more efficient, although this is a much lower priority than improving air separation.

3.3.1 Advanced O_2 Separation

One concept under investigation is air separation by an ionic transport membrane (ITM) integrated into the boiler system, a technology under development by Praxair, Inc. ITMs are non-porous ceramic membranes that selectively allow oxygen ions to pass through, and are driven by the O_2 partial pressure differential across the membrane (Chiesa, *et al.*, 2005). Operated in a stand-alone system, it takes a highly pressurized air feed (to maintain a high O_2 partial pressure differential) or very large membrane surface areas to achieve significant air separation, either of which is expensive. But when integrated with a boiler system, the ITM could operate with much less feed air pressurization and a smaller surface area, and could result in significant savings over a cryogenic ASU. In this type of arrangement, the coal combustion consumes the purified oxygen on the product side of the membrane as it comes out of the membrane, which helps to maintain a high driving force for producing additional oxygen. Figure 12 shows what a boiler with an integrated ITM might look like. The boiler is fed coal from the bottom, with ITM tubes and steam tubes on the walls.

Boiler-integrated ITM technology, if commercialized, could have considerable benefits. Praxair believes that the oxygen could be supplied to a boiler for one tenth the cost of a cryogenic ASU, and CO_2 could be potentially captured for as little as \$10/ton CO_2, including compression (Sirman, *et al.*, 2004). This may be an optimistic evaluation, however, and there are some serious issues that must be overcome. To operate in the severe environment of a boiler, a robust material is required that can handle compositional stress in the ITM tubes (Sirman, *et al.*, 2004). Temperature control of the membranes is both critical and difficult, carbon and ash deposition is problematic, and there remain serious questions about the long term integrity and reliability of the membrane components (Sirman, *et al.*, 2004).

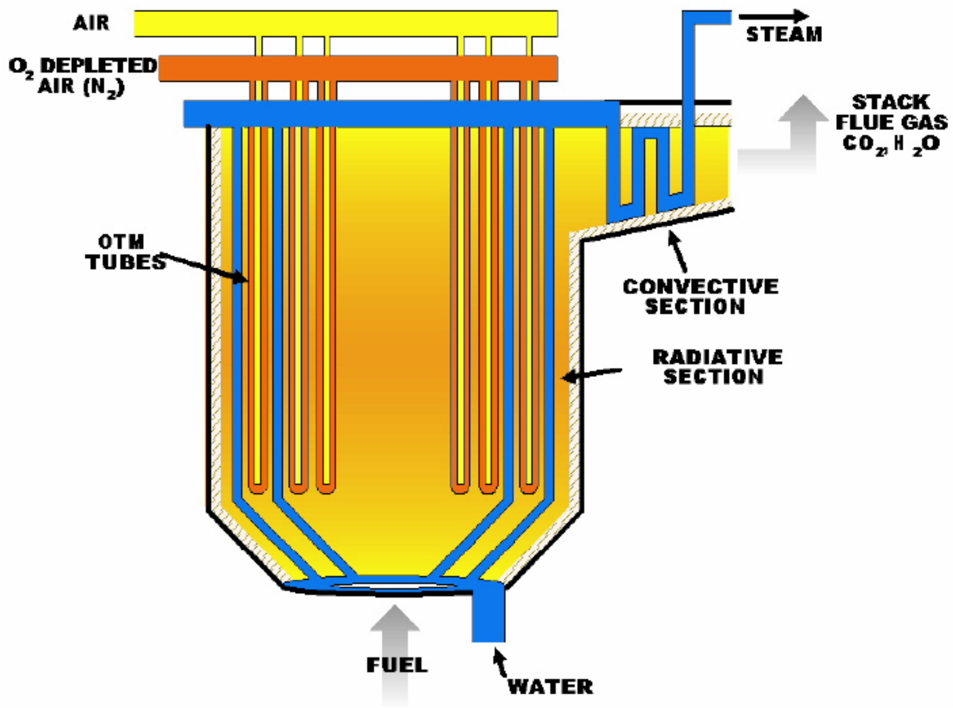

Figure 12. Boiler with Integrated Ionic Transport Membranes (Adapted from Sirman, *et al.*, 2004)

3.3.2 Chemical Looping Combustion

Chemical looping combustion (CLC) is another interesting concept for oxygen delivery (see Figure 13). This technology employs two interconnected fluidized bed reactors (air reactor and fuel reactor), in which oxygen is removed from air by an oxygen carrier by the following reaction in the air reactor, where Me = Metal (Ryden & Lyngfelt, 2004):

$$2Me + O_2 \rightarrow 2MeO \qquad (1)$$

In the second reactor (fuel reactor), the oxygen carrier is contacted with the fuel and combustion takes place by the following reaction:

$$C_nH_{2m} + (2n+m)MeO \rightarrow nCO_2 + mH_2O + (2n+m)Me \qquad (2)$$

The oxygen carrier is a metal oxide particle, usually based on copper, iron, manganese, or nickel, and delivers oxygen from the air reactor to the fuel reactor, and then is recycled to the air reactor to be enriched with oxygen again (Ryden & Lyngfelt, 2004). Reaction (1) is strongly exothermic, the heat from which is used to produce steam for power generation in turbines. Reaction 2 is usually slightly endothermic, but can be exothermic depending on which type of oxygen carrier is used. It is possible to generate some steam from the fuel reactor if an oxygen carrier with an exothermic reaction is used, but the bulk of the steam generation occurs in the air reactor.

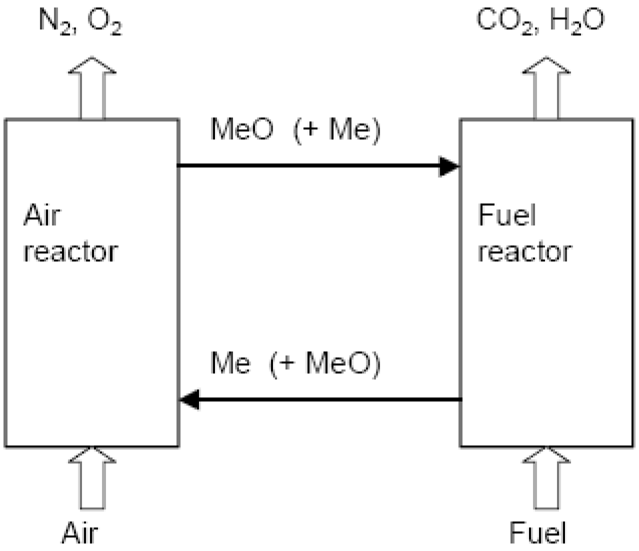

Figure 13. Conceptual Diagram of Chemical Looping Combustion System (Adapted from Adanez*, et al.,* 2004)

The fuel only comes in contact with oxygen from the carrier and never mixes with N_2, so that the products from the fuel reactor are simply CO_2 and H_2O. These can be easily separated and the CO_2 compressed for transport and storage. No cryogenic ASU is necessary and no major energy consuming separation processes are required.

Chemical looping combustion has been tested in systems using natural gas as a fuel. A very high fuel conversion can be attained in the fuel reactor, and a very high purity CO_2 stream is possible, with nearly 100% capture (Adanez, *et al.*, 2004). High retention of fines is achievable, and oxygen carrier particles have been found that neither decrease in reactivity nor particle strength over an operation time of 100 hours (Adanez, *et al.*, 2004).

It has been estimated that particle lifetime is on the order of 4,000 hours, with a cost of replacement on the order of \$1/ton CO_2 captured (Adanez, *et al.*, 2004).

There are some concerns about the use of this concept with solid fuel feedstock. It is much more difficult for the oxygen carriers to effectively deliver the O_2 to solid fuel particles, and there may be problems separating the oxygen carrier particles from ash particles after combustion. It is possible, and probably simpler, to combust coal gasification products in a CLC system.

3.3.3 Internal Flue Gas Recycle

There are several possible schemes for internal recycle of flue gas. Aspirating burners are special nozzles that are used to fire pulverized coal with an oxygen stream, which mimics air at the fuel jet. A new concept, known as dilute oxygen combustion, reacts a hot, dilute oxygen jet with a separate fuel jet to achieve uniform heating and ultra-low NO_x production in a unique boiler configuration, shown in Figure 14 (Kobayashi, 2001). In a similar design, the oxygen stream enters the boiler at the opposite corner of the boiler from the fuel jet, creating a circular flow regime. In tangential firing, oxygen and fuel are injected from the four corners of the boiler to create a circular flow, with fuel and oxygen injections alternating with height, as shown in Figure 15 (COEN, 2006).

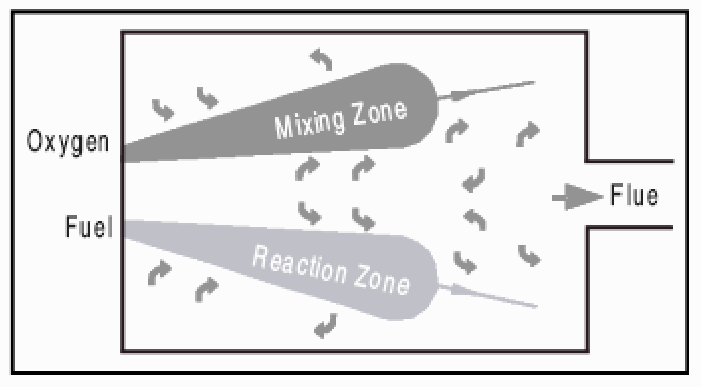

Figure 14. Dilute Oxygen Combustion System (Adapted from Kobayashi, 2001)

Figure 15. Tangential Firing Flow Regime (Adapted from Coen, 2006)

The advantage to internal flue gas recycle systems is that they eliminate the need for external ductwork and blowers, and they can reduce the flue gas volume. This could bring down the cost of a greenfield oxy-fired plant, but internal recycle systems may be difficult to achieve as a retrofit.

3.3.4 Clean Energy Systems, Inc. Rocket Engine Steam Cycle

A technology is currently being developed by Clean Energy Systems, Inc., in which gasified coal (see Section 4) is burned with oxygen in a unique steam generation system based on technology from the aerospace industry. This system relies on the injection of water during the combustion process for steam generation, as opposed to firing in a water-wall boiler to raise steam (as in conventional PC plants) or in a gas turbine with a heat recovery steam generator (as in an integrated gasification combined cycle). The resulting high energy gases drive multi-stage turbines to generate power, then pass through a condenser where the water is cooled and removed (see Figure 16 & Figure 17). Clean Energy Systems believes it could potentially reduce the cost of capture to one-tenth of the cost of a PC plant with an MEA system, (Clean Energy Systems, Inc., 2006).

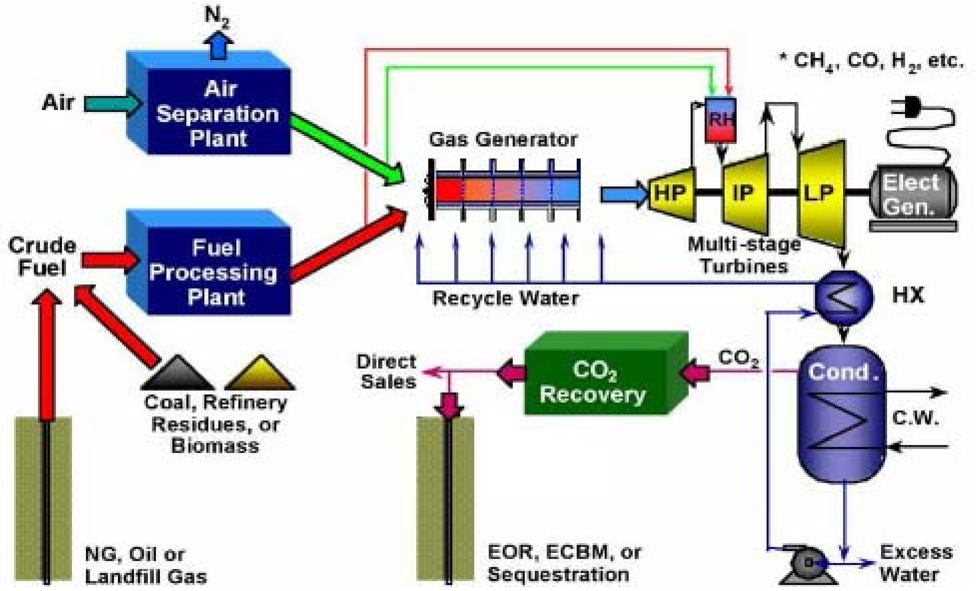

Figure 16. Process Flow Diagram for "Rocket" Style Steam Generation (Adapted from Clean Energy Systems, Inc., 2006)

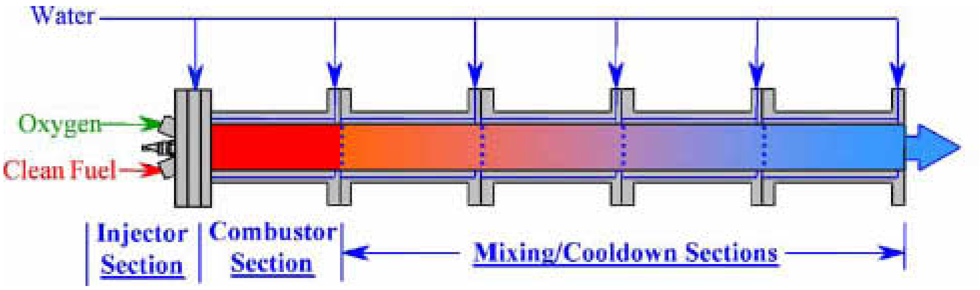

Figure 17. Close-up View of the Combustion Chamber/Steam Generator (Adapted from Clean Energy Systems, Inc., 2006)

This process may be advantageous for several reasons. The combustion technique, which provides precise, uniform mixing, as well as the injected water which controls local temperatures, both work to keep NO_x production to very low levels, so no additional process equipment is necessary for NO_x control (Clean Energy Systems, Inc., 2006). The mixing also allows for nearly exact stoichiometric oxygen supply, which means that the CO_2 stream is more pure after combustion and water removal, and removal of non-condensable gases may not be necessary (Clean Energy Systems, Inc., 2006).

The combustion chamber may also be cheaper than other alternatives, such as PC boilers and gas turbines with heat recovery steam generators (HRSG). PC boilers are large, and the steam tube systems are complex and require frequent maintenance, and HRSGs are also large and expensive. This combustion chamber would be compact and would preclude the need for a tube-based steam system or an HRSG. Additionally, this type of system is more efficient in transferring heat to the steam than conventional boilers and HRSGs, which are only 85-92% efficient.

The disadvantage to using this combustion technique with coal is that the coal must first be gasified, which requires large and costly equipment (see Section 4). An expensive and energy-intensive ASU is also required, and more oxygen is required than an oxygen-blown IGCC systems (U.S. DOE, 2002). CO_2 compression costs may also be higher than for other gasification-based capture technologies because of the low turbine exhaust pressures (U.S. DOE, 2002). There may also be separations required after combustion and water separation to prepare the CO_2 for transport and storage, although this depends on how pure the oxygen feed stream is and what the purity requirements are for the CO_2 stream.

3.4 Chapter Conclusions

Oxy-fired pulverized coal combustion with CO_2 capture is a viable option for CO_2 control, and appears to be competitive with MEA post-combustion systems both in terms of TPC and COE. State-of-the-art oxy-fired combustion systems use cryogenic ASU to produce O_2, external recycle of flue gases to control boiler temperature and heat flux characteristics, and a compression and cooling process with drying and flash systems to purify and compress the CO_2 for transport and storage. For a supercritical plant, oxy-firing with CO_2 capture increases TPC by 43% and increases COE by 46% over a similar plant with capture. While firing with oxygen actually increases the efficiency of the boiler, this is more than offset by the additional cost of the cryogenic ASU and CO_2 compression.

Because the cost of producing O_2 is so high, most efforts to improve oxy-fired CO_2 capture systems focus on the air separation process. While membrane systems are generally considered to be too expensive as stand-alone air separation systems, novel techniques for integrating them into the combustion process could reduce the cost of oxy-fired combustion. Chemical looping combustion is another novel concept for air separation that could lower the cost of CO_2 capture. The rocket engine steam system under development by Clean Energy Systems, Inc. still relies on a cryogenic ASU, but may provides gains in boiler efficiency and reduces O_2 demand enough that the cost of capture may be reduced.

As with post-combustion capture technologies, there is considerable uncertainty about which processes could lead to improvements in the cost of capture. It is not clear for example, that advantages provided by boiler-integrated ITM will offset the technical problems of putting ITMs in a boiler, and the performance of chemical looping combustion is relatively unproven in real operating conditions. In addition, the same difficulties with comparing processes and technologies persist, and seeing through the biases of the authors while reviewing the literature is also a problem.

4.0 Pre-Combustion Technology

The idea behind pre-combustion capture systems is that the CO_2 is easier to remove from a concentrated, high pressure stream prior to combustion than from a dilute stream at low pressure (as in post-combustion). To achieve this, coal is converted to synthesis gas (“syngas”), which is a mixture of primarily hydrogen and carbon monoxide. For a capture system, the carbon monoxide is converted to hydrogen gas and CO_2, the latter of which is separated for storage, while the former is combusted in a turbine for power. The syngas can also be utilized directly in a non-capture system. These types of systems are known as an integrated gasification combined cycles (IGCC), and can offer some significant benefits when used in a CO_2 capture context.

4.1 Overview

4.1.1 IGCC without CO_2 Capture

There are several types and configurations of IGCC systems, but all operate on the same premise (see Figure 18). Coal is gasified at high temperature and pressure with steam and oxygen, then cooled, cleaned of sulfur and particulates, and burned in a gas turbine for power. A portion of the heat remaining in the exhaust gas from the turbine is used to make steam in a HRSG, and the steam drives another turbine system, generating additional power.

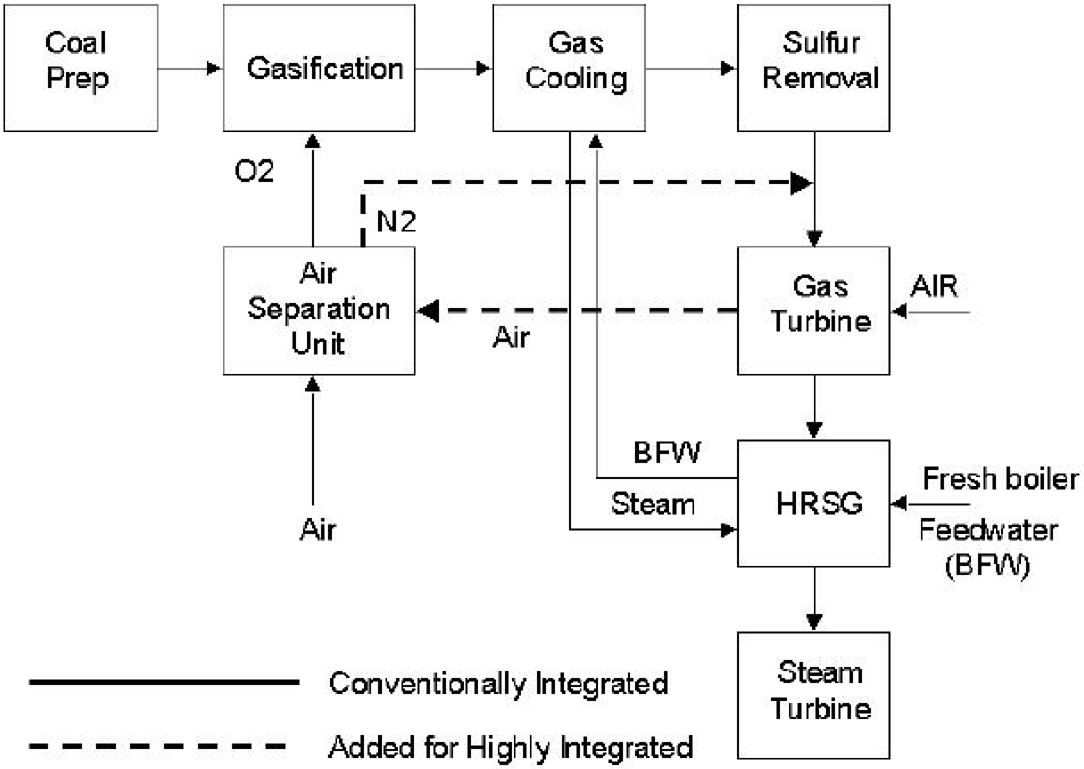

Figure 18. IGCC System without Capture (Adapted from Holt, 2001)

There are three major types of gasifiers in use today – moving bed, fluidized bed, and entrained flow, and each has their own advantages and disadvantages (see Figure 19) (Holt, 2001). In a moving bed reactor, steam and oxidant[4] are fed in the bottom of the gasifier, and they flow up through a bed of coal, which is fed from the top. The coal and steam/oxidant flow counter-currently past each other, and stages of the gasification process takes place throughout. A dry ash falls through a grate at the bottom of the vessel, and is removed there, although some systems can operate with a wet ash (slag) that flows out the bottom. Moving bed gasifiers are in use in South Africa, the U.S., Germany, Czech Republic, and China, although most uses are not for electric power production (Holt, 2001).

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[4] The oxidant for a gasifier is oxygen fed to the gasifier as either air or a purified (>95% pure) oxygen stream. Most gasifiers are fed purified oxygen.

In fluidized bed gasification, the steam and oxidant are fed from the bottom at such a rate that they mix the coal in the gasifier to a fluid-like consistency. Ash, which is typically removed as a dry solid or agglomerate, is removed from the bottom. These systems can process most coals, although are typically used with low quality coals (Holt, 2001). Of the three types of gasifiers, this type is the least widely employed today.

Entrained flow gasifiers operate with the oxidant and fuel both fed from the top and flowing co-currently to the bottom, where ash and syngas are removed. The residence time for both solids and gases is very brief (only a few seconds), and temperatures are very high. Ash is removed from the bottom as a wet slag. Because of the short residence time, a single entrained flow gasifier can produce the syngas needed for a commercial-scale operation, so most commercial IGCC plants use this technology (Holt, 2001).

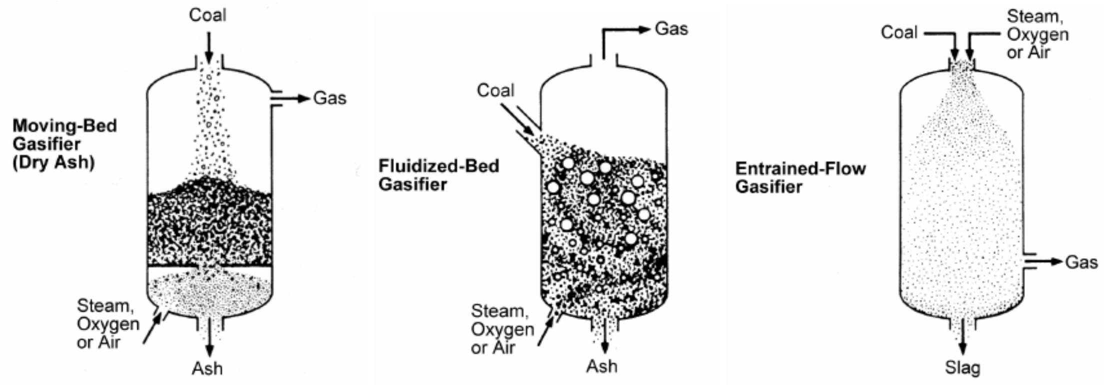

Figure 19. Three Major Types of Gasifiers - Moving Bed, Fluidized Bed, and Entrained Flow (Adapted from Holt, 2001)

The raw syngas can contain a considerable amount of sensible heat, particularly in the entrained flow gasifier that is popular for IGCC plants. This heat may be upwards of 15% of the energy in the coal, so the recovery of this heat can increase the overall efficiency of the plant (Holt, 2001). Some gasifiers have radiant heat exchangers on the walls of the vessel to produce steam, and some have convective heat exchangers directly following the gasifier to produce additional steam from the hot syngas. Heat exchangers can add substantial capital cost to a plant, but can markedly improve efficiency.

Raw syngas contains entrained particulates, HCN and NH_3 from fuel-bound nitrogen, and sulfur compounds primarily in the form of hydrogen sulphide (H_2S) and carbonyl sulphide (COS), and trace mercury and arsenic (Holt, 2001; Higman & van der Burgt, 2003). Virtually no NO_x is formed during gasification. Particulates are usually removed in a cyclone or candle filter, or a combination of the two. In some cases, a water quench is used. The nitrogenous compounds are removed in a water wash step, and the sulfur compounds are removed in Acid Gas Removal processes (Holt, 2001; Higman & van der Burgt, 2003). Mercury removal can be performed from syngas with the use of a sulfur-impregnated activated carbon bed, at an order of magnitude less cost than from a conventional PC power plant (Higman & van der Burgt, 2003). Although arsenic is not regulated as an emission, most arsenic is removed in either the slag in entrained-flow gasifiers, or in the syngas treatment wastewater (Higman & van der Burgt, 2003).

NO_x can form in the combustion turbine, and this is controlled by either saturating the cleaned fuel gas with water or by adding N_2, both of which are techniques to lower flame temperature(Holt, 2001). Current designs are able to limit NO_x levels to below 15 ppm, and some units can achieve single digits (Higman & van der Burgt, 2003).

The HRSG is a large heat exchanger in which heat from the combustion turbine exhaust gas is transferred to steam. The steam is used to generate power in a turbine system, similar to those used in post-combustion plants, although the steam is at lower temperatures and pressures. The exhaust gas is then vented to the atmosphere.

4.1.2 IGCC with CO_2 Capture

Unlike post-combustion capture from conventional PC plants, major changes must be made to the core process to capture CO_2 from and IGCC system (see Figure 20). Specifically, a water gas shift (WGS) reactor is added, in which CO reacts with H_2O to form H_2 and CO_2. Then a separation process, typically a physical or chemical absorption process, is used to remove the CO_2 from the "shifted syngas" stream. The CO_2 is then dehydrated for further compression, and the remaining gas stream of nearly pure H_2 is combusted in the gas turbine. An HRSG and steam cycle is also employed, as in IGCC without capture.

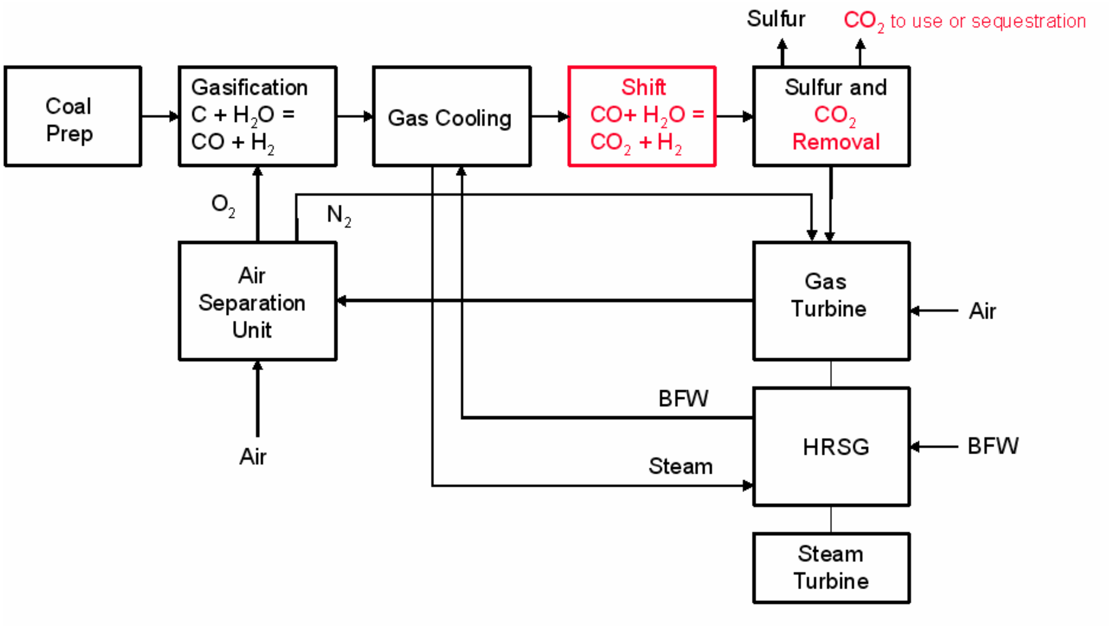

Figure 20. IGCC System with CO_2 Capture (Adapted from Phillips, 2005)

4.2 Current Technology/State of the Art

There are currently four coal IGCC systems in operation in Europe and the U.S., each between 250-300 MW_e (Deutch & Moniz, 2006). All of these units are without CO_2 capture, but have proven that IGCC projects can be successfully operated.

4.2.1 Technology Overview

A state-of-the-art IGCC design with CO_2 capture developed by the Electric Power Research Institute employs a slurry-fed, oxygen fired, entrained-flow gasifier (EPRI, 2000). Operating conditions are at pressures around 800 psig and temperatures between 2200-2500 °F, such that the ash melts and is removed as a slag (EPRI, 2000). The hot syngas is quenched with water to cool and humidify the stream to conditions suitable for the shift reaction. This step also removes chlorides and ammonia (EPRI, 2000). A candle filter is used to remove particulate matter prior to the shift reaction. Sulfur tolerant catalysts are used in the shift reactor, so that the shift can take place before sulfur removal[5]. A multi-stage Selexol absorption system is used to remove both CO_2 and H_2S, the latter of which is then separated and converted to purified sulfur for sale or disposal (EPRI, 2000). Selexol is a physical solvent consisting of a proprietary mixture of glycols, and can be very cheaply regenerated. The CO_2 is compressed and cooled for pipeline transport and storage, and the H_2-rich fuel gas is sent to the power block for electricity generation.

Figure 21 gives a simplified view of how a typical single-stage Selexol CO_2 capture system works (not including sulfur capture). The CO_2-rich shifted syngas, made up primarily of CO_2 and H_2, is contacted with a lean Selexol solvent in an absorption column. Here, the CO_2 is physically absorbed by the solvent at a pressure around 700 psia. For the purposes of this discussion, it should be assumed that the syngas stream has been previously cleaned of sulfur, although there are processes in which the sulfur and CO_2 are removed simultaneously. Other solvents which can also be used are chilled methanol (also known as Rectisol) or methyldiethanolamine (MDEA), a chemical solvent (Heintz, 2006). A relatively pure H_2 fuel stream leaves the top of the absorber and is prepared for energy conversion in a gas turbine or fuel cell, and a CO_2-rich solvent stream leaves the absorber bottom and goes to a two-stage flash tank system for regeneration. Most of the CO_2 (~90%) desorbs from the solvent in the first flash tank, where the pressure is reduced from around 700 psia to about 50 psia. The remainder of the CO_2 desorbs in the second flash tank at atmospheric pressure, and it is boosted to 50 psia, added to the larger CO_2 stream, and compressed to transportation and storage pressure. The CO_2-lean solvent is pumped back up to pressure and is sent back to the absorption tower for another cycle (EPRI, 2000).

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[5] Designs in which sulfur removal takes place before the shift reactor are less efficient than designs in which sulfer tolerant catalysts are used and sulfur clean-up takes place after the shift reaction. This is because the syngas stream must be cooled down for sulfur removal then later reheated, a process in which energy is lost. In addition, as the stream is cooled, steam required for the shift reaction condenses out of the syngas stream, and, therefore, additional steam must be added for the shift reaction.

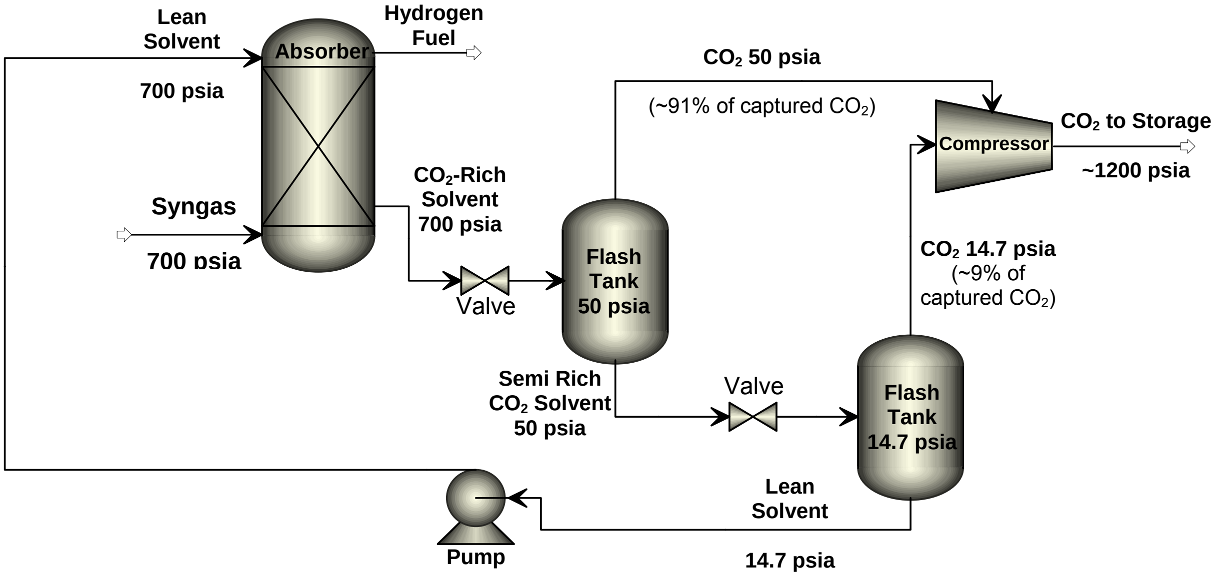

Figure 21. Simplified Flow Diagram of Pressure Swing Absorption Process (Numbers Adapted from EPRI, 2000)

4.2.2 CO_2 Capture Cost

Capturing CO_2 pre-combustion, of course, increases TPC and COE relative to an IGCC without capture. The increase, however, is less pronounced than for a conventional or oxy-fired PC plant, for two reasons. First, it is much easier and cheaper to remove CO_2 from a stream in which the partial pressure of the CO_2 is higher. Partial pressure is a function of both the concentration of CO_2 in the stream and the total pressure of the stream. For an IGCC system, the shifted syngas stream has both a concentration of CO_2 that is 2-3 times higher than a post-combustion flue gas stream and a total pressure that is 40-60 times higher, so the CO_2 partial pressure is almost two orders of magnitude higher. For this reason, a weakly-binding physical solvent such as Selexol can be used, allowing for a relatively non-energy intensive, and thus inexpensive, solvent regeneration[6] (Deutch & Moniz, 2006). The fuel gas stream is low volume and concentrated (in comparison with a post-combustion stream that includes nitrogen), so the additional equipment for capture is smaller than the additional equipment for a post-combustion system. Secondly, because the syngas is pressurized in the gasifier, and kept at an elevated pressure

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[6] Stronger binding solvents, such as the chemical solvent MEA, require more energy to remove the CO_2, and are advantageous for streams in which the CO_2 concentration is lower.

throughout the processing steps, less energy is required to compress it to transportation and storage conditions (Deutch & Moniz, 2006). Figure 21 shows that over 90% of the CO_2 removed is at about 50 psia (three times greater than atmospheric pressure), with the remainder at atmospheric pressure. As mentioned in Sections 2.2.3 and 3.2.3, the energy required for compression is quite high when the initial condition of the CO_2 is at atmospheric pressure, as in post-combustion or oxy-fired systems. Compared to those systems, about one-third of the compression energy is eliminated for an IGCC system. This is a substantial improvement given that the energy requirements of compression are about 40-45% of the energy penalty of capture for post-combustion and oxy-fired systems.

For a greenfield design, the TPC for capture is increased only about 32% and COE increased only 27% compared to an IGCC system with no capture (Deutch & Moniz, 2006). Figure 22 shows the increase in cost of electricity for an IGCC system with and without capture, including a supercritical PC with amine capture for comparison (Deutch & Moniz, 2006). The TPC for an IGCC plant with capture is 10% lower than the TPC for a supercritical PC plant with amine capture, and COE is 20% lower (Deutch & Moniz, 2006). Under the assumptions chosen by Deutch & Moniz, CO_2 capture appears to be less expensive from an IGCC than from a post-combustion PC, although for other cases or sets of assumptions, this may not hold true.

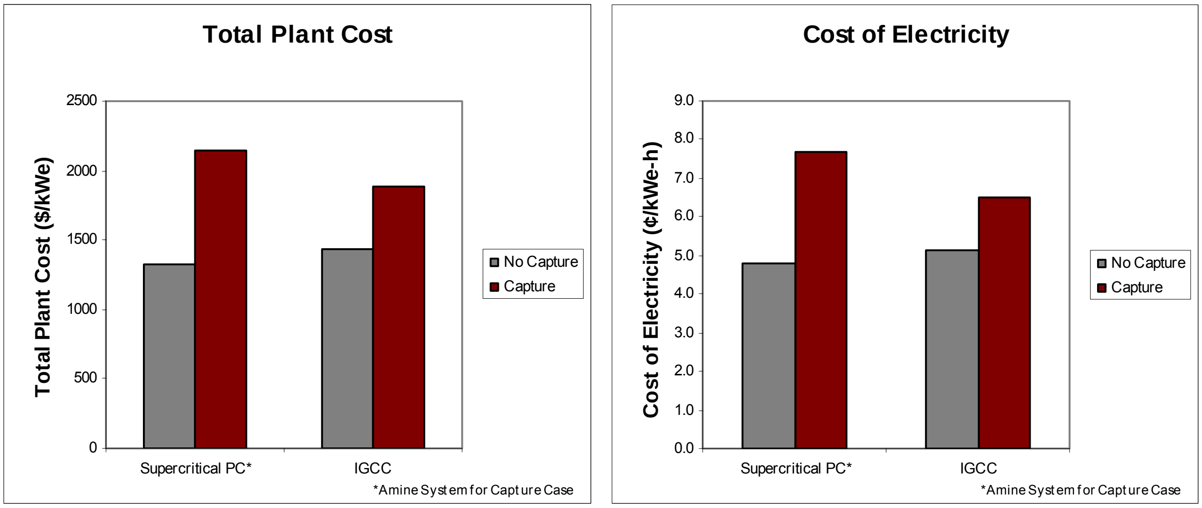

Figure 22. Total Plant Cost and Cost of Electricity for IGCC Systems with and without Capture, Supercritical with Amine Capture for Reference (Adapted from Deutch & Moniz, 2006)

4.2.3 Plant Efficiency Losses

As previously mentioned, the efficiency losses for an IGCC with capture are less than for PC systems with capture. The loss in efficiency is 7.2 percentage points, as compared to a 9.2 percentage point drop for post-combustion PC systems with capture, as shown in Figure 23 (Deutch & Moniz, 2006). The losses can be categorized into WGS reaction and other minor losses, CO_2 recovery losses, and CO_2 compression energy. The WGS reactor requires steam and energy, and the gasifier configuration is changed such that less steam is produced for power generation[7]. The CO_2 compression energy is the energy required to compress the CO_2 to conditions for transport and storage, and is lower than in post-combustion systems. The CO_2 recovery losses are attributable to the additional power required for the pumps, blowers, etc., in the Selexol unit. Figure 23 shows what typical losses are for an IGCC plant with capture and how these lower the overall efficiency of the plant.

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[7] Without capture, a radiant syngas cooler is used to generate additional steam. For a capture system, this is eliminated because the additional steam would be injected in the syngas stream for the shift reaction, so the syngas is directly quenched instead. The result is an approximately 2% decrease in overall plant efficiency.

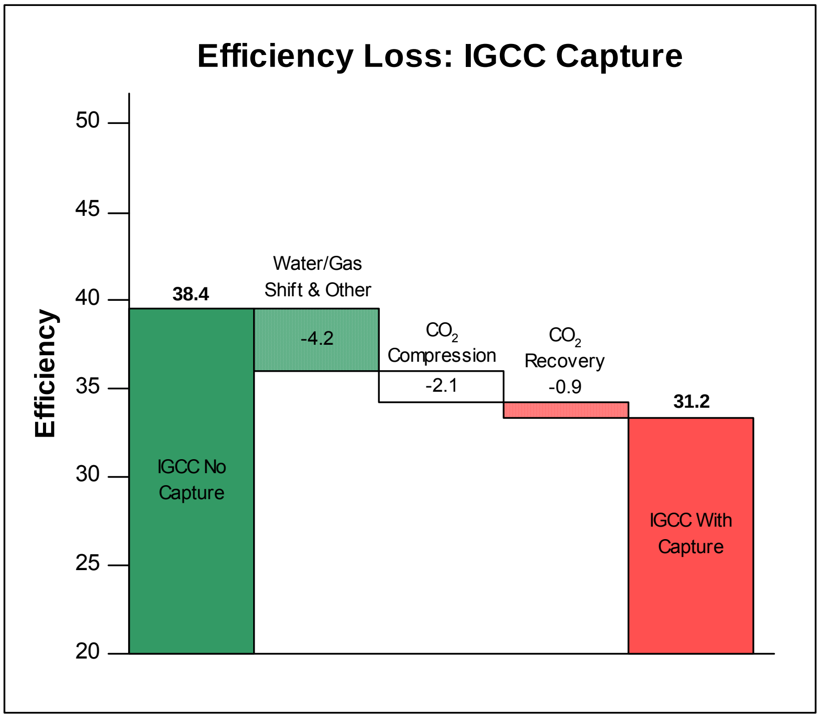

Figure 23. Efficiency Losses for an IGCC System with CO_2 Capture (Adapted from Deutch & Moniz, 2006)

4.2.4 Reliability and Operability Issues

Gasification of coal is an inherently capital-intensive process. As such, it is important that IGCC systems have high availability, in order to keep the cost of electricity competitive and recoup investment costs. This compounds the already high demand for availability and reliability of electricity consumers.

IGCC units have not had particularly good records of availability in electric power applications. This is because nearly all plants have been one-of-a-kind units, without the benefits of standardization and improvement over time, and because of a few widely publicized demonstration plants with less than impressive records on availability (Higman & van der Burgt, 2003). Gasification processes also require considerable operation and maintenance attention. However, it has been proven that they can offer very high reliability and availability with the proper foresight and if operated correctly. Although there are several substantial differences between liquid fed and coal fed gasifiers, there is a great deal of industrial experience with the former and with very high on-stream factors, up to 98% (Higman & van der Burgt, 2003). Such high availability might not be obtainable with a coal feed, but it shows reason to believe that competitive capacity factors are possible.

The problem with capturing CO_2 from an IGCC is that the capture equipment is central to the operation of the process as a whole. If there is a problem with any of the capture equipment, the whole process line may go down, and power production would come to a halt. This is in contrast to a post-combustion system in which the power-generating portion of the plant can operate if the capture system is out of operation, and the CO_2 can be vented to the atmosphere for a period of time. Problems with reliability due to the failure of CO_2 capture equipment are very unfavorable for plant operators from an economic perspective, and may present difficulties in grid operation that could affect many stakeholders, including consumers.

A bypass of the capture process units is impractical because everything downstream from the shift reactor is designed for a process with CO_2 capture. The syngas stream has a very different composition and volume without the shift reaction and CO_2 capture. This has an impact on the sulfur cleanup system, which would face very different operating conditions, and the gas turbine, which could have flame stability problems with such a different fuel stream.

Issues of reliability and availability hurt the competitiveness of IGCC (with or without capture) in relation to conventional PC systems. Many studies in which these technologies are compared assume a single capacity factor for both plant configurations, and this simply may not be a fair assumption. Small gains in capacity factor can equal big gains in economic performance, and the fact that PC plants may be able to attain a better capacity factor, particularly with CO_2 capture, could conceivably tip the balance in the favor of PC plants. There is still much uncertainty involved in this debate, and the performance of both types of plants with capture needs to be tested at large scale before any conclusive determination could be made.

4.3 Research Areas

There is a great deal of interest in understanding the potential of IGCC plants for bringing down the cost of capturing CO_2. Researchers are looking at a number of parts of the process in which to make improvements, including using superior sorbents, improving the water gas shift reaction, and using advanced energy conversion techniques.

4.3.1 Pressure Swing Absorption/Adsorption with Alternative Sorbents

Attempts are being made to improve the cost of separation of CO_2 from the fuel gas for standard IGCC process configurations. There is some room for improvement in this process step, although it must be kept in mind that the bulk of the cost of capture for an IGCC system lies in the energy requirements of the water gas shift reaction and the CO_2 compression energy. Energy requirements for the capture process itself, which can be attributed primarily to the regeneration energy of the Selexol absorbent and some fluid delivery energy, account for less than 15% of the total capture energy penalty. Systems which reduce capital costs of capture equipment would also be beneficial.

The use of pressure swing absorption has been described in Section 4.2.1 and in Figure 21, and is currently the process of choice for removing CO_2 from IGCC facilities. The problem with these processes is that the entire fuel gas stream must be cooled considerably before entering the Selexol unit, and even further if Rectisol is used (U.S. DOE, NETL, 2002). The stream is cooled from about 460°F after the low temperature shift reactor to about 100°F, which takes a substantial amount of cooling energy. If the CO_2 removal step could be performed at a higher temperature, it could be considerably less costly in terms of the energy required to reheat the gas stream for combustion. Researchers are looking at processes using a number of other solvents which may have advantages over the current favorites, Selexol and Rectisol, including the ability to function at higher temperatures.

Some fluorinated solvents are under investigation for use in pressure swing absorption systems such as that shown in Figure 21, including perfluoropolyethylene, perfluoropolypropylene, and perfluoroalkylpolysiloxanes. These physical solvents have the ability to selectively separate CO_2 from gaseous streams at high temperatures and pressures, potentially obviating the need for a cooling and reheat step (Heintz, *et al.*, 2005). They also have high chemical stability, high gas solubility, low vapor losses, and low regeneration energy requirements, which could make them attractive as replacements for Selexol or Rectisol.

Some other adsorbents include lithium silicate-based sorbents, such as Li_4SiO_4, and hydrotalcite-like compounds such as $[Mg_{0.73}Al_{0.27}(OH)_2](CO_3)_{0.135}\cdot mH_2O$ (Li, *et al.*, 2005; Hutson, *et al.*, 2004). The lithium silicate sorbent is effective at high temperatures, yields a high purity, high pressure CO_2 stream, is highly tolerant to syngas contaminants such as sulfur, and is effective across a broad range of CO_2 concentrations (Li, *et al.*, 2005). It is also chemically stable and is highly regenerable, so it appears to be promising as a CO_2 sorbent. The hydrotalcite-like compounds have very good CO_2 selectivity and capacity at high temperatures, but have relatively slow kinetic properties and show some loss of capacity with cycling (Hutson, *et al.*, 2004). These compounds, however, are very open to structural and chemical manipulation to improve characteristics. The kinetics and cycling properties must be better understood and advanced in order for them to be useful as CO_2 sorbents (Hutson, *et al.*, 2004).

The use of molecular sieves, activated carbon, and zeolites has also been investigated. It is not clear that these compounds show any advantages over current processes, however, because they require low temperatures similar to the Selexol process.

4.3.2 CO_2 Separation from Syngas by Hydrate Formation

A process is under development in which CO_2 is separated from a shifted syngas stream by taking advantage of the formation of gas hydrates rich in CO_2. The syngas stream, which consists primarily of CO_2 and H_2 is highly pressurized (~1000 psia) and then cooled to temperatures approaching 0 °C (Deppe, *et al.*, 2003). It is fed to a reactor with saturated water, in which ice crystals form, trapping the H_2S and CO_2 within the polyhedral structures (see Figure 24). The H_2 molecules are too small to be stabilized within the crystals, and are separated from the stream in a slurry/gas separator for use in power generation. The water/hydrate slurry is decomposed, producing high-pressure CO_2 for storage, and the water is re-saturated and recycled to the reactor (Deppe, *et al.*, 2003). Gaseous or liquid "promoters," including H_2S and some hydrocarbons, can be used to enhance hydrate formation such that the hydrates form at much lower pressures, saving pumping energy (Deppe, *et al.*, 2003).

The advantage to this process is that it doesn't require the use of large absorber towers or steam heated regenerators, but it requires significant capital and energy use in refrigeration (Deppe, *et al.*, 2003). Progress on the concept is still in the experimental phase, with the development of a pilot plant underway. It is possible that this process may be superior to current CO_2 capture techniques from IGCC fuel streams because it nearly eliminates the CO_2 compression step prior to storage. This may, however, be offset by the high pumping energy requirement for hydrate formation and the energy required for refrigeration.

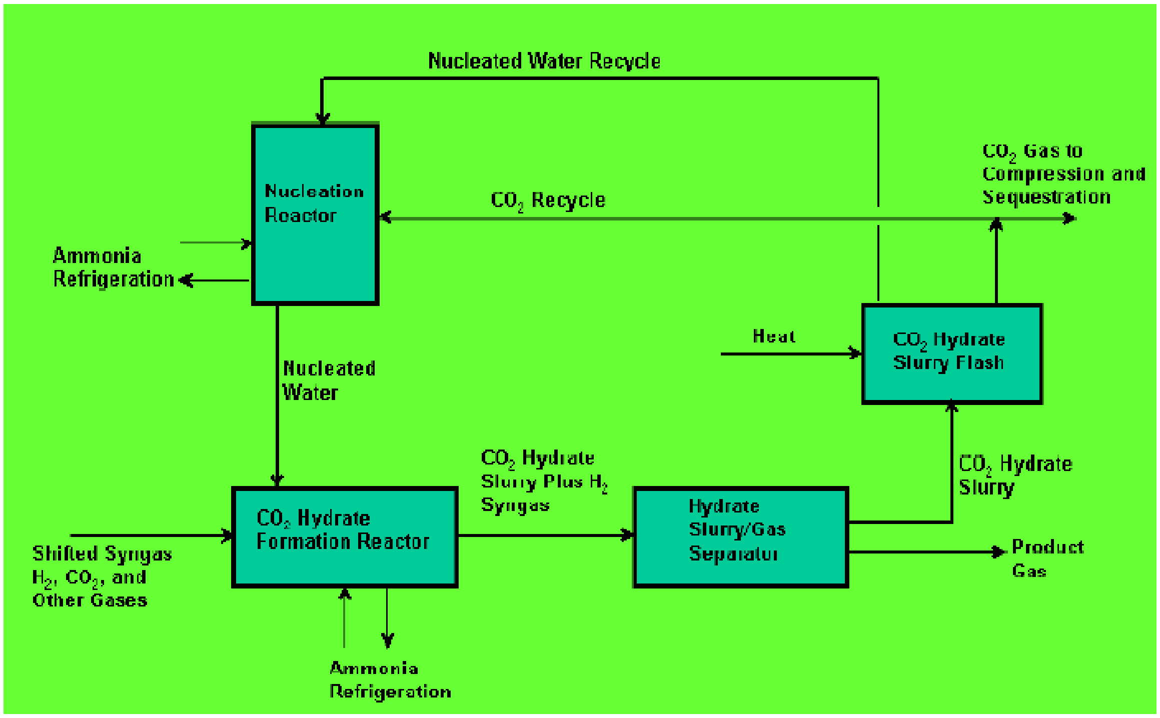

Figure 24. CO_2 Separation from Shifted Syngas Stream by the Formation of Hydrates (Adapted from Deppe *et al.*, 2003).

4.3.3 *Sorption Enhanced Water Gas Shift Reaction*

The water gas shift reaction is a major consumer of energy in the capture process, requiring nearly half of the energy required in the capture process. Improvements in the process could be very beneficial for the economics of the capture process as a whole.

A variation of the pressure swing absorption process that could be advantageous is to combine it with the WGS reaction. This can be done by performing the shift in a reactor with an adsorbent bed followed by an adsorbent/catalyst bed in a high temperature, high pressure process (see Figure 25). The first adsorbent bed removes CO_2, and the adsorbent/catalyst bed catalyzes the WGS reaction and simultaneously removes the CO_2 produced as the WGS reaction takes place (Allam, *et al.*, 2004). The reaction advances further to the products side, so more CO is shifted to H_2, and a purified H_2 fuel stream is produced. When the adsorbent is near its CO_2 capacity, it is regenerated by releasing the pressure and purging the bed with steam, producing a pure CO_2 stream. Multiple reaction/adsorption beds undergo cyclic process steps in combination to drive CO in the fuel gas to near extinction. The CO_2 adsorbent under consideration for this process is the hydrotalcite $Mg_6Al_2(OH)_{16}[CO_3]\cdot 4H_2O$ promoted by K_2CO_3 (Allam, *et al.*, 2004).

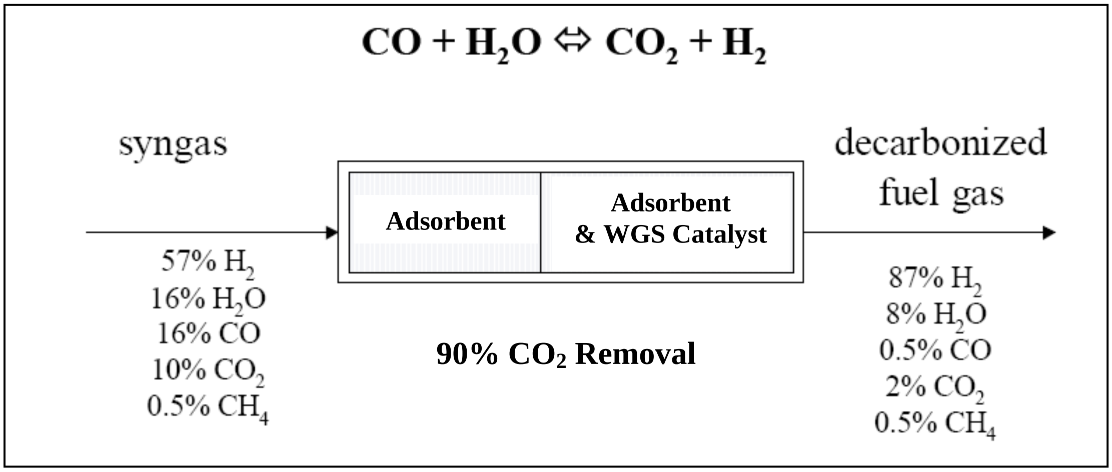

Figure 25. Simplified Diagram of a Sorbent Enhanced Water Gas Shift Reaction (Adapted from Allam, et al., 2004)

The advantages to this process are threefold (Allam, *et al.*, 2005). First, the WGS reaction is equilibrium limited, so removal of CO_2 during the reaction drives it further to the products side, so a more pure H_2 stream can be obtained with smaller reactors. Second, the process can be conducted at high temperatures and pressures, minimizing heat exchange equipment costs and reheat energy loss. And lastly, the H_2 fuel exits the reactors at high temperature and with excess steam, which is ideal for feed to a gas turbine for low NO_x formation and high process efficiency. The concept has been demonstrated and looks promising, but further characterization of process parameters at the industrial scale is needed (Allam, *et al.*, 2004).

4.3.4 Membrane-Enhanced Water Gas Shift Reaction

Similar to the sorption enhanced WGS process is the concept of enhancing the WGS reaction with the use of membranes (see Figure 26). In such a system, syngas is fed to a fixed bed reactor which has a membrane wall, at pressures around 500 psia. As H_2 is produced in the catalyzed WGS reaction, it is passed selectively through the membrane and is swept by N_2 gas to a turbine or fuel cell. The pressure drop across the membrane is approximately 435 psi, so the H_2 is produced at about 65-70 psi, so it must be compressed further for use in a gas turbine. The removal of the H_2 allows the WGS reaction to proceed further to the desired products side, and a purified, high pressure stream of CO_2 and H_2O is produced on the retentate side of the membrane. Water can easily be removed, and the CO_2 can be compressed for transport and storage. Some retentate (H_2 and CO) passes through the system un-reacted, and must be converted to power in a turbine, fuel cell, or converted to H_2 in an additional reactor step.

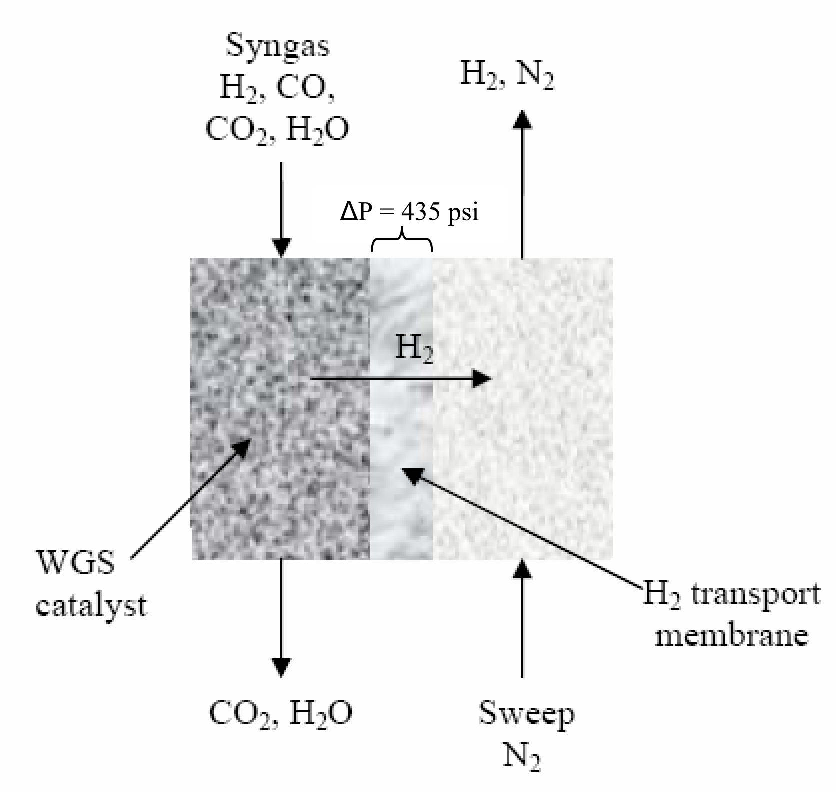

Figure 26. Section of Membrane Enhanced Water Gas Shift Reactor (Adapted from Lowe, *et al.*, 2004)

Metal alloy membranes have been tested and been found to have good flux and selectivity performance, and were able to withstand the high differential pressures required in a membrane reactor (Lowe, *et al.*, 2004). The membranes were alloys of Nb, Ta, V, Zr, Pd, and other Group IVB and VB elements, but other membrane materials, such as ceramics, are also possible (Lowe, *et al.*, 2004).

The membrane enhanced WGS reaction concept has some advantages over the Selexol and Rectisol processes (Lowe, *et al.*, 2004). It can be performed at high temperatures and pressures, saving energy. Also, because the CO_2 stream is at high pressure following the reaction and membrane separation, compression costs are lower than for a post-combustion or oxyfired system, which is a major advantage. Membrane enhanced WGS systems can also achieve higher CO_2 removal and a more pure H_2 fuel stream, and can decrease the amount and size of process equipment, saving money on capital costs. There are also a number of possible configurations for including membrane reactors in plants, including as an afterburner step for a fuel cell system (to be discussed in Section 4.3.5). Membrane enhanced WGS reactors show potential to be a lower cost CO_2 removal system, but membrane technology must be improved and costs lowered, and a commercial-scale demonstration must be made to show that the technology can be scaled up.

4.3.5 Fuel Cell Systems

In addition to technologies to directly separate CO_2 from the fuel gas stream, different techniques of energy conversion with CO_2 separation can also be used to improve the electricity production process. Fuel cells present the possibility of relatively low cost CO_2 capture. The efficiency attainable with a fuel cell system could greatly exceed what is now possible with IGCC systems, and the in situ fuel reforming capability of solid oxide and molten carbonate fuel cells could save some of the energy losses associated with the WGS reaction. The Selexol system could be eliminated, saving additional energy, but the CO_2 compression would still be a major cost and there are other problems that need to be overcome.

Solid Oxide Fuel Cells

The Solid Oxide Fuel Cell (SOFC) is a technology option which could potentially offer significantly higher efficiencies than gas turbine/combined cycle systems. It works by transferring oxygen ions from an air stream across a membrane, where they react with hydrogen molecules, producing water and two electrons (see Figure 27). The water is expelled from the system, and the electrons provide useable electric current. The membrane, in effect, performs the major N_2 separation for a system in which the CO_2 is captured. Solid oxide fuel cells operate at high temperatures, on the order of 1000 °C, and the electrolyte membrane is typically a Zirconium/Yttrium oxide (U.S. DOE, ER, 1993).

Solid oxide fuel cells are capable of processing a variety of fuels, including syngas, hydrocarbons, or hydrogen. In a coal fuelled system, a SOFC would be preceded by a gasifier and syngas cleaning steps. A water gas shift reactor could be used, but it is not necessary because the high operating temperature of the fuel cell enables in-situ fuel reforming to hydrogen (with the addition of steam), as shown in the “Fuel” stream of Figure 27 (U.S. DOE, ER, 1993). During reforming, CO_2 is formed, and it exits the anode side with H_2O and excess fuel (H_2 and CO). Because there is significant energy remaining in this stream, it is further processed in an “afterburner” step, which would typically be a catalyzed combustion process, followed by expansion in a gas turbine and a steam bottoming cycle.

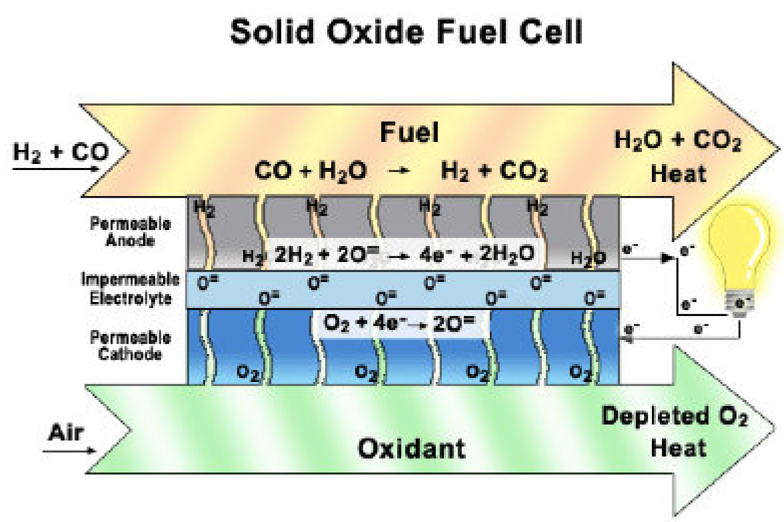

Figure 27. Schematic of Solid Oxide Fuel Cell (Adapted from PES Network, Inc., 2006)

For a system in which the CO_2 is captured, the fuel cell is operated in the same fashion, but the excess fuel is fired with pure (95%) oxygen in an afterburner, rather than with air, and the exhaust gases would not be expanded for energy recovery (see Figure 28). The exhaust gases are then almost entirely H_2O and CO_2, which can easily be separated and the CO_2 further compressed for transport and storage.

Some alternate steps have also been proposed for the afterburner step (Figure 28). One option is to include a shift reactor followed by an H_2 membrane separator, which converts the remaining CO to H_2 and CO_2. The H_2 is separated for recycle back to the fuel stream and the CO_2 is prepared for purification and compression (U.S. DOE, ER, 1993). The relatively low CO concentrations in the anode effluent may not justify a shift reactor, but there is sufficient H_2 in the effluent to warrant separation and recycle (U.S. DOE, ER, 1993).

Other afterburner steps have also been proposed, including an additional SOFC, an oxygen pump, a mixed oxide conductor, or combinations of these technologies (Lokurlu, *et al.*, 2004). An in-depth analysis of each of these options is not necessary, but it is important to note that there are other options for extracting additional energy from the excess fuel in the anode effluent. Relative investment cost and cost of electricity between the options is difficult to estimate because of the effects of variable economic factors can change the costs (i.e. fuel costs, CO_2 tax). One study of the relative costs of these options estimated that the investment cost and levelized cost of electricity for the technologies following the primary SOFC can be ranked in the following order: combustion/expansion/steam cycle < second SOFC < mixed oxide conductor < oxygen pump (Lokurlu, *et al.*, 2004).

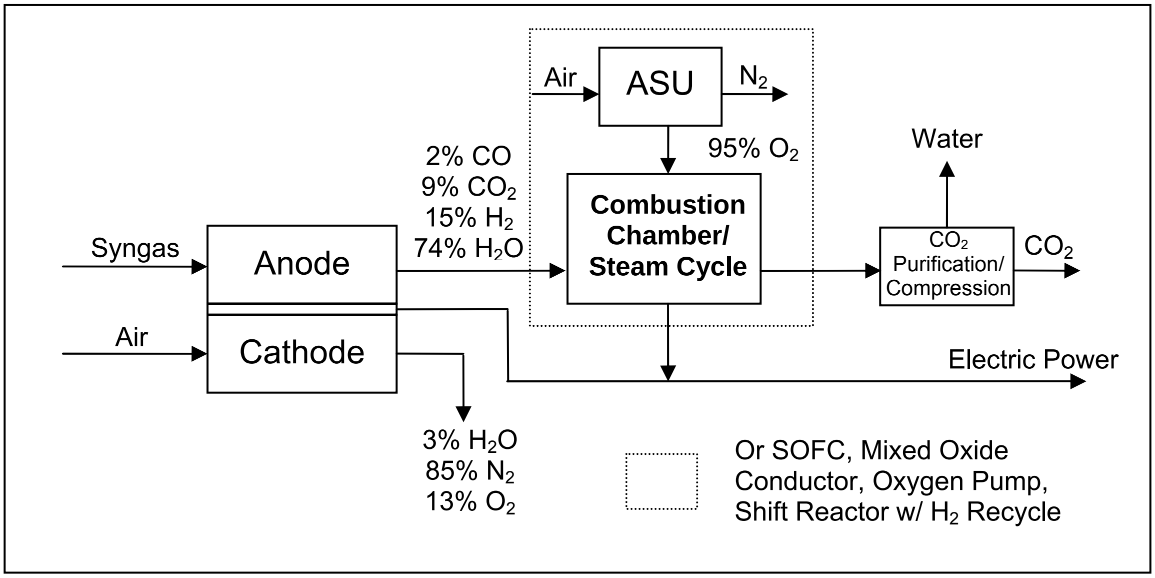

Figure 28. Solid Oxide Fuel Cell with CO_2 Capture (U.S. DOE, ER, 1993).

Another concept that could improve the overall performance of the process is integration with other parts of the process. For example, integrating the high temperature fuel cell with a high temperature air separation process, such as an ITM (see Section 3.3.1), could reduce the cost of providing O_2 to the gasifier or the gas turbine (U.S. DOE, ER, 1993).

Solid oxide fuel cell power plants can reach efficiencies of nearly 60% without CO_2 capture, and 50% with capture on a l*ower heating value* basis (U.S. DOE, NETL, 2002). Preliminary estimates put the investment cost of an SOFC/gas turbine plant without capture at about 20% greater than for a subcritical PC plant without capture (U.S. DOE, NETL, 2002). For a capture case however, the SOFC/gas turbine plant is comparable in price to an IGCC plant with capture, which is the least expensive capture plant (U.S. DOE, NETL, 2002). The levelized cost of electricity was estimated to be a bit lower than the IGCC plant (U.S. DOE, NETL, 2002). While SOFC plants may be nearly cost-competitive with PC and IGCC plants, particularly with CO_2 capture, there are still hurdles. Improvements must be made in the cost and durability of electrolytes. Operation and maintenance, and hence availability, are also an issue, as the components of an SOFC have a shorter lifetime than those in conventional power plants and will require outage time during replacement.

Molten Carbonate Fuel Cells

A molten carbonate fuel cell (MCFC) works in much the same way as an SOFC, except that the electrolyte is a different material and the reaction and mechanism for transferring ions are a bit different (see Figure 29). The electrolyte in an MCFC has a chemical formula of $MxCO_3$, where Mx is a metal, usually lithium or potassium (Itou, *et al.*, 2002). At temperatures in the range of 600-650°C, CO_2 and O_2 at the cathode create a carbonate ion (CO_3^{2+}) and two electrons. The ion diffuses through the $MxCO_3$ membrane to the anode, and the electrons provide useable power (Itou, *et al.*, 2002). At the anode, the carbonate ion reacts with H_2 to produce H_2O, CO_2, and heat. The CO_2 and H_2O can be easily separated, and the CO_2 compressed for transport and storage, with some CO_2 recycled to the cathode for consumption there. For use with coal as a fuel, the coal is first gasified, and the syngas reformed in the cell, as with the SOFC. Alternately, it is possible to have a direct carbon fuel cell, in which carbonate ion reacts with C, evolving pure CO_2 and heat, but it is difficult and costly to get a pure C stream (Steinberg, *et al.*, 2002).

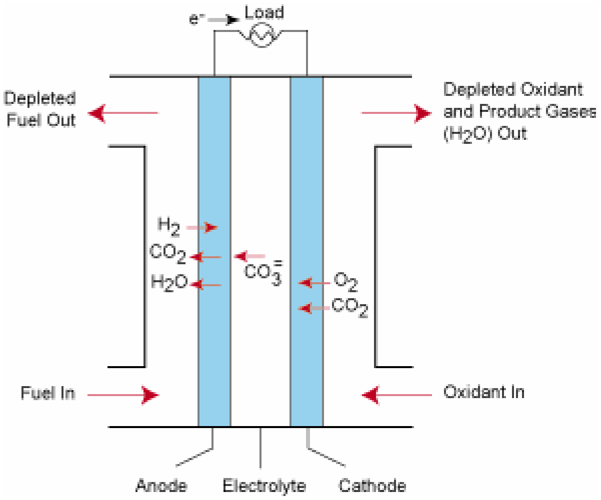

Figure 29. Schematic of Molten Carbonate Fuel Cell (Adapted from U.S. DOD Fuel Cell Projects, 2006)

The balance of the plant for a MCFC is very similar to that of the SOFC, with an "afterburner" system following the fuel cell. There are several small plants operating around the world, most of which are around the 250 kW_e scale, with one plant at the 1 MW_e scale (U.S. DOE, Webpage, 2006). The questions that remain are similar to those for SOFCs, and focus on the cost and durability of electrolytes, as well as materials corrosion.

4.4 Chapter Conclusions

Pre-combustion capture of CO_2 is a viable option for CO_2 control, and may have advantages over post-combustion systems. The current state-of-the-art systems use slurry-fed, oxygen fired, entrained-flow gasifiers with a water gas shift reaction and cold gas Selexol CO_2 capture. TPC for capture is increased only about 32% and COE increased only 27% compared to an IGCC system with no capture, which equates to a TPC 10% lower than for a supercritical PC plant with amine capture, and COE that is 20% lower. The major energy consumers are the water gas shift reaction and, to a lesser extent, CO_2 compression.

Several alternative sorbents have been investigated, and some may be able to offer an advantage over Selexol or Rectisol because they can be used at high temperatures. It is not yet clear, however, if they are superior to Selexol or Rectisol at this point. Separating

CO_2 by taking advantage of the formation of CO_2 hydrates in water has also been discussed, but would require cooling of the syngas, and my not be advantageous over current processes. Improving the yield of the water gas shift reaction through the use of a sorption enhanced or membrane enhanced process may also offer improvements to IGCC systems with capture. Using solid oxide or mixed carbonate fuel cells could greatly improve the overall plant efficiency, but require additional development.

IGCC systems with CO_2 capture may be able to reduce the cost of capture over post-combustion systems with MEA, but questions remain, particularly about the reliability and operability of IGCC systems. It is not yet clear if the advantages to IGCC outweigh the uncertainties. There are additional technological improvements to pre-combustion capture systems which may further reduce the cost of capture. As with post combustion and oxy-fired technologies, comparisons based simply on literature reviews are made difficult by high levels of uncertainty, the uses of different assumptions, and the inherent biases of the authors.

5.0 Discussion of Research and Development

Before discussing strategy for prioritizing CO_2 capture technology research and development efforts, a discussion of R&D theory and the role of government and private industry in the R&D process is necessary. It is also important to look at how R&D efforts are managed, both in government and private industry, and to investigate some of the tools that make management easier.

5.1 Types of Research & Development

A useful way to conceptualize R&D types is by creating a matrix in which the two broad purposes of research, improving basic understanding and finding practical applications, are plotted on the two axes (see Figure 30). Research which is purely for improving understanding of scientific phenomena is epitomized by the work done by Niels Bohr, who pursued a deeper comprehension of the workings of the atom (Deutch & Lester, 2004). R&D which is directed towards finding practical applications is exemplified by the work that Thomas Edison did in taking existing knowledge about the properties of electric currents and applying it to develop useful products, giving little thought to the underlying scientific implications (Deutch & Lester, 2004). Between these two extremes is a type of research that can be thought of as "use-inspired basic research." This is comparable to the work done by Louis Pasteur, who had a goal of treating disease in humans and animals and preventing the spoilage of milk, which led him to embark on investigations of the fundamental microbiological foundations of disease (Deutch & Lester, 2004). The bulk of CO_2 capture R&D will fall in this "Pasteurian" category, with the research being directed toward finding solutions to climate change risk, but still being relatively fundamental in nature. There may be some purely "Bohrian" research, and there will eventually be a great deal of "Edisonian" R&D if CO_2 capture technologies are adopted on a large scale.

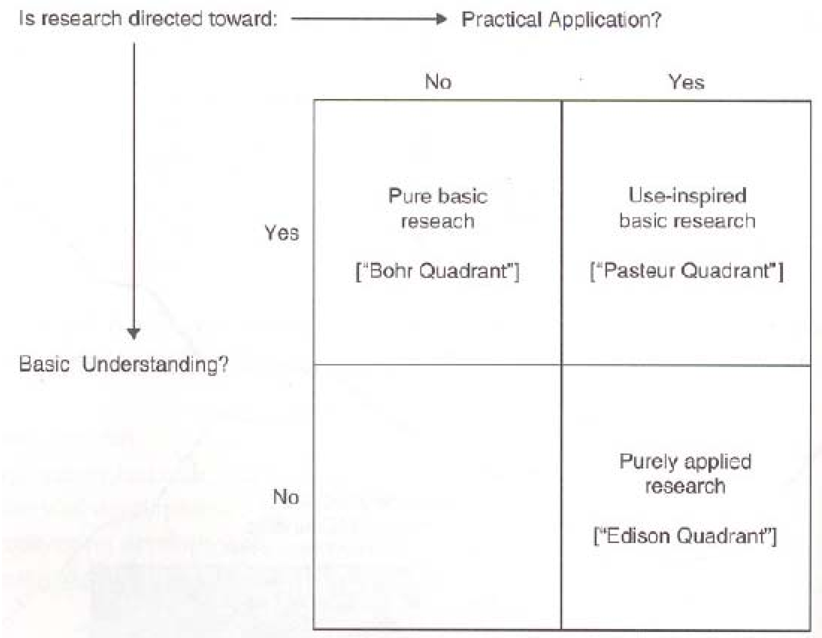

Figure 30. A Stokes Research and Development Matrix (Adapted from Deutch & Lester, 2004)

5.2 Role of Government and Industry in R&D

It is generally accepted that the role of federal government is to protect and improve the public welfare (Deutch & Lester, 2004). In this role, governments defend national security, take steps to improve the economic well-being of their citizens, and protect public health, safety and natural resources, and they use technology in various ways to meet these ends (Deutch & Lester, 2004). Private companies seek to maximize value from investments, serving both their shareholders and their customer base, and rely heavily on technology to do so. Because of the particularly heavy reliance on technology in the coal-based electric power industry and the uncertainty in terms of climate change risk, it is very important to both parties that innovation take place in the area of CO_2 capture technology. The question then arises over what the role of government and private industry players should be in the process of innovation, and what these groups should do to ensure that innovation occurs.

Governments should clearly take a role in use-inspired basic research or applied R&D when it supports a specific national purpose, or when they are a specific user of the technology that is being advanced (Deutch & Lester, 2004). Research to advance CO_2

capture technology fits a national purpose, reducing climate change risk, so it is clear that there should be some level of government involvement in the more applied types of research. A final, but very important, area in which government support for R&D is warranted is in basic research, from which the discoveries that drive much innovative activity arise (Deutch & Lester, 2004).

Much of the time, however, there is little reason for serious government involvement in R&D, particularly applied R&D. Private firms will generally invest in their own R&D if they expect a sufficient payoff. In the case of CO_2 capture technology, if firms expect climate change legislation, they will have incentive to advance the technology such that it will help them remain profitable even with CO_2 limitations.

5.3 Managing R&D Efforts as a Portfolio

With several development pathways and multiple technology options to choose from within each pathway, limited resources must be allocated such that a company interested in CO_2 capture technology will have a number of options available to them in the future. A balance must be struck such that enough technologies are actively being developed to provide future options, but not so many that scarce resources are spread too thin, diminishing the chances that any single technology will reach maturity. Decisions must be made over which CO_2 capture technologies should be pursued, which should be accelerated, and which should be cut. Prioritizing research advancements in CO_2 capture technology is essentially a portfolio management problem.

The optimal technology portfolio will have a number of different projects in various stages of development at any given time, and will balance risk versus return and short-term versus long-term advancements (Cooper, *et al.*, 2001). The portfolio can be thought of as a pipeline of technology development, with raw concepts at one end, and useable technologies produced at the other end (see Figure 31). Research and development efforts move potential technologies from concepts to finished products, and the portfolio management process is used to determine which technologies are pushed through the pipeline and how fast, and which are abandoned and when.

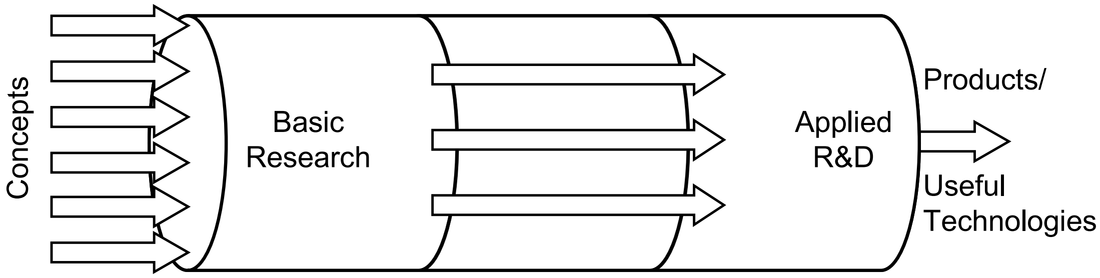

Figure 31. Technology Development Pipeline.

The management of a technology portfolio cannot occur in the dark. There must be a structured approach to understanding each technology, determining its place in the technology development pipeline, and deciding what to do with it. Using technology assessments and project development tools can provide the information and structure required to effectively manage a portfolio. There are a number of tools available, each having its own purpose and its unique strengths and weaknesses. Government and private industry stakeholders should carefully choose a set of portfolio management tools that supports their strategy and their unique outlook, and fits within their aversion to their specific set of risks.

5.4 Portfolio Management Tools

5.4.1 Technology Readiness Levels

Several approaches for assessing the potential of technologies have been experimented with by a number of different organizations. NASA developed a system of "Technology Readiness Levels" (TRLs) in the 1980's to provide a consistent comparison of maturity between different types of technology, and continues to use a refined version of it today (Mankins, 1995). The Department of Defense (DOD) adopted the TRL approach in 2004, although the Air Force Research Lab had been using them since the 1990's.

The NASA TRL system has nine levels, TRL 1 through TRL 9, as summarized in Table 3. Technologies are advanced from TRL 1 up through TRL 9 as they are developed. The specific language of the TRLs shows how they are tailored for typical NASA technologies, which are based primarily on flight in a space environment. The DOD adapted the language of the TRL to suit their needs and their operating environment, but essentially accepted the same system.

TRL 1	Basic principles observed and reported
TRL 2	Technology concept and/or application formulated
TRL 3	Analytical and experimental critical function and/or characteristic proof-of-concept
TRL 4	Component and/or breadboard validation in laboratory environment
TRL 5	Component and/or breadboard validation in relevant environment
TRL 6	System/subsystem model or prototype demonstration in a relevant environment
TRL 7	System prototype demonstration in a space environment
TRL 8	Actual system completed and “flight qualified” through test and demonstration
TRL 9	Actual system “flight proven” through successful mission operations

Table 3. NASA TRL Model (Mankins, 1995)

In 1999, the U.S. General Accounting Office (GAO) produced a report describing their study of how technology development and transition are treated differently between the DOD and private industry. It showed that technology assessment systems such as TRLs can successfully aid in decision-making if properly applied, and can aid in bringing technologies to maturity with fewer cost and schedule over-runs (U.S. GAO, 1999). The GAO report also revealed that technologies for which product development began before the technology was sufficiently mature (i.e. projects that were hurried to launch) tended to have less favourable outcomes.

Technologies for DOD are generally developed first by outside organizations, and then transferred to DOD project management and funding once a certain maturity level has been reached. The GAO observed that, due to budget and deadline pressures, the maturity level of early-stage technologies was often overstated so transfer to DOD could occur sooner, which led to a higher failure rate. The GAO report recommended the adoption of a disciplined, knowledge-based approach for technology assessment centered around the use of TRLs, with the requirement that technologies reach a high level of maturity (analogous to a TRL of 7) before DOD commits to development and production (U.S. GAO, 1999).

The situation with CO_2 capture technologies is quite similar in nature to the transfer process that occurs in DOD development programs, although the roles are reversed. For CO_2 capture technology, most of the early stage development is done in government labs or with government funding, while later-stage development is done primarily by private industry, with a "transfer" of leadership when private firms are satisfied that the technology has reached a certain level of maturity[8]. During the writing of this thesis, it was observed that the early-stage technology developers seem to often overstate the maturity or the potential of their CO_2 capture technology, presumably to make their project appear attractive to funders. To avoid the problems encountered by DOD when rushing technologies to deployment, it would be sensible for CO_2 capture technologies that are being researched with governmental funding to have their maturity assessed according to a TRL-like system.

The GAO also found that, in successful commercial sector organizations, product development for manufacture and marketing does not usually take place until technology development is complete (U.S. GAO, 1999). Because private firms must remain profitable to survive, they took a more conservative approach, allowing technologies to mature and prove their performance characteristics before any additional resources were spent to bring them to manufacture and production stages. To keep with the GAO's second recommendation, and in light of this finding, technologies which are being developed with governmental funding should be brought to a relatively high TRL number before private industry players should be expected to take a leadership role in bringing them to market.

Other groups have used TRLs, and identified problems with applying them to different technology categories. Researchers at the Carnegie Mellon Software Engineering Institute have explored using TRLs for some software products, and identified

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[8] The roles are reversed because the characteristics of the market are different for CO_2 capture technologies than for DOD technologies, and the end-users are also different. The market for capture technologies is driven by the prospect of government regulation of CO_2, which would force private firms to invest scarce resources in technologies for which they would be the end-user. For DOD technologies, the market is driven by well-financed government demand for advanced weaponry, which incentivizes outside firms to develop early-stage technologies for which the government will be the end-user.

shortcomings due to the differences between the characteristics of the software products and NASA's technologies (Smith, 2005). Researchers have also adapted the TRL system for use with intelligent systems such as robots, intelligent vehicles, and teleoperated devices. The additional sources of uncertainty and complexity in the requirements for these systems have prompted researchers to include measurement standards complementary to the NASA and DOD TRL model in their evaluation system (Meystel, *et al.,* 2003). Because the characteristics of and requirements for CO_2 capture technologies are unique, a TRL system specific to CO_2 capture technologies should be developed.

Using the NASA model as a basis, a first-attempt TRL model specific to CO_2 capture technologies is shown in Table 4 (Mankins, 1995). It includes the progression of the technology from a scientific principle and technology concept to laboratory-scale, bench-scale, and full-scale prototypes, and then to full deployment. These steps are intended to reflect the actual sequence of steps that a CO_2 capture technology would go through as it is developed and deployed. The final TRL incorporates the demonstration of economic viability, which is not included in NASA and DOD TRL models, but is an important factor for CO_2 capture technologies.

TRL 1	Basic scientific principles observed and reported
TRL 2	Technology concept and/or application formulated
TRL 3	Analytical and experimental critical function and/or proof-of-concept validated
TRL 4	Component and/or process validated at laboratory scale
TRL 5	Component and/or process validated at pilot scale
TRL 6	System/subsystem model or prototype demonstrated at pilot scale
TRL 7	System prototype demonstrated at full scale
TRL 8	Actual system integrated into a full-scale plant and successfully deployed
TRL 9	Actual system market proven through economically successful industrial operations

Table 4. TRL Model Adapted for CO_2 Capture Technologies

5.4.2 "Gate"-Style Models

Many private sector organizations have their own processes to guide product development. General Electric's "Tollgate" system and ABB's "Gate" model are two good examples, and there are several others (Chao & Ishii, 2005). The GE model is shown in Table 5.

TG 1	Identify need and develop concepts
TG 2	Perform economic feasibility studies and select best options
TG 3	Obtain customer feedback and refine approach
TG 4	Develop proposal/program plans
TG 5	Define launch requirements
TG 6	Prepare to launch
TG 7	Perform detailed design and manufacturing plan
TG 8	Prepare for validation
TG 9	Complete validation
TG 10	Product support and identify opportunities for improvement

Table 5. General Electric "Tollgate" Model (Chao & Ishii, 2005)

These systems are meant to be a focused, formal, and disciplined approach to prioritizing and managing projects in a portfolio (Chao & Ishii, 2005). Each gate is a decision point at which the project is either *continued with or without changes*, or *terminated*, based on an assessment of its benefit, status, risk, and resource and technological considerations (Chao & Ishii, 2005). These models have been successful in ensuring consistent implementation of process standards, enforcing discipline, managing investment risk, and synchronizing project work.

For “gate” style project management models, there is a delicate balance between adding structure to the technology development process and adding cumbersome bureaucratic barriers. The rules for each step must be demanding enough that managers and technologists are forced to stop and consider the value of the project they are pursuing, its place in the overall strategy of the organization, and potentially even the strategy of the organization as a whole. At the same time, valuable time and money cannot be wasted on unnecessary and overbearing administrative steps.

Gate project management tools are valuable for delivering to market technologies that are already mature and proven, and thus are best applied by private industry for technologies that would have a high TRL number. They are not practical for developing early-stage research concepts where the uncertainty of technical success is high. Gate models should be incorporated into the product development process by private firms who seek to bring CO_2 capture technologies with proven technical performance characteristics to market.

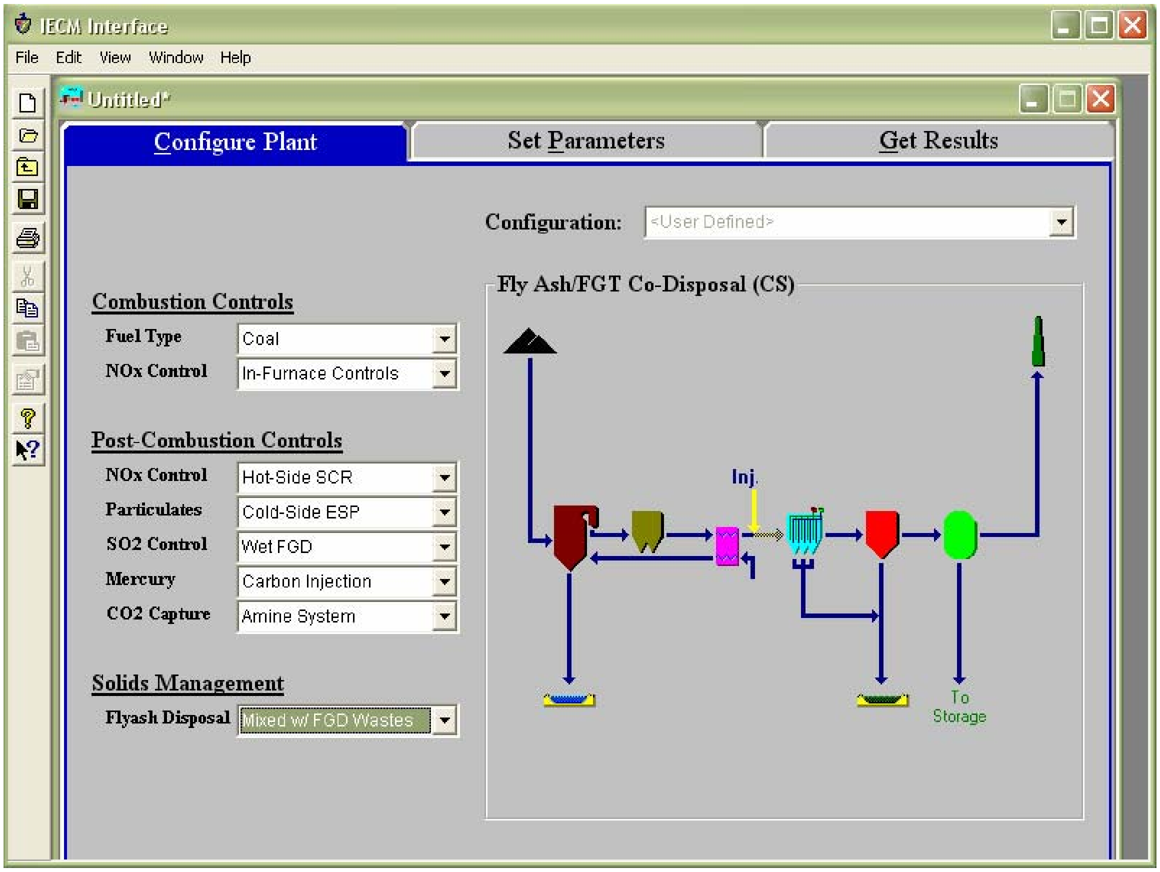
5.5 Analytical Tools

Technology Readiness Level and Gate models can provide the framework for developing technology, but there still must be methods for obtaining reliable information when deciding which technologies to include in the portfolio. Analytical tools can be very useful for providing such information for portfolio management decisions. The tools can vary greatly in their purpose, applicability, and format, but generally they seek to quantitatively analyze technologies or activities to understand the dynamics of cost, performance, and reliability by considering technical, financial, policy, scale, learning, and other factors. Information from these tools can be used to aid in the portfolio management process by giving reasonable preliminary estimates of cost, material requirements, expected performance, emissions output, and other factors. Some analytical tools can also make an estimate of the economic or emissions impact that a technology can have if it is successful.

There are a number of different analytical tools, each filling a different niche in the information it is capable of providing. None of them are perfect, none of them are universally applicable, and they are only as strong as the assumptions upon which the calculations are based. Also, there is a distinct trade-off between sophistication and ease of use; those that make very detailed calculations and provide very precise output require more detailed and rigorous inputs, placing additional burden on the user. It is very important that the analytical tool to be used is selected thoughtfully and applied appropriately in order to get information that is useful and reliable.

5.5.1 Integrated Environmental Control Model

A good example of an analytical tool is the Integrated Environmental Control Model (IECM), which was developed for the Department of Energy by researchers at Carnegie Mellon University. The IECM can furnish the user with valuable information about the energy and mass flows (including air pollutants, reagent requirements, and solid wastes) and the economic factors (including capital cost, operating and maintenance costs, and levelized cost of electricity) of coal-fuelled power plants of various configurations in a matter of minutes (U.S. DOE, National Energy Technology Laboratory, 2001). In a simple Windows-based interface, the user enters information about the type of coal plant and the air emission control technologies, including for NO_x, SO_2, particulate matter, mercury, and CO_2, and enters key operating parameters (see Figure 32). The program re-calculates mass and energy balances and economic estimates, and displays results in several useful formats. The IECM is fast, powerful, and can provide an excellent basis for comparison between competing technologies.



Configuration: <User Defined>

Combustion Controls

Fuel Type: Coal
NOx Control: In-Furnace Controls

Post-Combustion Controls

NOx Control: Hot-Side SCR
Particulates: Cold-Side ESP
SO2 Control: Wet FGD
Mercury: Carbon Injection
CO2 Capture: Amine System

Solids Management

Flyash Disposal: Mixed w/ FGD Wastes

Figure 32. IECM User Interface Input Screen (Integrated Environmental Control Model, 2005)

IEA GHG R&D Programme Rapid Assessment Program

An analytical tool which is even more relevant for CO_2 capture technology assessment is an Excel-based calculator developed by a team from the IEA GHG R&D Programme in the UK (Haines, *et al.*, 2005). This tool screens novel CO_2 capture schemes to assess viability and performance by using standardized sources of data and performing some simple calculations. Viability is evaluated by assessing the state of technology development , the complexity of the flow scheme, the types of materials required, the severity of process conditions, and the safety and environmental aspects of the technology (Haines, *et al.*, 2005). Performance is evaluated by assessing CO_2 emissions, fuel consumption, capital and operating costs, process complexity, severity of conditions, construction materials, natural resource requirements, development requirements, and safety and environmental impacts (Haines, *et al.*, 2005). Viability and performance are mapped on a chart with two axes, much like the bubble diagrams discussed in Section 5.4.4, to provide a visual representation of the absolute and comparative potential that each technology option offers. This analytical tool can be very useful in helping to better understand the strengths and weaknesses of competing processes, and in screening out new processes which have little chance of commercial success (Haines, *et al.*, 2005). It is useful for technologies which are in the early stages of development.

5.5.2 CO_2 Capture Project Common Economic Model

A similar analytical tool is the Common Economic Model for comparing different CO_2 capture technologies that has been developed for the CO_2 Capture Project (Melien, 2005). This model applies a common set of approaches and methods in cost estimation and economic screening of CO_2 capture technologies, including a common discount factors, pre-tax analyses, and emissions taxes (Melien, 2005). It takes into account site-specific scenarios, comparative case analysis, significant non-capture costs, multi or byproduct outputs, technology comparisons, and generic pricing factors (Melien, 2005). This model makes a “best estimate” of cost levels and operational performance for technologies at the time of commerciality, for technologies that are either commercially available or very close to being available. Capture cost and avoided cost of CO_2 is calculated based on capital cost, operating cost, and energy costs of the capture system up to the point of delivery of CO_2 (Melien, 2005). Transportation and storage costs are addressed separately, in a sensitivity analysis. An example of an output from the model is shown in

Figure 33, where the terms on the x-axis are the different CO_2 capture technologies that were compared[9].

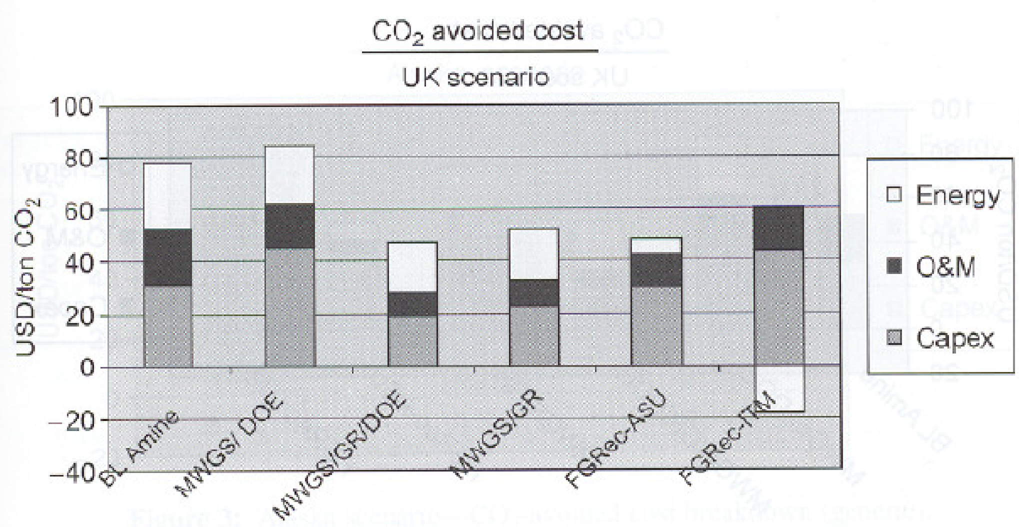


Figure 33. Sample Output from CO_2 Capture Project Common Economic Model (Melien, 2005).

This model is very useful for comparing technologies that are at the "products" end of the technology development pipeline. It is applicable to specific situations in which an industrial operation is planned, a number of CO_2 capture technologies could be chosen, and a decision must be made in the near term. It is not useful for screening new or novel technology options.

There are other analytical tools available, such as the chemical process models of coal-fired power plants, with and without CO_2 capture, that are developed during the course of larger DOE-funded studies (U.S. DOE, NETL, 2002). Typically, the results of government-funded studies are publicly available, including the analytical models which were used to develop results. These may be of limited scope, but could still be useful in portfolio management.

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[9] BL Amine = Post-combustion MEA system; MWGS/DOE = Pre-combustion membrane WGS system with DOE membrane; MWGS/GR/DOE = Pre-combustion membrane WGS system with GRACE and DOE membrane; MWGS/GR = Pre-combustion membrane WGS system with GRACE and Pd-membrane; FGRec-ASU = Oxy-fired with flue gas recycle and cryogenic ASU; FGRec-ITM = Oxy-fired with flue gas recycle and ITM.

5.5.3 Quantitative Tools

There are a number of quantitative and financial tools which can be useful in assessing the value of CO_2 capture technologies and in making decisions regarding portfolio management, each having their own characteristics and applications. Some examples are Net Present Value analyses, the "Expected Commercial Value" model and the "Bang-For-Buck Index" developed by Cooper, as well as the "Productivity Index" model, the "Options Pricing Theory" model, the "Dynamic Rank-Ordered Lists" model, and various other customized scoring models. (Cooper, *et al.*, 2001).

Quantitative tools are often simple to use, and provide distinct answers that make comparison between technologies clear and easy to understand. It is very important to be aware, however, that these tools are only as good as the assumptions upon which they are based, and they often do not capture all of the aspects which should be considered when evaluating technologies. If the strengths and weaknesses of quantitative and financial tools are well understood and the tools are applied consistently and appropriately, however, they can be very powerful and effective in maintaining a successful technology development portfolio.

5.5.4 Risk vs. Reward Assessments

Finding the correct balance of risk and reward is an essential part of managing an R&D portfolio, and should be considered by government and industry when developing CO_2 capture technologies. Using a chart to display some metric of risk versus reward is a common way of visually communicating the risk/reward profile of a technology, in an absolute sense and in relation to other technologies. Figure 34 shows an example of what a risk/reward diagram might look like, in this case for a company that produces a variety of household and beauty items.

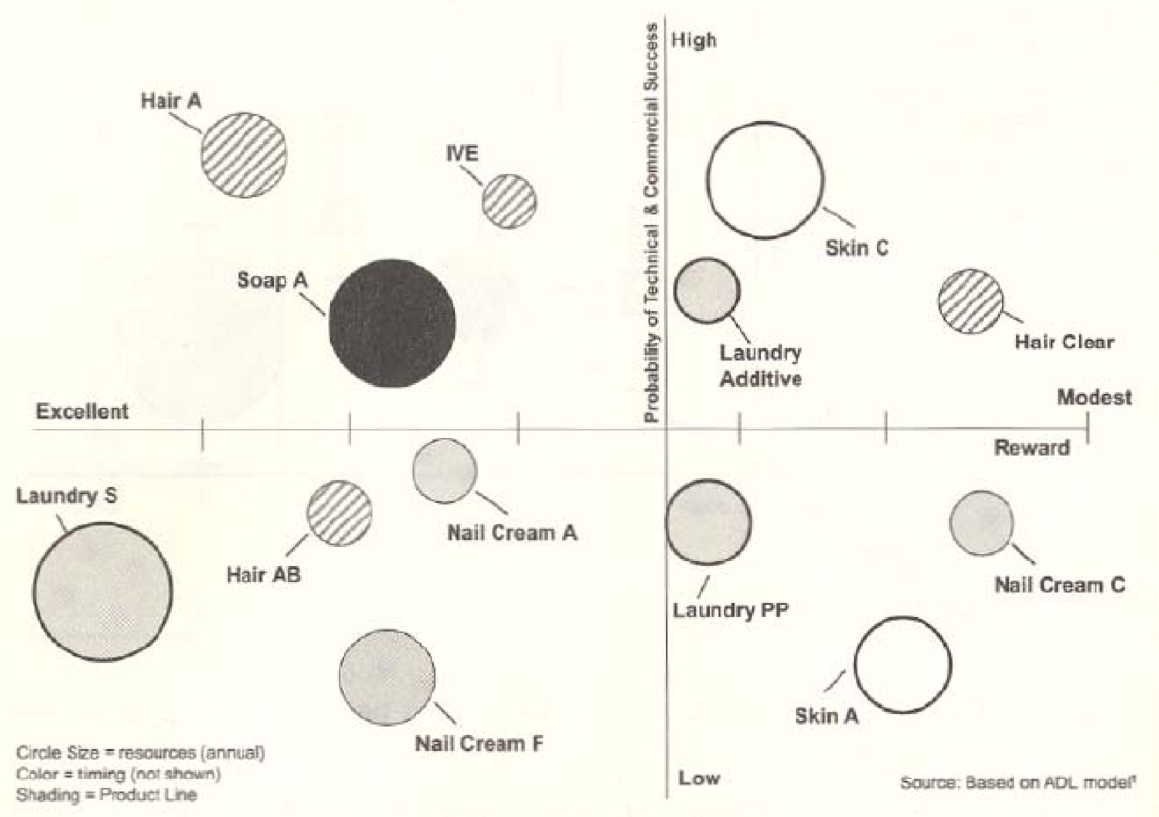


Figure 34. Example of a Risk/Reward Diagram (Adapted from Cooper, *et al.*, 2001).

There are several variants of the risk/reward chart, in which different metrics are used, but the essential characteristic is that some valuation of risk is placed on one axis, and reward on the other axis (Cooper, *et al.*, 2001). Metrics may differ depending on who is using the chart, and what type of research is being performed. For example, a government lab performing basic research should rate technologies based on probability of technical success, while private firms doing late-stage development should be concerned with commercial success. The size of the bubbles on the chart, as well as colors and shading schemes can also communicate other pieces of information, such as the estimated resources required to develop the project, levels of uncertainty surrounding data on the technology, and importance in strategy, among others.

For CO_2 capture technologies, a qualitative assessment of reward should suffice, although a quantitative metric such as potential capture cost in \$/ton CO_2 might also be valuable. Risk should be defined qualitatively, and should depend on who is developing the chart.

It is beyond the scope of this thesis to attempt to place the collection CO_2 capture technologies on a risk/reward diagram, but that is an exercise which should be undertaken by both government and industry researchers.

5.5.5 Subjective Assessments

Technology readiness levels, gate product development models, and other analytical tools can only offer so much information to decision-makers, and cannot be 100% accurate in their assessments. There will always be factors which cannot accounted for by even the most sophisticated decision-making tools. Additionally, there may not always be one right answer when it comes to choosing between technology options and when deciding whether to accelerate or abandon a technology. For these reasons, there must still be some reliance on subjective assessments of CO_2 capture technologies. Expert analysis from individuals with extensive industry experience will always be valuable, and should be used to fill in gaps in information when using other portfolio management tools, if not be given a leading role in the decision-making process.

Analytical Tools Conclusions

The value in using analytical tools is that they can provide information that is very useful in decision-making at a relatively low cost. Unfortunately, there are relatively few such tools available for general use, and many of those that are available are still under development. Generating additional analytical tools, particularly those which specialize in evaluating CO_2 capture technologies specifically, would be very useful for plant owners and operators, regulators, researchers, environmental groups, and other interested parties. The availability of such tools could provide decision makers with information on potential technology options quickly and inexpensively, could offer valuable support in the CO_2 technology portfolio management process, and could reduce the uncertainty surrounding the potential of novel capture technologies. It should be a top priority in CO_2 capture technology research, both for government and industry, to develop additional analytical tools.

5.7 Chapter Conclusions

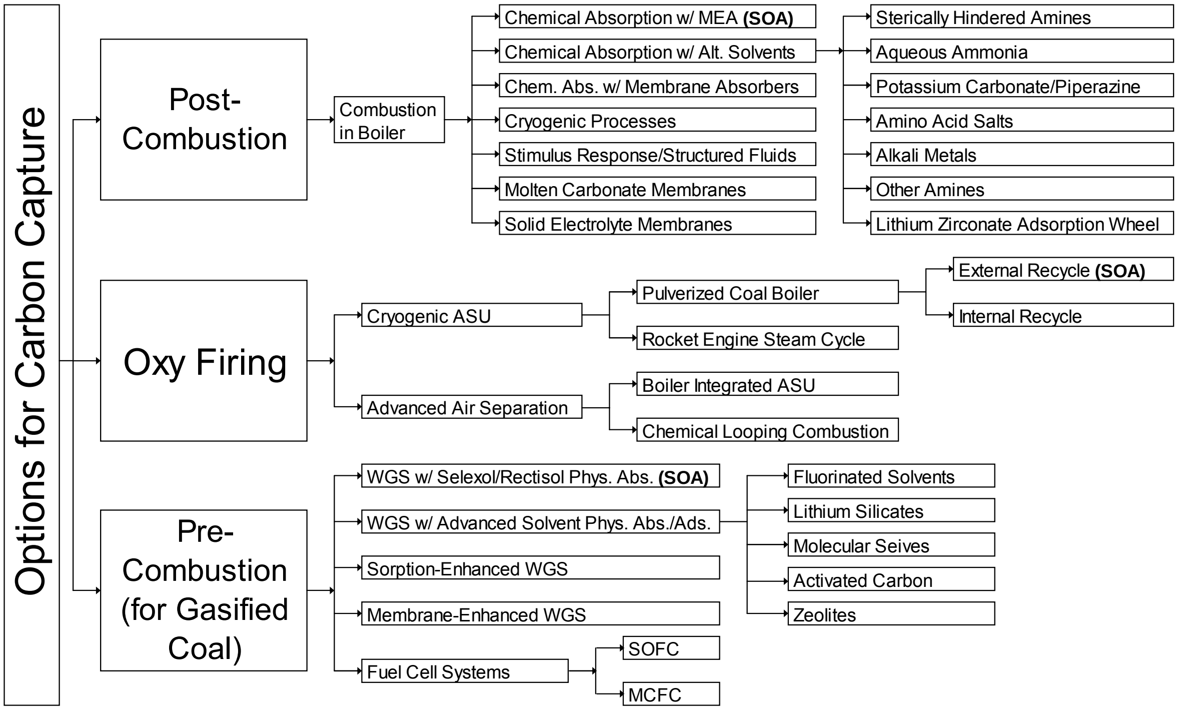
There are different types of R&D, ranging from pure basic research, which seeks to answer fundamental questions about the nature of scientific phenomena, to pure applied research, which seeks to exploit scientific phenomena to achieve practical ends. Government and private industry have different purposes in performing R&D activities, and should pursue a different mix of R&D types. Both, however, should actively maintain a portfolio of technologies that are “in the pipeline,” and should use portfolio management tools to aid in the process of making technology decisions. There are a number of portfolio management tools available, each having their own strengths and weaknesses. Improving the management tools and increasing the reach and capacity of analytic tools is a major and worthwhile task in itself, and could lead to better decision-making in the future and better use of limited R&D resources.

6.0 Conclusions and Recommendations

As detailed in Section 1.2, the question this thesis seeks to answer is:

> **“How should research and development efforts in CO_2 capture technologies for the coal-fuelled electric power industry be prioritized and advanced?”**

Chapters 2, 3, & 4 have outlined the technology options available for capturing CO_2. There are three primary pathways to viable capture systems for the coal power industry – post-combustion, oxy-fired, and pre-combustion capture. Within these three domains, there are a number of technology options that are under development. The goal for these technologies is to reduce the impact of CO_2 capture on total plant cost, cost of electricity, and plant efficiency. Figure 35 shows the key technology options and pathways available today for CO_2 Capture.



SOA = State-of-the-Art

Figure 35. Schematic Representation of the Technology Options and Pathways for CO_2 Capture

Chapter 5 has summarized the different types of research and development efforts and their objectives, and has discussed the roles of different groups in pursuing these efforts. A suite of decision-making tools for systematically managing technology development projects were also examined.

Based on the assessment of technologies available for CO_2 capture from coal-powered plants, the following conclusions can be drawn:

- There are three primary pathways to capture available today – post-combustion capture from flue gases, oxy-fired combustion, and pre-combustion capture from fuel.

- Within these pathways there are a number of technological options at various stages of development for improving the process and reducing the cost of capture

- Given the tools available today, it is a major effort to assess the potential of the technologies and to compare different technologies.

- There are no clear technology winners.

When taken with the conclusions from the investigation of research types, roles, and management tools, a set of recommendations can be set out for prioritizing research efforts in CO_2 capture technologies:

- A portfolio of technologies should be pursued, including technologies from across the three different pathways and at various stages of development.

- Government portfolios should focus primarily on early-stage technology concepts and basic research.

- Government organizations should use TRLs and a variety of analytical tools to aid in portfolio management.

- Industrial firms' portfolios should focus primarily on late-stage technologies which are being pushed to commercialization.

- Industrial firms should use gate models and a variety of analytical tools to aid in portfolio management.

- A major near-term effort should be made to improve current and develop new analytical tools, with the goal of improving the outcome of long-term decision-making.

Hence, the answer to the overarching question outlined at the beginning of this section is:

> **"Because there are several pathways that include multiple technologies at various stages of development, high levels of uncertainty surrounding the technologies, and no clear winners, government and industry stakeholders must pursue portfolios of technologies using appropriate portfolio management tools and analytical tools, balancing risk and reward and long term versus short term needs."**

We are at a crossroads in terms of moving CO_2 capture technology forward. New builds in the coal-fired power industry are expected over the next several years in the U.S., and China is currently installing coal capacity at the rate of one large plant per week. Decisions made today will have an impact on which CO_2 capture options will be available in the future. It is important that well-informed strategic policies are put in place and that practical decisions are made today, in both the public and private sector, to ensure that CO_2 capture technology is sufficiently capable of meeting future needs for the U.S. and other international interests. Government and industrial technology developers must put forth a sustained effort to advance CO_2 capture technologies, and it is hoped that the insights provided in this thesis will contribute to that endeavour.

7.0 References

1. Adanez, J., Hurst, P., Lyngfelt, A., Kronberger, B., Morin, J.-X. (2004), "The Grace Project: Development of Oxygen Carrier Particles for Chemical-Looping Combustion. Design and Operation of a 10kW Chemical-Looping Combustor," Presented at the 7th International Conference on Greenhouse Gas Technologies, Sept. 5-9, 2004, Vancouver, Canada.

2. Allam, R., Chiang, R., Hufton, J., Weist, E., White, V., Middleton, P. (2004), "Power Generation with Reduced CO_2 Emissions via the Sorption Enhanced Water Gas Shift Process," Presented at the Third Annual Conference on Carbon Capture and Sequestration," May 3-6, 2004, Alexandria, VA.

3. Allam, R., Chiang, R., Hufton, J., Weist, E., White, V., Middleton, P. (2005), "Development of the Sorption Enhanced Water Gas Shift Process," *Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project*, Elsevier, Ltd., Oxford, UK.

4. Bozzuto, C., Gupta, J.C., Guha, M., Johnson, H., Liljedahl, G., Marion, J., ya Nsakala, N., Palkes, M., Plasysnki, S. (2001), "Engineering Feasibility of CO_2 Capture on an Existing U.S. Coal-Fired Power Plant," Presented at the First National Conference on Carbon Sequestration, May 15-17, 2001, Washington D.C.

5. Buhre, B.J.P., Elliot, L.K., Sheng, C.D., Gupta, R.P., Wall, T.F. (2005), "Oxy-fuel Combustion Technology for Coal-fired Power Generation," *Progress in Energy and Combustion Science*, 31, pp. 283-307.

6. Chao, L.P., Ishii, K. (2005), "Design Process Error-Proofing: Benchmarking Gate and Phased Review Life-Cycle Models," Presented at IDETC/CIE 2005, Long Beach, CA, USA, September 24-28, 2005.

7. Chiesa, P., Consonni, S., Napoletano, S., Romano, M. (2005), "Decarbonized Electricity Production from Coal by Means of Oxygen Transport Membranes," Presented at the Fourth Annual Conference on Carbon Capture and Sequestration," May 2-5, 2005, Washington, D.C.

8. Chinn, D., Choi, G.N., Degen, B., Richen, P.L., Wen, H. (2005), "CO_2 Removal from Power Plant Flue Gas – Cost Efficient Design and Integration Study," an excerpt from *Carbon Dioxide Capture for Storage in Deep Geologic Formations, Vol 1.*, Elsevier Ltd, Oxford, UK.

9. Ciferno, J.P., DiPietro, P., Tarka, T. (2005), "An Economic Scoping Study for CO_2 Capture Using Aqueous Ammonia," Prepared for U.S. Department of Energy, National Energy Technology Laboratory.

10. Clean Energy Systems, Inc. (2006), Clean Energy Systems, Inc. webpage "The Technology," downloaded 03/09/2006 from http://www.cleanenergysystems.com/2005/technology.html.

11. Clodic, D., El Hitti, R., Younes, M., Bill, A., Casier, F. (2005), "CO_2 Capture by Anti-Sublimation Thermo-Economic Process Evaluation," Presented at the 4th Annual Conference on Carbon Capture & Sequestration, May 2-5, 2005, Alexandria, VA, USA.

12. Coen. (2006), "BIF Boiler Regulations and Technology," downloaded 4/12/2006 from http://www.coen.com/i_html/white_bif.html.

13. Coker, D., Figueroa, J., Green, D.A., Gupta, R.P., McMichael, W.J., Nelson, T.O., Portzer, J.W. (2005), "Dry Regenerable Carbonate Sorbents for Capture of Carbon Dioxide from Flue Gas," Presented at the Fourth Annual Conference on Carbon Capture and Sequstration, May 2-5, 2005, Washington, D.C.

14. Cooper, R.G., Edgett, S.J., Kleinschmidt, E.J. (2001), *Portfolio Management for New Products (2nd Edition)*, Perseus Publishing Services, Cambridge, MA.

15. Cullinane, J.T., Oyenekan, B.A., Lu, J, Rochelle, G. T. (2002), "Carbon Dioxide Capture by Absorption with Potassium Carbonate," NETL funded project, University of Texas at Austin.

16. Deppe, G., Tam, S.S., Currier, R.P., Young, J.S., Anderson, G.K., Le, L., Spencer, D.F. (2003), "Developments in the SIMTECHE Process – Separation of CO_2 from Coal Syngas by Formation of Hydrates," Presented at the Second Annual Conference on Carbon Capture and Sequestration, Alexandria, VA, May 5-8, 2003.

17. Deutch & Moniz. (2006), "The Future of Coal," MIT Laboratory for Energy and the Environment, Cambridge, MA.

18. Deutch, J.M., Lester, R.K. (2004), *Making Technology Work: Applications in Energy and the Environment*, Cambridge University Press, Cambridge, UK.

19. Electric Power Research Institute. (2000), "Evaluation of Innovative Fossil Fuel Power Plants with CO_2 Removal," An interim report published December 2000, Palo Alto, CA.

20. Eom, T.H., Lee, J.B., Oh, J.M., Ryu, C.K., Yi, C.K. (2005), "Development of Na and K-Based Sorbents for CO_2 Capture from Flue Gas," Presented at the Fourth Annual Conference on Carbon Capture and Sequstration, May 2-5, 2005, Washington, D.C.

21. Feron, P.H.M., ten Asbroek, N. (2004), "New Solvents Based on Amino-Acid Salts for CO_2 Capture from Flue Gases," Presented at the 7th International Conference on Greenhouse Gas Technologies, Sept. 5-9, 2004, Vancouver, Canada.

22. Fisher, K.S., Beitler, C., Figueroa, J.D., Jassim, M., Rochelle, G., Rueter, C. (2005), "Integrating MEA Regeneration with CO_2 Compression to Reduce CO_2 Capture Costs," Presented at the Fourth Annual Conference on Carbon Capture and Sequstration, May 2-5, 2005, Washington, D.C.

23. FLUOR (2004), "Potential for Improvement in Power Generation with Post-Combustion Capture of Carbon Dioxide," Interim Final Report prepared for IEA GHG R&D Programme, Report No. August 2004-08-10.

24. FLUOR. (2004), "Improvement in Power Generation with Post-Combustion Capture of CO_2," IEA Greenhouse Gas R&D Programme, Report No. PH4/33.

25. Gibbins, J., Roberts, C.A., Panesar, R., Kelsall, G. (2004), "Potential for Improvement in Power Generation with Post-Combustion Capture of CO_2," Interim report, IEA GHG R&D Programme.

26. Granite, E.J., & O'Brien, T. (2005), "Review of Novel Methods for Carbon Dioxide Separation from Flue and Fuel Gases," *Fuel Processing Technology*, No. 86, pp. 1423-1434.

27. Haines, M.R., Skinner, G.F., Maunder, A.D. (2005), "Rapid Assessment of Novel CO_2 Capturing Power Plants," Presented at the 7th International Conference on Greenhouse Gas Technologies, Sept. 5-9, 2004, Vancouver, Canada.

28. Heintz, Y., Lemoine, R.O., Sehabiague, L., Morsi, B.I., Jones, K.L. Pennline, H.W. (2005), "CO_2 Capture Under Elevated Pressures and Temperatures Using Fluorinated Solvents," Presented at the AICHE 2005 Annual Meeting, Cincinnati, OH, Oct. 30- Nov. 4, 2005.

29. Herzog, H., & Golomb, D. (2004), "Carbon Capture and Storage from Fossil Fuel Use," *Encyclopedia of Energy*, Elsevier, Article No. NRGY: 00422.

30. Herzog, H., Golomb, D., Zemba., S. (1991), "Feasibility, Modeling and Economics of Sequestering Power Plant CO_2 Emissions in the Deep Ocean," *Environmental Progress*, Vol. 10, No. 1.

31. Herzog, H.J. (2002), "Carbon Sequestration: Analysis of Research Activities," A report to the Electric Power Research Institute, Palo Alto, CA.

32. Higman, C., van der Burgt, M. (2003), "Gasification," Elsevier Science, Burlington, MA, USA.

33. Hoff, K.A., Juliussen, O., Ma'mun, S., Svendsen, H.F. (2004), "Selection of New Absorbents for Carbon Dioxide Capture," Presented at the 7th International Conference on Greenhouse Gas Technologies, Sept. 5-9, 2004, Vancouver, Canada.

34. Holt, N. (2001), "Integrated Gasification Combined Cycle Power Plants," *Encyclopedia of Physical Science and Technology*, Sept. 2001.

35. Hutson, N., Attwood, B., Reynolds, S., Gadre, S., Ebner, A., Ritter, J. (2004), "Separation and Capture of CO_2 Using a High Temperature Pressure Swing Adsorption System," Presented at the Third Annual Conference on Carbon Capture and Sequestration," May 3-6, 2004, Alexandria, VA.

36. Iijima, M., Ishida, K., Kamijo, T., Mimura, T., Yagi, Y., Yonekawa, T., Yoshiyama, R. (2004), "Improvements of Carbon Dioxide Capture Technology from Flue Gas," Presented at the 7th International Conference on Greenhouse Gas Technologies, Sept. 5-9, 2004, Vancouver, Canada.

37. Ing, Häge, H.C. (2006), "Balancing the Triangle of Economy, Security, and Environment in an Open European Energy Market," Presented at Energy Paths – Horizon 2050, Vienna, Austria, March 16th, 2006.

38. Integrated Environmental Control Model. (2005), Developed by Carnegie Mellon University for the U.S. DOE, National Energy Technology Laboratory. Publicly available at http://www.iecm-online.com/index.htm.

39. Itou, K., Tani, H., Ono, Y., Kasai, H., Ota, K. (2002), "High Efficiency CO_2 Separation and Concentration System by Using Molten Carbonate," Presented at the 6th International Conference on Greenhouse Gas Technologies, Oct. 1-4, 2002, Kyoto, Japan.

40. Jordal, K., Anheden, M., Yan, J., Stromberg, L. (2005), "Oxyfuel Combustion for Coal-Fired Power Generation with CO_2 Capture – Opportunities and Challenges," Presented at the 7th International Conference on Greenhouse Gas Technologies, Sept. 5-9, 2004, Vancouver, Canada.

41. Judkins, R.R. & Burchell, T.D. (2001), "CO_2 Removal From Gas Streams Using a Carbon Fiber Composite Molecular Sieve," Presented at the First National Conference on Carbon Sequestration, Washington, DC, May 14-17 2001.

42. Kobayashi, H., Deneys, A.C., Riley, M.F. (2001), "Praxair's Dilute Oxygen Combustion Technology for Pyrometallurgical Applications," *JOM : The Journal of the Minerals, Metals & Materials Society*. Vol 53, Issue 5, pp. 21-24.

43. Li, W., Turk, B.S., Gangwal, S.K., Nelson, T.O., Gupta, R.P. (2005), "Novel Lithium Silicate-based Sorbents for High Temperature Carbon Dioxide Removal," Presented at the Fourth Annual Conference on Carbon Capture and Sequestration," May 2-5, 2005, Washington, D.C.

44. Lokurlu, A., Bakke, K., Blum, L., Heidug, W., Li, K-J., Riensche, E. (2004), "CO_2 Sequestration from Solid Oxide Fuel Cells: Technical Options and Costs," Presented at the 7th International Conference on Greenhouse Gas Technologies, Sept. 5-9, 2004, Vancouver, Canada.

45. Lowe, C., Mundschau, M., Xie, X. (2004), "Hydrogen Membrane Selection for a Water Gas Shift Reactor, Phase II," Presented at the Third Annual Conference on Carbon Capture and Sequestration," May 3-6, 2004, Alexandria, VA.

46. Mancuso, L., Farina, G.L., Domenichini, R. (2005), "CO_2 Capture in Low-Rank Coal Power Plants," Draft Report, IEA Greenhouse Gas R&D Programme, July 2005.

47. Mankins, J.C. (1995), "Technology Readiness Levels: A White Paper," NASA, Office of Space Access and Technology, Advanced Concepts Office.

48. Melien, T. (2005), "Economic and Cost Analysis for CO_2 Capture Costs in the CO_2 Capture Project Scenarios," *Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project*, Elsevier, Ltd., Oxford, UK.

49. Meystel, A., Albus, J., Messina, E., Leedom, D. (2003), "Performance Measures for Intelligent Systems: Measures of Technology Readiness," A white paper presented at the Performance Metrics for Intelligent Systems Workshop, Gaithersburg, MD, Sept. 16-18, 2003.

50. PES Network, Inc. (2006), "Solid Oxide Fuel Cells," downloaded 4/13/2006 from http://www.freeenergynews.com/Directory/FuelCell/SolidOxide/.

51. Phillips, J. (2005), "Integrated Gasification Combined Cycles with CO_2 Capture," Electric Power Research Institute presentation.

52. Resnik, K.P., Yeh, J.T., Pennline, H.W. (2004), "Aqua Ammonia process for Simultaneous Removal of CO_2, SO_2, and NO_x," *International Journal of Environmental Technology and Management*, Vol. 4, Nos. 1/2.

53. Roberts, *et al.*. (2005), "Potential for Improvement in Power Generation with Post-Combustion Capture of CO_2," Presented at The International Conference on Greenhouse Gas Control Technologies, Vancouver, Canada, 5-9 September, 2005.

54. Rochelle, Gary. (2005), Gary Rochelle of University of Texas (Austin) personal communication with Howard Herzog of MIT Laboratory for Energy and the Environment, March 7, 2005.

55. Ryden, M., Lyngfelt, A. (2004), "Hydrogen and Power Production with Integrated Carbon Dioxide Capture by Chemical-Looping Reforming," Presented at the 7th International Conference on Greenhouse Gas Technologies, Sept. 5-9, 2004, Vancouver, Canada.

56. Simmonds, M., Miracca, I., Gerdes, K. (2005), "Oxyfuel Technologies for CO_2 Capture: A Techno-Economic Overview," Presented at the 7th International Conference on Greenhouse Gas Technologies, Sept. 5-9, 2004, Vancouver, Canada.

57. Sirman, J., Simmonds, M., Switzer, L., Thompson, D. (2004), "Oxygen Transport Membranes – An Enabling Technology for Cost Effective CO_2 Capture," Presented at the Third Annual Conference on Carbon Capture and Sequestration," May 4, 2004, Washington, D.C.

58. Smith, J.D. (2005), "An Alternative to Technology Readiness Levels for Non-Developmental Item Software," Carnegie Mellon Software Engineering Institute, presented at the 38th Hawaii International Conference on System Sciences, Jan. 3-6, 2005.

59. Steinberg, M., Cooper, J.F., Cherepy, N. (2002), "High Efficiency Carbon and Hydrogen Fuel Cells for CO_2 Mitigated Power," Presented at the 6th International Conference on Greenhouse Gas Technologies, Oct. 1-4, 2002, Kyoto, Japan.

60. The Babcock and Wilcox Company (2006), "Demonstration of the Oxy-combustion Process for CO_2 Control at the City of Hamilton," Presented at the Americal Coal Council 2006 Mercury & Multi-Emissions Conference, March 16, 2006.

61. U.S. Department of Defense, Fuel Cell Projects. (2006), "Fuel Cell Information Guide," Downloaded April 14th, 2006 from http://dodfuelcell.cecer.army.mil/molten.html.

62. U.S. Department of Energy, National Energy Technology Laboratory. (2002),"Advanced Fossil Power Systems Comparison Study," Morgantown, WV.

63. U.S. Department of Energy, Office of Energy Research. (1993), "A Research Needs Assessment for the Capture, Utilization and Disposal of Carbon Dioxide from Fossil Fuel-Fired Power Plants," Vol II, July 1993.

64. U.S. Department of Energy. (2006), "Molten Carbonate Fuel Cell Technology," Downloaded April 14, 2006 from

http://www.fossil.energy.gov/programs/powersystems/fuelcells/fuelcells_moltencarb.html.

65. U.S. DOE, National Energy Technology Laboratory. (2001), "The Integrated Environmental Control Model," A Project Fact Sheet, available at http://www.netl.doe.gov/technologies/publications/factsheets/project/proj147.pdf

66. U.S. GAO (1999), "Better Management of Technology Development can Improve Weapon System Outcomes," A Report to the Chairman and Ranking Minority Member, Subcommittee on Readiness and Management Support, Committee on Armed Services, U.S. Senate, Washington D.C., July 30, 1999.

67. Williams, A., Pourkashanian, M., Jones, J.M., Skorupska, N. (2000), *Combustion and Gasification of Coal*, Taylor & Francis, New York, NY.