



THE CARBON CAPTURE AND SEQUESTRATION: TECHNOLOGY OVERVIEW

*M.D.S. PIRZADA and F.N PIRZADA

Chemistry Division, PINSTECH, P.O. Nilore, Islamabad, Pakistan

Carbon capture and sequestration (CCS) technologies remove carbon dioxide from flue gases. It is then stored instead of being released into the atmosphere. CCS has the potential to mitigate global warming by capturing carbon dioxide (CO₂) at its major production centres such as fossil fuel power plants. Large scale capture of CO₂ has already been achieved commercially. The CCS is technically feasible and fairly well developed but to date no large-scale power plant is being operated with a full carbon capture and storage system. Compared to a plant without CCS, one with CCS can cut CO₂ emissions to the atmosphere by approximately 80-90%. However, the energy required to accomplish CCS increases the fuel needs of a coal-fired plant by about 25%. This, combined with the total system costs significantly increases the cost of energy. This makes CSS currently a relatively expensive mitigation option. Still if fossil fuels remain a major part of the energy mix, the global exigency to reduce carbon dioxide emissions laid under Kyoto protocol can make CCS an attractive option. This article discusses the possibilities and limitations of CCS. The technical and economic uncertainties and obstacles in the implementation of CCS have been illustrated. The status of industrial-scale storage projects in operation and those in the pipeline has also been reviewed.

Keywords: Carbon capture, Sequestration, Kyoto protocol

1. Introduction

There is overwhelming scientific evidence that climate change is a serious global threat [1]. There is a need therefore to intensify measures to combat climate change.

The effect of climate change and global warming on the world economy has recently been studied and evaluated in great detail by Sir Nicholas Stern [2]. Stern states: "our actions over the coming few decades could create risks of major disruption to economic and social activity, later in this century and in the next, on a scale similar to those associated with the great wars and the economic depression of the first half of the 20th century."

As greenhouse gases are retained by the atmosphere for longer periods, it is anticipated that their atmospheric concentrations will continue to rise for several decades. Consequently, the average global temperatures will keep increasing [3]. The likely consequences in the foreseeable future include persistent sea-level rise and associated increase in the occurrence of extreme storm surges [4]. In some areas changing rainfall patterns, inundation, and spread of infectious diseases will increase the risks of famine and high mortality.

Nowadays, there is a growing consensus among the environmentalists that rising concentrations of greenhouse gases in the atmosphere are contributing to the already visible signs of climate change. Human activities, especially burning of fossil fuels, are the main contributors to the anthropogenic share in the overall concentrations of the long-lived greenhouse gases.

In addition to the climate change, greenhouse gases and particle soot affect body's respiratory and cardiovascular systems. Many studies have established aggravated asthma, bronchitis, emphysema, lung and heart diseases, and respiratory allergies as a direct cause of air pollution. A recent study has found that only in USA, the CO₂ may increase annual air pollution deaths by about 1000 per 1 K rise in CO₂-induced temperature [5]. According to the WHO the number of deaths per year attributed to outdoor pollution is 28,700. The impact of air pollution is measured by an index that combines the time lived with a disability and the time lost due to premature mortality – the Disability Adjusted Life Year (DALY). The estimated outdoor DALY value for Pakistan is 2.3 [6]. This places Pakistan among the top 10 on the pollution-impact list.

*Corresponding author : thepirzada@yahoo.com

Presently the fossil fuels are providing 86% of the world's energy [8]. The trend that is likely to continue for many decades. The statistics indicate that global consumption of fossil fuel is still escalating and the global carbon dioxide emissions rising. Among the fossil fuels, coal is the most abundant. It also has the most widely distributed reserves. Coal is mined in over 100 countries. The largest reserves are found in the USA, Russia, Australia, China, India and South Africa. Table 1 shows the Production of Coal by Country and year. Pakistan has large coal deposits mostly in the Thar coal field in Sindh. The proven global reserves of coal are around 998 billion tonnes [8], enough to sustain the current production rate for 155 years. According to British Petroleum statistics, coal was the fastest growing fossil fuel in 2007 for the fifth year in a row [9]. In 2007, China was building about two coal fired power plants every week [10]. The large reserves make coal a popular candidate to meet the energy demand of the global community in the foreseeable future. Unfortunately coal has the highest CO₂ emissions per unit of energy produced. This suggests that global carbon dioxide production may keep on rising for many decades.

2. The Challenge of Emission Reduction

The mitigation of adverse environmental impacts due to global warming and consequent climate change requires the reduction of CO₂ emissions in the atmosphere. Energy sector is the major source of CO₂. The reduction in CO₂ emissions can be achieved through a number of parallel approaches e.g. enhanced energy conservation, and increasing the share of renewable energy sources. Efforts and investments to significantly increase the share of renewable energy to satisfy the primary energy demand remain ineffective mainly being expensive and hence non-competitive. Apparently the pressure to reduce CO₂ emissions will increase with time; this will eventually require carbon capture from fossil fuels. This makes incorporating advanced technologies in fossil fuel-based energy generation system imperative. Success in this effort will allow sustainable growth without abandoning the fossil energy sources [11].

2.1. Carbon capture and sequestration

Carbon capture and sequestration (CCS) is defined as the capture of CO₂ from fossil fuel-using sources, and its storage in secure reservoirs instead of releasing it in the atmosphere. Another common term used for this approach is carbon capture and storage. Carbon sequestration complements two other major approaches for greenhouse gas reduction, namely improving energy efficiency and increasing use of non-carbon energy sources. There is growing interest this option because of its potential to cope with large-scale energy production [12].

Table 1. Production of coal by country and year (million tonnes) [9].

Country	2003	2004	2005	2006
Indonesia	114.3	132.4	146.9	195.0
Poland	163.8	162.4	159.5	156.1
Germany	204.9	207.8	202.8	197.2
South Africa	237.9	243.4	244.4	256.9
Russian Feder	276.7	281.7	298.5	309.2
Australia	351.5	366.1	378.8	373.8
India	375.4	407.7	428.4	447.3
United States	972.3	1008.9	1026.5	1053.6
PR China	1722.0	1992.3	2204.7	2380.0
Total World	5187.6	5585.3	5886.7	6195.1

This approach if applied successfully will help exploit the huge potential of fossil fuels without increasing the CO₂ burden of the atmosphere, and thereby mitigating global climate change. The storage period should be long enough to exceed the period of peak fossil fuel exploitation, so that if CO₂ is finally released in the air this should happen at a time when the peak atmospheric CO₂ concentrations have already passed.

2.2. Capture processes

Various processes are used for CO₂ capture. The capture technologies are typically classified as post-combustion, pre-combustion, and oxy-fuel combustion. Active R&D is in progress on several options for improving each of these processes. All of these processes are energy as well as capital intensive. There is uncertainty about which of these technologies has the potential to reduce the cost of CO₂ capture and help meet future challenges.

According to IPCC estimates, for 90 percent CO₂ capture from a power plant, the fuel

consumption will increase by 11 to 40 percent and the power production costs by 20–85 percent, depending on the technology and the fuel [1]. The cost reduction remains a fundamental challenge. The use of the available technology for CO₂ capture in the near future will therefore in large part will be determined with regard to costs. The foremost processes are briefly described below [13].

2.3. Post-combustion process

Post-combustion involves separating CO₂ from the exhaust gas from the power plants using chemical cleaning. The process works on the principle of chemical absorption. The flue gas is bubbled through the solvent that preferentially removes the CO₂ from it. Later processing in a regenerator separates the gas from the solvent. For CO₂ absorption, mono ethanol amine (MEA) is the most commonly used solvent. The schematic of the process is shown in Fig. 1.

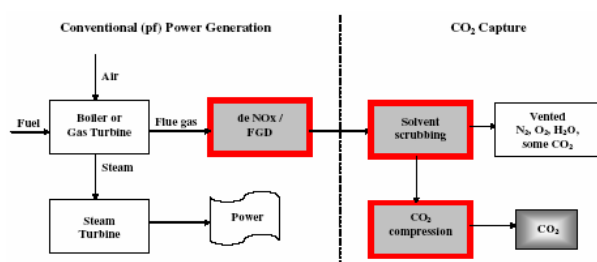


Figure 1. Schematic of post-combustion capture process, with additional unit operations For carbon capture showed bold [14].

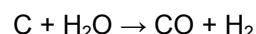
Since the separation is done from the exhaust gas, this technology can, in principle, be employed in existing power plants without major modifications of the power plant system. Post-combustion is the most mature technology, although there are still significant uncertainties surrounding its use.

Other alternate processes like membrane separation, cryogenic fractionation, and adsorption using molecular sieve are less energy efficient and comparatively expensive. The R&D on ionic liquid membranes that beat polymers in terms of CO₂ selectivity and permeability at higher temperatures is in progress [12].

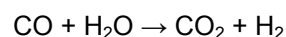
2.4. Pre-combustion process

The-combustion technology entails capturing of CO₂ before combustion. Pre-combustion

capture is the preferred method in coal gasification units. Gasification is a process that converts carbonaceous materials e.g. fossil fuels, biomass or organic waste (wood, plastic etc.) into a mixture of carbon monoxide and hydrogen. This gas mixture is called synthesis gas or syngas and is itself a fuel. The syngas is better fuel as more energy contained in the fuel can be extracted. The process involves reacting the raw material at elevated temperatures >700°C with a controlled amount of oxygen and/or steam.



The resulting carbon monoxide reacts with water to form carbon dioxide and hydrogen, a reversible reaction called as water gas shift reaction.



The CO₂ is separated from a mixture of CH₄, H₂, or a mix of CO and H₂ gases after gasification stage (See Fig 2). The CO₂ is captured using methanol or poly (ethylene glycol). The method is ideally suited for integrated coal gasification combined cycle power plants (ICGC). The separation of CO₂ from this fuel stream in essence results in a “decarbonised fuel” which means that on burning the exhaust gas from this fuel will have very little CO₂. Pre-combustion requires modification of gas turbines and is considered to be a more complex technology than post-combustion.

2.5. Oxyfuel combustion process

Fossil fuel burnt in air results in a mixture of flue gases that is mainly N₂ with 3-15% of CO₂. The separation of CO₂ from this mixture as mentioned earlier is capital and energy intensive. Another option is to burn the fossil fuel in pure or enriched oxygen. This results in a flue gas stream containing mostly CO₂ and H₂O. The water vapors can be easily condensed, and the CO₂ can be compressed for later processing. Figure 3 shows a schematic of the process.

The emerging oxyfuel combustion process has its own characteristic constraints. The oxygen supply requires an air separation unit. This is an extremely energy-intensive process, and the corresponding technology is quite costly. Furthermore the present day gas turbines exhibit

very poor performance with oxygen combustion. This demands new types of turbines that are efficient to oxygen combustion. Oxy-fuel is thus still a developing technology.

The factors that dictate the selection of a particular method include, the concentration of CO₂ in the gas stream, the pressure of the gas stream, and whether the fuel is solid or gas. Post-combustion capture is typically used at power plants. Pre-combustion capture technologies are considered better for coal gasification units, fertilizer manufacturing and in hydrogen production. Oxy-fuel combustion is still in the demonstration phase.

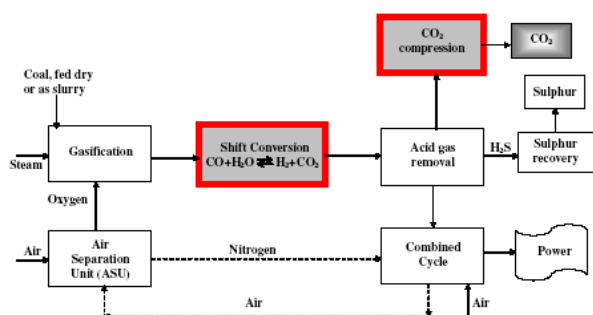


Figure 2. Schematic of pre-combustion capture process, with additional unit operations for carbon capture showed bold [14]

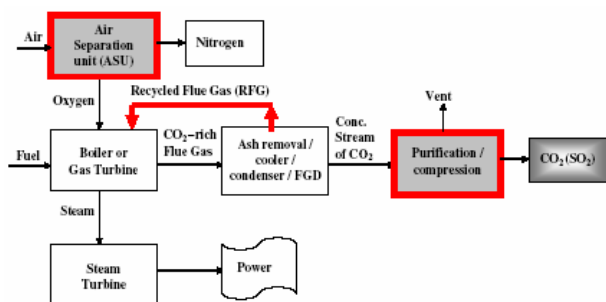


Figure 3. Schematic of oxy-fuel (Oxyf) process, with additional unit operations for carbon capture showed bold [14].

3. Transportation of CO₂

CO₂ must be transported from the CO₂ source to the CO₂ storage site. CO₂ is transported as liquid. It requires the conversion of gas to liquid by compression or a combination of compression and cooling. Transportation is carried out in controlled conditions to avoid solid stale and subsequent clogging of pipes or equipment. Both

pipelines and ships can be used for transportation. Transportation by pipeline being simpler is more common.

Pipeline transport of CO₂ is largely similar to the transport of oil and gas. The technologies are well proven with an extensive construction and operation experience in variety of terrestrial environments. The experience of transportation in marine environment is however limited.

Choice of means of transport depends on the volume of emissions, the distance from the source to the storage place and the type of storage. Presently pipeline transport is considered simpler and cost-effective.

3.1. Storage systems

The choice of a particular storage system is determined by several criteria. These include:

- Storage period
- Cost of transportation and storage
- Safety and reliability
- Environmental impact, and
- Conformity with the national/ international laws and regulations.

Currently geologic sinks are the foremost storage options. Geologic storage options include deep saline formations, depleted oil and gas reservoirs, formations for enhanced oil recovery operations, and un-minable coal seams [14].

3.2. Depleted oil and gas reservoirs

Injecting CO₂ into depleted oil and gas fields has already been practiced for many years with the purpose of disposing of "acid gas," a mixture of CO₂, H₂S, and other by-products of oil and gas exploitation and refining. The process requires a sufficiently isolated reservoir with adequate porosity.

3.3. Enhanced oil recovery (EOR) operations

Different gases like such as CO₂, natural gas, or nitrogen used for EOR operations. Upon injection into the reservoir the gas expands and thereby pushes additional oil to a production wellbore. In addition it gets dissolved in the oil results in viscosity reduction and consequently increasing its fluidity. From half to two-thirds of the injected gas returns with the produced oil and

is reused. The rest is trapped in the oil reservoir. Much of the CO₂ injected into the oil reservoir is only temporarily stored. EOR is a mature technology. In US alone 72 such projects are producing ~200,772 barrels (bbl) of oil per day. Canada, Hungary, Turkey, and Trinidad are other countries where EOR is being exercised [15].

3.4. Abandoned coal mines

The captured CO₂ can also be stored in the abandoned or uneconomic coal mines. The gas can diffuse through the pore structure of coal and get adsorbed. Compared to CH₄, the coal has double affinity for CO₂; the process therefore can be used to enhance the recovery of coal bed methane. This process has become a significantly important component of natural gas supply in the United States, producing nearly 7% of the nation's total natural gas production.

3.5. Deep saline formations

Saline formations containing mineralized brines have been used for storage of chemical wastes. Deep saline formations because of their large volumes and their common occurrence have enormous storage potential for CO₂. Compared to the oil fields or coal mines the storage in saline aquifers has no side product. The dissolution into fluids and the reaction with minerals present in the host formation to form solid compounds such as carbonates helps in immobilization of CO₂. It is estimated that CO₂ could be trapped for millions of years, and the well-maintained sites can retain over 99% of the injected CO₂ over 1,000 years [1].

3.6. Deep ocean storage

In this approach, liquid CO₂ is directly injected into the water column at depths around 3,000 m. At these depths the liquid CO₂ becomes heavier than seawater and sinks to the ocean bottom to form a "CO₂ lake." The Ocean represents the largest potential sink for anthropogenic CO₂. The ocean already holds an estimated 40,000Gt C in its surface layer. By comparison the atmosphere and terrestrial biosphere hold merely 750 GtC and 2,200 GtC respectively.

Unlike the surface layer the deep ocean water is unsaturated with respect to CO₂. An anthropogenic CO₂ burden of twice the atmospheric concentration if injected into the deep ocean will change the ocean carbon

concentration by less than 2%, and change its pH by less than 0.15.

3.7. The dynamics of ocean storage

For cost considerations CO₂ would be released in the liquid phase. Because of the hydrostatic pressure, the density of CO₂ increases with the depth of injection. If liquid CO₂ is released above 500m depth the hydrostatic pressure is less than 50 atmospheres, liquid CO₂ transforms into vapor phase and makes its way to the atmosphere. Between 500-3,000 m, liquid CO₂ rises to surface by buoyancy. The hydrodynamic modeling has shown that liquid CO₂ dispersed at this depth into droplets of less than ~ 1 cm diameter completely dissolves before rising 100 m. At depths larger than 3,000m liquid CO₂ becomes denser than seawater. If released there, it sinks to the bottom of the ocean forming a CO₂ lake. At temperatures less than 101C and pressures greater than 44.4 atmospheres CO₂ reacts with water to form a solid hydrate. In case of droplets a thin film of hydrate is formed at the surface.

There are two approaches to injecting CO₂ into the ocean.

- i. To Inject CO₂ at 1,500–3,000 m depth, and
- ii. To inject CO₂ below 3,000 m, where it will form a "CO₂ Lake"

The first technique results in higher dilution and therefore minimizes local environmental impacts. The second technique promises minimum leakage to the atmosphere.

Table 2. Costs of energy with and without CCS (2002 US\$ per kwh) [1].

	NC	PC	IGC
Without capture (reference plant)	0.03 - 0.05	0.04 - 0.05	0.04 - 0.06
With capture and geological storage	0.04 - 0.08	0.06 - 0.10	0.06 - 0.09
With capture and Enhanced oil recovery	0.04 - 0.07	0.05 - 0.08	0.04 - 0.08

Researchers are also working on an alternate option that of bringing seawater into contact with

flue gases from a CO₂ source. This CO₂-rich water can then be brought into contact with powdered carbonate minerals resulting in corresponding bicarbonate. This approach does not require deep injection and no pH changes result. Its drawbacks include the need for large amounts of water and carbonate minerals. Various other methods of CO₂ separation and capture from power plants and other industrial sources have been proposed and are areas of active investigation in various research laboratories e.g. mineralization and biomineralization. Ongoing research and development is analyzing the technical potential and economic feasibility of these and other novel concepts for carbon capture and sequestration [16-19].

3.8 Chemical conversion

The captured CO₂ can be used by the chemical industry as a raw material. One such utility is the synthesis of urea (>10 Mt C p.a.). However, the amount that can be utilized is a very small fraction of current global anthropogenic emissions that is nearly 7 Gt C per year.

NC: Natural gas combined cycle, PC: Pulverized coal, IGC: Integrated gasification combined cycle

4. Cost and Environmental Safety

The injection of CO₂ in a geological reservoir starts a phase where control of CO₂ is handed over to the forces of nature. However, understanding of these forces and their interactions is rather limited. This raises serious questions of risks to human health and the impact on the environment. The studies are still in progress to evaluate the likelihood and potential impacts associated with leaks, long-term diffusion and accumulation.

Capturing and compressing CO₂ are energy and cost intensive processes. The capturing of CO₂ accounts for about three-fourths of the total cost of a carbon capture, storage, transport, and sequestration system. The CCS processes would require an additional ~ 25% for a coal-fired plant and ~15% for a gas-fired plant. This combined with the extra cost of storage transportation is estimated to increase the costs of energy from a power plant with CCS by 30-60% depending on size of the plant and its relative location from the

sequestering location. The cost of energy with and without CCS has been compared in Table 2 [1].

5. Conclusions

1. While currently relatively expensive, CCS is technically feasible option to mitigate global warming. CCS could be attractive if it is desired to retain fossil fuels as part of the energy mix while reducing carbon emissions.
2. Near-term prospects favor CCS with storage in depleted oil and gas reservoirs. Deep aquifers may provide an attractive longer-term-storage option. Ocean storage has huge potential but poses various technical uncertainties.
3. CO₂ sequestration is not an unproven technology. In fact, the United States alone is sequestering about 8.5 million tons of carbon for enhanced oil recovery each year. The critical issue in this regard is that currently sequestering cost makes the electricity prohibitively expensive. A considerable cost reduction is a prerequisite for the general acceptance and consequent extensive implementation of this philosophy/approach.
4. Experts agree that global potential of reservoirs exceeds the sequestration requirements of CO₂. More work is needed however to establish the effectiveness and safety of proposed reservoirs.
5. Opportunities for future cost reductions will include the investigation of innovative technologies, including new types of power plants and power cycles. Moreover, system-level analyses should be performed to minimize not only capture costs, but also the sequestration costs associated with transportation and injection.
6. The R&D can enhance the efficiency and effectiveness of many candidate processes making some of these processes cost-effective, even free. This is because the process enhancements and high-value byproducts can offset the cost of the CO₂ storage operations.

In order to utilize the huge coal reserves for global power needs without increasing CO₂ emissions, low cost technologies must be developed for capturing CO₂ from power plants.

To date, there is no ongoing R&D program in the area of CO₂ capture and sequestration in our country. Our scientists and engineers are enriched with the valuable experience in the field of adsorption chemistry, chemical processing and transportation of oil and gas. An expected growing share in the future energy mix of the country combined with the global research interest in this area will hopefully draw the attention of our scientist, engineering and energy planners of Pakistan.

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