Carbon Dioxide: Capturing and Utilization

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1. Introduction

The global warming issue is one of the most important environmental issues that impacts on the very foundations of human survival.

One person emits about 20 tons of CO₂ per year. Combustion of most carbon-containing substances produces CO₂. Energy utilization in modern societies today is based on combustion of carbonaceous fuels, which are dominated by the three fossil fuels: coal, petroleum, and natural gas. Complete oxidation or combustion of any carbon-based organic matter produces CO₂.

Carbon dioxide makes up just 0.035 percent of the atmosphere, but is the most abundant of the greenhouse gases (GHG) which include methane, nitrous oxide, ozone, and CFCs. All of the greenhouse gases play a role in protecting the earth from rapid loss of heat during the nighttime hours, but abnormally high concentrations of these gases are thought to cause overall warming of the global climate. Governments around the world are now pursuing strategies to halt the rise in concentrations of carbon dioxide and other greenhouse gases (Climate Change 2007). Presently it is estimated that more than 30 billion metric tons of CO₂ is generated annually by the human activities in the whole world. It is reported that approximately 80 percent of the total which is about 24 billion tons is unfortunately originated from only 20 countries. Table 1 shows a list of the most contributed countries in CO₂ emissions. In addition to the efforts for reduction of CO₂, a new technology to collect and store CO₂ is being aggressively developed. The technology is so called CCS which means Carbon dioxide Capture & Storage. Many scientists have concluded that the observed global climate change is due to the greenhouse gas effect, in which man-made greenhouse gases alter the amount of thermal energy stored in the Earth's atmosphere, thereby increasing atmospheric temperatures. The greenhouse gas produced in the most significant quantities is carbon dioxide. The primary source of man-made CO₂ is combustion of fossil fuels. Stabilizing the concentration of atmospheric CO₂ will likely require a variety of actions including a reduction in CO₂ emissions. Since the Industrial Age, the concentration of carbon dioxide in the atmosphere has risen from about 280 ppm to 377ppm, a 35 percent increase. The concentration of carbon dioxide in Earth's atmosphere is approximately 391 ppm by volume as of 2011 and rose by 2.0 ppm/yr during 2000-2009. Forty years earlier, the rise was only 0.9 ppm/yr, showing not only increasing concentrations, but also a rapid acceleration of concentrations. The increase of concentration from pre-industrial concentrations has again doubled in just the last 31 years.

Rank	Country	Annual CO ₂ emissions (in 1000 Mt)	% of global total
1	China	7,031,916	23.33%
2	United States	5,461,014	18.11%
3	India	1,742,698	5.78%
4	Russia	1,708,653	5.67%
5	Japan	1,208,163	4.01%
6	Germany	786,660	2.61%
7	Canada	544,091	1.80%
8	Iran	538,404	1.79%
9	United Kingdom	522,856	1.73%
10	South Korea	509,170	1.69%
11	Mexico	475,834	1.58%
12	Italy	445,119	1.48%
13	South Africa	435,878	1.45%
14	Saudi Arabia	433,557	1.44%
15	Indonesia	406,029	1.35%
16	Australia	399,219	1.32%
17	Brazil	393,220	1.30%
18	France	376,986	1.25%
19	Spain	329,286	1.09%
20	Ukraine	323,532	1.07%
21	Poland	316,066	1.05%
22	Thailand	285,733	0.95%
23	Turkey	283,980	0.94%
24	Taiwan	258,599	0.86%
25	Kazakhstan	236,954	0.79%
26	Egypt	210,321	0.70%
27	Malaysia	208,267	0.69%
28	Argentina	192,378	0.64%
29	Netherlands	173,750	0.58%
30	Venezuela	169,533	0.56%
31	Pakistan	163,178	0.54%
32	United Arab Emirates	155,066	0.51%
33	Other countries	3,162,011	11.34%
World		29,888,121	100%

Table 1. List of countries by 2008 emissions (IEAW, 2010)

Carbon dioxide is essential to photosynthesis in plants and other photoautotrophs, and is also a prominent greenhouse gas. Despite its relatively small overall concentration in the atmosphere, CO₂ is an important component of Earth's atmosphere because it absorbs and emits infrared radiation at wavelengths of 4.26 μm (asymmetric stretching vibrational mode) and 14.99 μm (bending vibrational mode), thereby playing a role in the greenhouse effect, although water vapour plays a more important role. The present level is higher than at any time during the last 800 thousand years and likely higher than in the past 20 million years.

To avoid dangerous climate change, the growth of atmospheric concentrations of greenhouse gases must be halted, and the concentration may have to be reduced (Mahmoudkhani & Keith, 2009).

There are three options to reduce total CO₂ emission into the atmosphere:

- Reduce energy intensity
- Reduce carbon intensity, and
- Enhance the sequestration of CO₂.

The first option requires efficient use of energy. The second option requires switching to using non-fossil fuels such as hydrogen and renewable energy. The third option involves the development of technologies to capture, sequester and utilize more CO₂.

2. Sources of CO₂

About 85% of the world's commercial energy needs are currently supplied by fossil fuels. A rapid change to non-fossil energy sources would result in large disruption to the energy supply infrastructure, with substantial consequences for the global economy. The technology of CO₂ capture and storage would enable the world to continue to use fossil fuels but with much reduced emissions of CO₂, while other low- CO₂ energy sources are being developed and introduced on a large scale. In view of the many uncertainties about the course of climate change, further development and demonstration of CO₂ capture and storage technologies is a prudent precautionary action. Global emissions of CO₂ from fossil fuel use were 23684 million tons per year in 2001. These emissions are concentrated in four main sectors: power generation, industrial processes, the transportation sector and residential and commercial buildings, as shown in Figure 1(a) (IEA, 2003) also, Figure 1 (b and c) depicts the distribution of the flue gases produced by these fuels showing that the major part of the effluent gases is N₂, H₂O, CO₂, and O₂, respectively (Moghadassi et al., 2009).

Fig. 1. (a) The emissions contribution of CO₂ from fossil fuels use in 2001, total emissions 23684 Mt/y and typical power station flue gas compositions, by the use of (a) coal and (b) natural gas as a fuel.

Table 2 shows the worldwide large stationary CO₂ sources emitting more than 0.1 Mt CO₂ per year. Most of the emissions of CO₂ to the atmosphere from the electricity generation and industrial sectors are currently in the form of flue gas from combustion, in which the CO₂ concentration is typically 4-14% by volume, although CO₂ is produced at high concentrations by a few industrial processes. In principle, flue gas could be stored, to avoid

emissions of CO₂ to the atmosphere it would have to be compressed to a pressure of typically more than 10 MPa and this would consume an excessive amount of energy. Also, the high volume of flue gas would mean that storage reservoirs would be filled quickly. For these reasons it is preferable to produce a relatively high purity stream of CO₂ for transport and storage; this process is called CO₂ capture (Lotz & Brent, 2008).

<i>Process</i>	<i>Number of sources</i>	<i>Emissions (Mt CO₂ per year)</i>
Fossil fuels		
Power	4942	10539
Cement production	1175	932
Refineries	638	798
Iron and steel industry	269	646
Petrochemical industry	470	379
Oil and gas processing	Not available	50
Other sources	90	33
Biomass		
Bioethanol and bioenergy	91	303
Total	13466	7887

Table 2. Worldwide large stationary CO₂ sources emitting more than 0.1 Mt CO₂ per year (Lotz & Brent, 2008).

2.1 CO₂ large point sources

Power generation is the largest source of CO₂ which could be captured and stored. However, substantial quantities of CO₂ could also be captured in some large energy consuming industries, in particular iron and steel, cement and chemicals production and oil refining.

2.1.1 Cement production

The largest industrial source of CO₂ is cement production, which accounts for about 5% of global CO₂ emissions. The quantity of CO₂ produced by a new large cement kiln can be similar to that produced by a power plant boiler. About half of the CO₂ from cement production is from fuel use and the other half is from calcination of CaCO₃ to CaO and CO₂. The concentration of CO₂ in the flue gas from cement kilns is between 14 and 33 vol%, depending on the production process and type of cement. This is higher than in power plant flue gas, so cement kilns could be good candidates for post-combustion CO₂ capture. It may be advantageous to use oxyfuel combustion in cement kilns because only about half as much oxygen would have to be provided per tone of CO₂ captured. However, the effects on the process chemistry of the higher CO₂ concentration in the flue gas would have to be assessed (Henriks et al., 1999).

2.1.2 Iron and steel production

Large integrated steel mills are some of the world's largest point sources of CO₂. About 70% of the CO₂ from integrated steel mills could be recovered by capture of the CO₂ contained in blast furnace gas. Blast furnace gas typically contains 20% by volume CO₂ and 21% CO, with the rest being mainly N₂. An important and growing trend is the use of new processes for

direct reduction of iron ore. Such processes are well suited to CO₂ capture (Freund & Gale, 2001).

2.1.3 Oil refining

About 65% of the CO₂ emissions from oil refineries are from fired heaters and boilers (Freund & Gale, 2001). The flue gases from these heaters and boilers are similar to those from power plants, so CO₂ could be captured using the same techniques and at broadly similar costs. The same would be true for major fired heaters in the petrochemical industry, such as ethylene cracking furnaces.

2.1.3.1 Hydrogen and ammonia production

Large quantities of hydrogen are produced by reforming of natural gas, mainly for production of ammonia-based fertilizers. CO₂ separated in hydrogen plant is normally vented to the atmosphere but it could instead be compressed for storage. This would be a relatively low cost method of avoiding release of CO₂ to the atmosphere. It could also provide useful opportunities for the early demonstration of CO₂ transport and storage techniques.

2.1.3.2 Natural gas purification

Some natural gas fields contain substantial amounts of CO₂. The CO₂ concentration has to be reduced to ~2.5% for the market, so any excess CO₂ has to be separated. The captured CO₂ is usually vented to the atmosphere but, instead, it could be stored in underground reservoirs. The first example of this being done on a commercial scale is the Sleipner Vest gas field in the Norwegian sector of the North Sea (Torp & Gale, 2002).

2.1.3.3 Energy carriers for distributed energy users

A large amount of fossil fuel is used in transport and small-scale heat and power production. It is not practicable using current technologies to capture, collect, and store CO₂ from such small scale dispersed users. Nevertheless, large reductions could be made in CO₂ emissions through use of a carbon-free energy carrier, such as hydrogen or electricity. Both hydrogen and electricity are often considered as a carrier for energy from renewable sources. However, they can also be produced from fossil fuels in large centralized plants, using capture and storage technology to minimize release of CO₂. Production of hydrogen or electricity from fossil fuels with CO₂ storage could be an attractive transitional strategy to aid the introduction of future carbon free energy carriers (Audus et. al., 1996).

3. Kyoto protocol

The global warming issue forces us to make efforts to use resources and energy efficiently and to reconsider socioeconomic activities and lifestyles that involve large volumes of production, consumption and waste. In June 1992, the Rio de Janeiro United Nations Conference on Environment and Development agreed on the United Nations Framework Convention on Climate Change (UNFCCC), an international treaty aiming at stabilizing greenhouse gas concentrations in the atmosphere. Greenhouse gases such as carbon dioxide (CO₂) or methane are considered responsible for global warming and climate change. Table 3

<i>Gas</i>	<i>Global warming Potential*</i>	<i>Contribution to global warming</i>	<i>Major sources</i>
Energy-originated CO ₂	1	76%	From fossil fuels both from direct consumption of heating oil, gas, etc. and indirect from fossil fuels for electricity production.
Non-energy-originated CO ₂			From use of limestone, incineration of waste, etc. in industrial processes.
CH ₄ –(Methane)	21	12%	From anaerobic fermentation, etc. of organic matter in paddy fields and waste disposal sites.
N ₂ O - (Nitrous oxide)	310	11%	Generated in some manufacturing processes for raw materials for chemical products, the decomposition process of microorganisms in livestock manure, etc.
HFC- (Hydrofluoro-carbons)	140-11700	<1%	Used in the refrigerant in refrigeration and air conditioning appliances, and in foaming agents such as heat insulation materials, etc.
PFC- (Perfluoro Carbons)	7400	<1%	Used in manufacturing processes for semiconductors, etc.
SF ₆ – (Sulfur hexafluoride)	25000	<1%	In cover gas when making a magnesium solution, manufacturing of semiconductors and electrical insulation gas, etc.
*Global Warming Potential expresses the extent of the global warming effect caused by each greenhouse gas relative to the global warming effect caused by a similar mass of carbon dioxide.			

Table 3. The global warming potential and major sources subject to the Kyoto protocol.

is a list of most important gases and their global warming potential according to the Kyoto protocol. In 1997, world leaders negotiated the so-called Kyoto protocol as an amendment to the UNFCCC. Under the protocol, industrialized countries committed themselves to a concrete and binding reduction of their collective greenhouse gas emissions (5.2% by 2012 compared to 1990 levels). Currently and within the framework of the UNFCCC, international negotiations try to establish new reduction goals for the post-2012 second commitment period. The December 2009 Copenhagen conference is expected to fix a concrete agreement (UNFCCC, 1992).

The Kyoto Protocol puts a cap on the emissions of these 6 greenhouse gases by industrialized countries (also called Annex I Parties) to reduce their combined emissions by at least 5% of their 1990 levels by the period 2008-2012. In order to minimize the cost of reducing emissions, the Kyoto Protocol has provided for 3 mechanisms that will allow industrialized countries flexibility in meeting their commitments:

- International emissions trading (ET) – trading of emission permits (called Assigned Amount Units or AAUs) among the industrialized countries.
- Joint Implementation (JI) – crediting of emission offsets resulting from projects among industrialized countries (called Emission Reduction Units or ERUs).
- Clean Development Mechanism (CDM) – crediting of emission offsets resulting from projects in developing countries (called Certified Emission Reductions or CERs).

4. Carbon Capture and Storage (CCS)

Carbon capture and storage (CCS) technologies offer great potential for reducing CO₂ emissions and mitigating global climate change, while minimizing the economic impacts of the solution. It seems that along with development of clean technologies, which are a long time program, the need for an emergency solution is vital. Capturing and storage of carbon dioxide is an important way to reduce the negative effects of the emissions. There are several technologies for CCS, some currently are used in large capacities and some are in the research phases. These technologies can be classified, based on their maturity for industrial application, into four classes (IPCC, 2006):

1. “*Mature market*” such as industrial separation, pipeline transport, enhanced oil recovery and industrial utilization.
2. “*Economically feasible*” such as post-combustion capture, pre-combustion capture, tanker transport, gas and oil fields and saline aquifers.
3. “*Demonstration phase*” such as oxy-fuel combustion and enhanced coal bed methane.
4. “*Research phase*” such as ocean storage and mineral carbonation.

Table 4 shows the predicted amounts of CO₂ emission and capture from 2010 to 2050.

Table 5 shows the planned CO₂ capture and storage projects including the location, size, capture process, and start-up date. Figure 2 demonstrates an overview of CO₂ capture processes and systems (IPCC, 2006). There are three known method for capturing of CO₂ in fossil fuels combustion systems. They are applicable in the processes where the main purpose is heat and power generation such as power generation stations. Following is a brief description of there three important capturing processes (WRI, 2008).

<i>Type of data</i>	<i>Sector</i>	<i>2010</i>	<i>2020</i>	<i>2030</i>	<i>2040</i>	<i>2050</i>
CO ₂ emission	Power production	12014	13045	10999	7786	4573
	Industry	5399	5715	5277	4385	3493
	Transportation	7080	8211	8237	6733	5228
	Other sources	4589	4894	5072	5072	5072
	Total	29083	31864	29586	23976	18367
CO ₂ capture	Power production	0	340	2750	5963	9176
	Industry	0	66	699	1591	2483
	Transportation	0	148	1046	2550	4055
	Other sources	0	0	0	0	0
	Total	0	554	4494	10104	15713
Accumulated CO ₂ capture (all sectors)		0	1672	28468	104262	236151

Table 4. Predicted CO₂ emission and capture globally in million tones. (Stangeland, 2007).

<i>Project Name</i>	<i>Location</i>	<i>Feedstock</i>	<i>Size (MW, except as noted)</i>	<i>Capture Process</i>	<i>Start-up Date</i>
Total Lacq	France	Oil	35	Oxf	2008
Vattenfall Oxyfuel	Germany	Coal	30/300/1000*	Oxf	2008–15
AEP Alstom Mountaineer	USA	Coal	30	Poc	2008
Callide-A Oxy Fuel	Australia	Coal	30	Oxf	2009
GreenGen	China	Coal	250/800**	Prc	2009
Williston	USA	Coal	450	Poc	2009–15
Kimberlina	USA	Coal	50	Oxf	2010
NZEC	China	Coal	Undecided	Undecided	2010
AEP Alstom Northeastern	USA	Coal	200	Poc	2011
Sargas Husnes	Norway	Coal	400	Poc	2011
Scottish & Southern Energy Ferrybridge	UK	Coal	500	Poc	2011–12
Naturkraft Kårstø	Norway	Gas	420	Poc	2011–12
Fort Nelson	Canada	Gas	Gas Process	Prc	2011
ZeroGen	Australia	Coal	100	Prc	2012
WA Parish	USA	Coal	125	Poc	2012
UAE Project	UAE	Gas	420	Prc	2012
Appalachian Power	USA	Coal	629	Prc	2012
Wallula Energy Resource Center	USA	Coal	600–700	Prc	2013
RWE power Tilbury	UK	Coal	1600	Poc	2013
Tenaska	USA	Coal	600	Poc	2014
UK CCS Project	UK	Coal	300–400	Poc	2014
Statoil Mongstad	Norway	Gas	630 CHP	Poc	2014
RWE Zero CO ₂	Germany	Coal	450	Prc	2015
Monash Energy	Australia	Coal	60,000 bpd	Prc	2016
Powerfuel Hatfield	UK	Coal	900	Prc	Undecided
ZENG Worsham-Steed	USA	Gas	70	Oxf	Undecided
Polygen Project	Canada	Coal/ Pcoke	300	Prc	Undecided
ZENG Risavika	Norway	Gas	50–70	Oxf	Undecided
E.ON Karlshamn	Sweden	Oil	5	Poc	Undecided

* 30/300/1000 = Pilot (start time 2008)/Demo/Commercial (anticipated start time 2010–2015)

** 250/800 = Demo/Commercial

bpd = barrels per day; CHP = combined heat and power; Pcoke = petroleum coke; Prc= Pre-combustion; Poc= Post-combustion; Oxf= Oxi-fuel

Table 5. Planned CO₂ capture and storage projects (MIT, 2008).

4.1 Post-combustion capture

In order to separate the CO_2 from the other flue gas components and concentrate the CO_2 , it is necessary to add a capture and a compression system (for storage and transport) to the post-combustion system. Advanced post-combustion capture technologies also require significant cleaning of the flue gas before the capture device particularly, sulfur levels have to be low (less than 10 ppm and possibly lower) to reduce corrosion and fouling of the system.

Figure 3 shows a simple block diagram for post-combustion capture from a power plant.

Fig. 2. Overview of CO_2 capture processes and systems.

Fig. 3. Post-Combustion Capture from a Pulverized Coal-Fired Power Plant.

4.2 Pre-combustion capture

Pre-combustion capture involves the removal of CO_2 after the coal is gasified into syngas, but before combustion in an Integrated coal Gasification Combined Cycle (IGCC) unit (Figure 4). The first step involves gasifying the coal. Then, a water-gas shift reactor is used to convert carbon monoxide in the syngas and steam to CO_2 and hydrogen. The CO_2 is removed using either a chemical or a physical solvent, such as Selexol™, and is compressed. The hydrogen is combusted in a turbine to generate electricity. Because of technical problems, only 4 GW of IGCC power plants have been built worldwide until the end of 2007.

Fig. 4. Pre-Combustion Capture on an IGCC Power Plant.

4.3 Oxy-fuel combustion

Oxy-fuel combustion involves the combustion of fossil fuels in an oxygen-rich environment (nearly pure oxygen mixed with recycled exhaust gas), instead of air. This reduces the formation of nitrogen oxides, so that the exhaust gas is primarily CO_2 and is easier to separate and remove (Figure 5). An air separation unit supplies oxygen to the boiler where it mixes with the recycled exhaust gas. After combustion, the gas stream can be cleaned of PM, nitrogen oxides, and sulfur. After condensing out the water, the flue gas has a CO_2 concentration that is high enough to allow direct compression. As of 2008, oxy-fuel power

Fig. 5. Oxy-Fuel Combustion with Capture.

plants are in the early stages of development with pilot-scale construction currently underway in Europe and in North America as shown in Table 5 (MIT, 2008).

5. CO₂ removal from gaseous streams

There are three incentives to remove CO₂ from a process stream:

- CO₂ is being removed from a valuable product gas, such as H₂, where it is eventually emitted to the atmosphere as a waste by-product.
- CO₂ is recovered from a process gas, such as in ethanol production, as a saleable product. However, only a modest fraction of the CO₂ produced is marketed as a saleable product, and much of this CO₂ finds its way to the atmosphere because the end use does not consume the CO₂.
- CO₂ is recovered simply to prevent it from being released into the atmosphere, but, this necessarily requires sequestration of the recovered CO₂.

Processes to remove CO₂ from gas streams vary from simple treatment operations to complex multistep recycle systems.

Most of these processes were developed for natural gas sweetening or H₂ recovery from syngas. Recently, interest has built on the capture of CO₂ from flue gas, and even landfill gas and coal bed methane gas. In addition, flue gas, coal bed methane and some landfill gases contain O₂ that can interfere with certain CO₂ separation systems. This complication is generally not present in natural gas, most landfill gas, or H₂ systems. Table 6 lists the licensors of CO₂ separation processes as of 2004 (Ritter & Ebner, 2007; Hydrocarbon Processing, 2004).

For these reasons, commercial CO₂ gas treatment plants are usually integrated gas processing systems; few are designed simply for CO₂ removal. Four different CO₂ removal technologies are widely practiced in industry. These are 1) absorption, both chemical and physical, 2) adsorption, 3) membrane separation, and 4) cryogenic processes (Kohl & Nielsen, 1997). Table 7 shows CO₂ separation techniques including the use of them in CO₂ capture processes.

5.1 Absorption processes

The overwhelming majority of CO₂ removal processes in the chemical and petrochemical industries take place by absorption (see Table 6).

The chemical process industries (CPI) remove CO₂ to meet process or product requirements (e.g., the production of natural gas, ammonia or ethylene oxide manufacturing). A variety of liquid absorbents are being used to remove CO₂ from gas streams.

Absorption processes for CO₂ removal generally can be divided into two categories: (a) *chemical absorption* where the solvent (commonly alkanolamines) chemically reacts with CO₂ and (b) *physical absorption* where the solvent only interacts physically with CO₂ (such as methanol in Rectisol Process and glycol ethers in Selexol Process).

In many industrial applications, combinations of physical solvents and reactive absorbents may be used in tandem. The solvents include monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), methyldiethanolamine (MDEA), and diglycolamine

Licensors	System	Primary Goal	CO ₂ in Tail-gas	Capacity per Unit	Plants world wide
Linde AG	PSA-H ₂	H ₂ -(P)	30-60%	1-100 MMscfd	250
Technip	PSA-H ₂	H ₂ -(P)	30-60%	-	240
Uhde	PSA-H ₂	H ₂ -(P)	30-60%	-110 MMscfd	60
Haldor Topsoe A/S	PSA-H ₂	H ₂ -(P)	30-60%	-20 MMscfd	31
UOP LLC (Polybed)	PSA-H ₂	H ₂ -(P)	30-60%	-200 MMscfd	700
CB&I Howe-Baker	PSA-H ₂	H ₂ -(P)	30-60%	1-280 MMscfd	170
Foster Wheeler	PSA-H ₂	H ₂ -(P)	30-60%	1-95 MMscfd	100
Lurgi Oel-Gas-Chemie GmbH	PSA-H ₂	H ₂ -(P)	30-60%	1-200 MMscfd	105
Air Products (PRISM)	PSA-H ₂	H ₂ -(P)	30-60%	15-120 MMscfd	50
Uhde GmbH	PSA-NH ₃	H ₂ -(P)	30-60%	500-1800 mtpd	14
Haldor Topsoe	PSA-NH ₃	H ₂ -(P)	30-60%	650-2050 mtpd	60
Kellogg Brown & Root, Inc	PSA-NH ₃	H ₂ -(P)	30-60%	-1850 mtpd	200
Axens	Adsorption	GC+CO ₂ -(R)	1-98%	-	60
Shell Global Solutions International B.V (ADIP)	Scrub (MDEA, DIPA)	AG-(R)	1-98%	-	400
Prosernat-IFP Group Tech. (Advanced Amines)	Scrub (DEA, MDEA)	AG-(R)	1-98%	0.3-25.2 Nm ³ /d	120
BASF AG (aMDEA)	Scrub (MDEA)	AG-(R)	1-98%	3.5-700 MMscfd	230
UOP LLC (Amine Guard FS)	Scrub (amine)	AG-(R)	1-98%	-500 MMscfd	500
UOP LLC (Bentfield)	Scrub (DEA-K ₂ CO ₃)	AG-(R)	1-98%	-500 MMscfd	700
Exxon Mobil Research & Eng. Co. (FIEXSORB)	Scrub (amine)	AG-(R)	1-98%	-	49
Fluor Enterprises, Inc. (Econamine)	Scrub (DGA) H ₂ -(P)	CO ₂ -(R)	+99%	3-400 MMscfd	55
Fluor Enterprises, Inc. (Econamine FG Plus)	Scrub (MEA)	CO ₂ -(R)	+99%	-300 mtpd	24
Advantica Ltd. (LRS-10)	Scrub (LRS10-K ₂ CO ₃)	CO ₂ -(R)	+99%	-	30
Lurgi Oel-Gas-Chemie GmbH (Rectisol)	Scrub (Methanol)	AG-(R)	1-98%	-	100
UOP LLC (Selexol)	Scrub (DME, PEG)	AG-(R,P)	1-98%	-	55
Shell Global Solutions International B.V (Sulfinol)	Scrub (sulfolane, amine)	AG-(P)	1-98%	-	200
Air Liquide (Medal)	Membrane	CO ₂ H ₂ O-(R)	2-70%	1-1000 MMscfd	several
NATCO Group Inc. (CYNARA)	Membrane	CO ₂ -(R)	-95%	5-750 MMscfd	30
UOP LLC (Separex)	Membrane	AG-(R)	-	-	50
Merichem Chem & Refineries Services (AMINEX)	HFMFC	AG-(R)	1-98%	-	10

Table 6. Major Licensors of CO₂ separation processes from gaseous streams (Hydrocarbon Processing, 2004.)

<i>Separation techniques</i>	<i>Post-combustion</i>	<i>Oxy fuel-combustion</i>	<i>Pre-combustion</i>
Chemical & physical absorption	Chemical solvents	-	Physical solvents Chemical solvents
Membrane	Polymer - Ceramic-Hybrid - Carbon	Polymer	Polymer- Ceramic Palladium
Adsorption	Zeolites Active carbons Molecular sieves	Zeolites - Activated carbons - Adsorbents (O ₂ /N ₂)	Zeolites - Activated carbons - Aluminum and silica gel
Cryogenic	-	Distillation	-

Table 7. CO₂ separation techniques (IEAGHG, 2011).

(DGA). Ammonia and alkaline salt solutions are also used as absorbents for CO₂. Water is used as a CO₂ absorbent, but only at high pressures where solubility becomes appreciable. However, in all cases solvent recycling is energy and capital intensive. Among the solvents, MEA has the highest capacity and the lowest molecular weight. It offers the highest removal capacity on either a unit weight or a unit volume basis. When only CO₂ is to be removed in large quantities, or when only partial removal is necessary, a hot carbonate solution or one of the physical solvents is economically preferred. MEA has good thermal stability, but reacts irreversibly with COS and CS₂.

DEA has a lower capacity than MEA and it reacts more slowly. Although its reactions with COS and CS₂ are slower, they lead to different products that cause fewer filtration and plugging problems. TEA has been almost completely replaced in sour gas treating because of its low reactivity toward H₂S. DGA has the same reactivity and capacity as DEA, with a lower vapor pressure and lower evaporation losses. DIPA, which is used in the Sulfinol and Shell Adip processes to treat gas to pipeline specifications, can remove COS and is selective for H₂S removal over CO₂ removal. MDEA selectively removes H₂S in the presence of CO₂, has good capacity, good reactivity, and very low vapor pressure. As a result, MDEA is a preferred solvent for gas treating.

Flue gas from combustion processes associated with burners, flaring, incineration, utility boilers, etc. contain significant amounts of CO₂. However, as discussed above, this CO₂ is generally of low quality because its concentration tends to be low, the flue gas is very hot, and it contains a variety of other gaseous species and particulates that make CO₂ recovery difficult and expensive.

Fluor Enterprises Inc. has 24 Econamine FG plants operating worldwide and producing a saleable CO₂ product for both the chemical and food industries. Randall Gas Technologies, ABB Lummus Global Inc. has four installations of similar technology operating on coal fired boilers. Two of these plants produce chemical grade CO₂ and the other two plants produce food grade CO₂. Mitsubishi Heavy Industries Ltd. also has commercialized a flue gas CO₂ recovery process, based on their newly developed and proprietary hindered amine solvents (KS-1, KS-2 and KS-3).

5.2 Adsorption processes

The adsorption processes include pressure swing adsorption (PSA), temperature swing adsorption (TSA), and hybrid PSA/TSA. Only a few classes of adsorbents and adsorption

processes are being used to remove CO₂ from gas streams. These adsorbents include aluminosilicate zeolite molecular sieves, titanosilicate molecular sieves, and activated carbons. Other classic adsorbents are being used to remove contaminants from CO₂ streams destined for commercial use. In this case, the adsorbents include activated carbons for sulfur compounds and trace contaminant removal, silica gels for light hydrocarbon removal, and activated alumina, bauxite, and silica gels for moisture removal. Of the CO₂ producing processes listed in Table 6, only H₂, syngas, NH₃, fermentation ethanol, natural gas, and combustion are beginning to use adsorption processes for removing or purifying CO₂.

By-product CO₂ from H₂ production via methane steam reforming is recovered using PSA in lieu of absorption. The PSA unit offers advantages of improved H₂ product purity (99-99.99 vol% H₂, 100 ppmv CH₄, 10-50 ppmv carbon oxides, and 0.1-1.0 vol% N₂) with capital and operating costs comparable to those of wet scrubbing.

Modern PSA plants for H₂ purification generally utilize layered beds containing 3 to 4 adsorbents (e.g., silica gel or alumina for water, activated carbon for CO₂, and 5A zeolite for CH₄, CO, and N₂ removal). Depending on the production volume requirements, from four to sixteen columns are used in tandem. The PSA unit is operated at ambient temperature with a feed pressure ranging between 20 and 60 atm. Hydrogen recovery depends on the desired purity, but ranges between 60 and 90%, with the tail gas (i.e., the desorbed gas containing H₂O, N₂, CO₂, CH₄, CO, and H₂) generally being used as fuel for the reformer.

Although PSA systems are increasingly used for H₂ recovery, they yield a by-product CO₂ stream that is only about 50 vol% pure. Low purity makes this tail gas stream less attractive as a commercial CO₂ source.

As the composition of natural gas varies widely depending on the location of the well (the CO₂ concentration in natural gas varies between 3 and 40 vol%; but it could be as high as 80 vol%), and because of the complexity and variability of the composition of natural gas, a train of separation processes, including adsorption, absorption, cryogenic and membrane separation, may be used to process it into pipeline quality methane.

Although the traditional process for removing CO₂ has been the amine process, but PSA technology is beginning to supplant some of the absorption technology in natural gas treatment, especially in the so called shut-in natural gas wells that previously contained too much N₂ to justify processing.

To remove CO₂ from coal bed methane, Engelhard Corporation uses molecular gate adsorption technology with a more traditional PSA mode with compressed feeds ranging in pressure 80-800 psig. Similarly, Axens has commercialized natural gas purification technology, based on alumina and zeolite molecular sieve adsorbents and a TSA regeneration mode. The alumina removes trace and bulk contaminants in the natural gas other than CO₂ through both chemisorption and physisorption mechanisms. The zeolite molecular sieve serves to remove CO₂ and other contaminants via physisorption. Axens has over 60 installations operating worldwide that treat a variety of natural gas and industrial process streams. Table 8 shows the performance characteristics of some common sorbents for CO₂ separation.

Sorbent	Capacity	Feed composition	Ref.
Aqueous ammonia	1.20 g CO ₂ /g NH ₃	15vol% CO ₂ , 85vol%N ₂	Yeh <i>et al.</i> , 2005
Aminated mesoporous silica	0.45–0.6 molCO ₂ /mol amine	100% CO ₂	Knowles <i>et al.</i> , 2005
Aminated SBA-15	1528–4188 μmol CO ₂ /g sorbent	10%CO ₂ , 90% He, with 2% H ₂ O	Gray <i>et al.</i> , 2005
PEI-impregnated MCM-41	45 ml (STP) CO ₂ /g adsorbent	15% CO ₂ , 4%O ₂ , 81% N ₂	Xu <i>et al.</i> , 2005
PEI-impregnated MCM-41	246 mg CO ₂ /gPEI or 82 mg CO ₂ /g sorbent	N/A	Xu <i>et al.</i> , 2002; Song <i>et al.</i> , 2006
Anthracite activated carbon	65.7 mg CO ₂ /g adsorbent	N/A	Maroto-Valer <i>et al.</i> , 2005
Lithium silicate	360 mg CO ₂ /g sorbent	100% CO ₂	Kato <i>et al.</i> , 2005

Table 8. The CO₂ sorbent performance.

5.3 Membrane processes

Membrane technology for separating gas streams is attractive for many reasons:

1. It neither requires a separating agent nor involves phase changes.
2. No processing costs associated with regeneration and phase change.
3. The systems involve small footprints compared to other processes.
4. They require low maintenance.
5. They are compact and lightweight and can be positioned either horizontally or vertically, which is especially suitable for retrofitting applications.
6. They are modular units and allow for multi-stage operation.
7. They have linear scale up costs (Takht Ravanchi *et al.*, 2009a; Takht Ravanchi & Kargari, 2009).

The major drawbacks associated with this technology are the low capacity and poor thermal properties of the current commercial available membranes. Membranes are an appealing option for CO₂ separation, mainly because of the inherent permeating properties. CO₂ is a fast diffusing gas in many membrane materials, such as glassy and rubbery polymers, molecular sieves, and several other inorganic materials. On the other hand, CO₂ also has a relatively high molecular weight and a large quadruple moment, enabling it naturally to adsorb more strongly to or dissolve at much higher concentrations in these membrane materials compared to many other gas species. These properties give rise to very high CO₂ permeation rates and selectivities over many other gas species, sometimes even higher than H₂ and He. Membrane systems potentially or actually commercialized for gas separations are listed in Table 6. Of the CO₂ producing processes listed, only natural gas production, to a lesser extent landfill gas production, H₂, syngas, and NH₃ production are beginning to use membrane processes for removing or purifying CO₂.

One of the great challenges in membrane-based CO₂ separation technology is the lack of membranes with simultaneous high permeability and selectivity. A wide range of selectivity/permeability combinations are provided by different membrane materials, but for gas separation applications, the most permeable polymers at a particular selectivity are of interest, and the highly permeable polymers exhibit moderate to low selectivity values.

On the other hand, in the application of a membrane with a specific permeability, to meet the desired selectivity using the multi-stage gas separation process is often unavoidable.

Up to now, many studies have been carried out to increase the performance of polymeric membranes. According to these researches, the most important methods for increasing the performance of polymeric membranes are as follows (Sanaeepur et al., 2011a, 2011b; Ebadi et al., 2010, 2011):

1. Incorporation of flexible and polar groups such as amines, carboxyles.
2. Mixing with a carrier (fixed carrier membranes) such as type 1 amino group as a CO₂ carrier.
3. Using a soft segment such as poly (dimethyl siloxane).
4. Addition of a compatibilizer such as polystyrene-block-poly (methylmethacrylate) in polymethylmethacrylate/poly methyl ether blends.
5. Polymer blending and interpenetrating polymer networks.
6. Chemical cross-linking and load-bearing network creation via covalent linkages.
7. Structural modification of block copolymers by block copolymerization with a polymer having specific mechanical properties that form a nanostructure, which has physical cross-linkages with favorite properties.
8. Free volume increasing by adding (nano) particles to polymer matrices.

The first commercial cellulose acetate membrane units for CO₂ removal from natural gas were implemented only few years after the introduction in 1980 of the first commercial PRISM membrane air separation system developed by Monsanto. By the end of the 1980s companies such as Natco (Cynara), UOP (Separex) and Kvaerner (Grace Membrane Systems) were producing membrane plants for this purpose. A few years later, more selective polyimides and only recently polyaramides were slowly introduced to displace the old cellulose acetate systems. Today, commercial membrane technology for CO₂ separation is largely based on glassy polymeric materials (cellulose acetate, polyimides, and polyaramides). Currently, the membrane market devoted to CO₂ separation from natural gas is about 20%, which is only 2% of the total separations market for natural gas. Membranes are used in situations where the produced gas contains high levels of CO₂. However, the membranes are very sensitive to exposure to C5+ hydrocarbons present in wet natural gas streams because these compounds immediately degrades performance and can cause irreversible damage to the membranes. Membranes for large-scale recovery of CO₂ from, for example, natural gas for use as a salable product are a relatively recent development. A variety of membranes, including ones with separating layers made of cellulose acetate, polysulfone, and polyimide, are used for this purpose. Air Products and Chemicals and Ube are marketing membrane systems for EOR and landfill gas upgrading, respectively and they have been commercialized for H₂ purification in reforming processes. For example, membrane processes, such as the POLYSEP membrane systems developed by UOP and the PRISM membrane systems developed by Monsanto and now sold by Air Products and Chemicals recover H₂ from various refinery, petrochemical and chemical process streams. Both are based on polymeric asymmetric membrane materials composed of a single polymer or layers of at least two different polymers, with the active polymer layer being a polyimide. The PRISM system is based on a hollow fiber design and POLYSEP is a spiral-wound, sheet-type contactor. Both are used to recover H₂ from refinery streams at purities ranging from 70 to 99 vol% and with recoveries ranging from 70 to 95%. Relatively

pure H_2 containing a very low concentration of CO_2 leaves these units in the low pressure permeate stream. This stream can be sent to a methanator for CO_2 removal and further purification. The high-pressure retentate stream, consisting of H_2 and CO_2 with low concentrations of CO and CH_4 , can be used as fuel.

Figure 6 shows the currently status of the developed membranes for separation of CO_2 from N_2 streams as the selectivity (α) versus permeability (P).

Fig. 6. Upper bound correlation for CO_2/N_2 separation (Robeson, 2008).

Another attractive membrane system is so called “Liquid Membrane” (LM) which have been found many applications in chemical engineering, medicinal and environmental processes (Kaghazchi et al., 2006, 2009; Kargari et al., 2002, 2003a, 2003b, 2003c, 2003d, 2004a, 2004b, 2004c, 2004d, 2004e, 2005a, 2005b, 2006a, 2006b, 2006c ; Mohammadi et al., 2008; Nabieyan et al., 2007; Rezaei et al., 2004).

Separation of gases by LM is a new field in separation science and technology. Separation of olefin/paraffin gases are very attractive and cost effective (Takht Ravanchi, 2008a, 2008b, 2008c, 2008d, 2009a, 2009b, 2009c, 2010a, 2010b, 2010c). CO_2 removal from gas streams especially natural gas is important for increase the heating value of the natural gas and limiting the CO_2 emission in the combustion systems (Heydari Gorji, 2009a, 2009b).

The advantage of the LM over solid (organic or inorganic) membranes are ease of operational conditions and very higher selectivities (in the order of several hundreds), but the instability problems of the LM have limited the industrial applications of this attractive technology.

5.4 Cryogenic liquefaction processes

Recovery of CO_2 by cold liquefaction has the advantage of enabling the direct production of very pure liquid CO_2 , which can be readily transported. The disadvantages associated with

the cryogenic separation of CO₂ are the amount of energy required in refrigeration, particularly in dilute gas streams, and the requirement to remove gases, such as water and heavy hydrocarbons, that tend to freeze and block the heat exchangers.

Liquefaction technology for CO₂ recovery is still incipient. Cryogenic CO₂ recovery is typically limited to streams that contain high concentrations of CO₂ (more than 50 vol%), but with a preferred concentration of > 90 vol%. It is not considered to be a viable CO₂ capture technology for streams that contain low concentrations of CO₂, which includes most of the industrial sources of CO₂ emissions. Cryogenic separation of CO₂ is most applicable to high-pressure gas streams, like those available in pre-combustion and oxyfuel combustion processes. Cryogenic CO₂ recovery is increasingly being used commercially for purification of CO₂ from streams that already have high CO₂ concentrations (typically > 90%). Of the CO₂ producing processes listed in Table 6, only ethanol production and H₂, syngas, and NH₃ production utilize cryogenic processes for removing or purifying CO₂.

Currently, Costain Oil, Gas & Process Ltd. has commercialized a CO₂ liquefaction process with around seven units installed worldwide. The process is assisted by membrane technology to treat streams with CO₂ fractions greater than 90 vol.%

Recently, Fluor Enterprises Inc. also developed a CO₂ liquefaction process called CO₂LDSEP. This technology exploits liquefaction to separate CO₂ from H₂ and other gases in the tail gas of a H₂ purification PSA unit. Table 9 demonstrates the CO₂ capture technologies advantages and challenges.

6. CO₂ conversion, utilization and fixation

One way to mitigate carbon dioxide emission is its conversion and fixation to value-added products. The main processes for carbon dioxide conversion and fixation in chemical industries are:

- a. Hydrogenation
- b. Oxidative Dehydrogenation
- c. Oxidative Coupling of Methane
- d. Dry Reforming of Methane

CO₂ is not just a greenhouse gas, but also an important source of carbon for making organic chemicals, materials and carbohydrates (e.g., foods). As will be discussed below, various chemicals, materials, and fuels can be synthesized using CO₂, which should be a sustainable way in the long term when renewable sources of energy such as solar energy is used as energy input for the chemical processing.

Some general guidelines for developing technologies for CO₂ conversion and utilization can be summarized as below:

- Select concentrated CO₂ sources for CO₂ capture and/or utilization; aim for on-site/nearby uses if possible.
- Use CO₂ to replace a hazardous or less-effective substance in existing chemical processes for making products with significant volumes.
- Use renewable sources of energy or 'waste' energy for CO₂ conversion and utilization whenever possible.

<i>CO₂ Capture Technology</i>	<i>Capturing method</i>	<i>Advantages</i>	<i>Challenges</i>
Pre-Combustion	Physical Solvent	<ul style="list-style-type: none"> • Recovery process does not require heat. • Common for same solvent to have high H₂S solubility, allowing for combined CO₂/H₂S removal. • System concepts for CO₂ recovery with some steam stripping and delivery at a higher pressure may be optimized for power systems. 	<ul style="list-style-type: none"> • CO₂ pressure is lost during flash recovery. • Must cool down synthesis gas for CO₂ capture, then heat it back up again and re-humidify for firing to turbine. • Low solubilities can require circulating large volumes of solvent, resulting in large pump loads. • Some H₂ may be lost with the CO₂.
	Solid Sorbent	<ul style="list-style-type: none"> • CO₂ recovery does not require heat. • Common for H₂S to also have high solubility in the same sorbent (combined CO₂/H₂S capture). • System concepts for CO₂ recovery with some steam stripping and delivery at a higher pressure may be optimized for power systems. 	<ul style="list-style-type: none"> • CO₂ pressure is lost during flash recovery. • Must cool synthesis gas for CO₂ capture, then heat it back up again and re-humidify for firing to turbine. • Some H₂ may be lost with the CO₂.
	H ₂ /CO ₂ Membrane	<p>H₂ or CO₂ Permeable Membrane:</p> <ul style="list-style-type: none"> • No steam load or chemical attrition. <p>H₂ Permeable Membrane Only:</p> <ul style="list-style-type: none"> • Can deliver CO₂ at high-pressure, greatly reducing compression costs. • H₂ permeation can drive the CO shift reaction toward completion – potentially achieving the shift at lower cost/higher temperatures. 	<ul style="list-style-type: none"> • Membrane separation of H₂ and CO₂ is more challenging than the difference in MW implies. • Due to decreasing partial pressure differentials, some H₂ will be lost with the CO₂. • In H₂ selective membranes, H₂ compression is required and offsets the gains of delivering CO₂ at pressure. In CO₂ selective membranes, CO₂ is generated at low pressure requiring compression.
	Water Gas Shift Membrane	<ul style="list-style-type: none"> • Promote higher conversion of CO and H₂O to CO₂ and H₂ than in a conventional WGS reactor. • Reduce CO₂ capture and H₂ production costs. • Increase net plant efficiency. 	<ul style="list-style-type: none"> • Single stage WGS with membrane integration • Improved selectivity of H₂ or CO₂ • Optimize membranes for WGS reactor conditions
Post-Combustion	Solvent	<ul style="list-style-type: none"> • Chemical solvents provide a high chemical potential necessary for selective capture from streams with low CO₂ partial pressure. • Wet-scrubbing allows good heat integration and ease of heat management (useful for exothermic reactions). 	<ul style="list-style-type: none"> • Trade off between heat of reaction and kinetics. • Energy required to heat, cool, and pump nonreactive carrier liquid (usually water) is often significant. • Vacuum stripping can reduce regeneration steam requirements, but is expensive.

<i>CO₂ Capture Technology</i>	<i>Capturing method</i>	<i>Advantages</i>	<i>Challenges</i>
Oxy-fuel Combustion	Solid Sorbent	<ul style="list-style-type: none"> Chemical sites provide large capacities/fast kinetics (capture from low CO₂ partial pressure streams). Higher capacities on a per mass or volume basis than similar wet-scrubbing chemicals. Lower heating requirements than wet-scrubbing. Dry process—less sensible heating requirement than wet scrubbing process. 	<ul style="list-style-type: none"> Heat required to reverse chemical reaction (although generally less than in wet-scrubbing cases). Heat management in solid systems is difficult, which can limit capacity and/or create operational issues when absorption reaction is exothermic. Pressure drop can be large in flue gas applications. Sorbent attrition.
	Membrane	<ul style="list-style-type: none"> No steam load. No chemicals. Simple and modular designs. 'Unit operation' versus complex 'process.' 	<ul style="list-style-type: none"> Tend to be more suitable for processes like IGCC. Trade off between recovery and product purity. Requires high selectivity. Poor economy of scale. Multiple stages/ recycle streams may be required.
	Cryogenic Distillation & Solid Sorbent	<ul style="list-style-type: none"> The combustion products are CO₂ and water. The relatively pure CO₂ is easily separated thus making the sequestration process less expensive. 	<ul style="list-style-type: none"> Current cryogenic air separation plants to produce O₂ are expensive and energy intensive. High costs of CO₂ recycle. Converting air-fired systems to oxygen fired. High temperatures can degrade boiler materials. Requires high temperature materials. Excess flue gas constituents contaminating sequestration stream (O₂, SO₂, NOx, Hg).

Table 9. CO₂ capture technologies advantages and challenges (DOE/NETL 2010)

- Convert CO₂ along with other co-reactants into chemical products that are industrially useful at significant scale.
- Fix CO₂ into environmentally benign organic chemicals, polymer materials or inorganic materials.
- Electric power generation with more efficient CO₂ capture and conversion or utilization.
- Take value-added approaches for CO₂ sequestration coupled with utilization.

CO₂ is used as refrigerant for food preservation, beverage carbonation agent, supercritical solvent, inert medium (such as fire extinguisher), pressurizing agent, chemical reactant (urea, etc.), neutralizing agent, and as gas for greenhouses.

Solid CO₂ (dry ice) has a greater refrigeration effect than water ice. Dry ice is also usually much colder than water ice, and the dry ice sublimates to a gas as it absorbs heat. It should be noted that the use of CO₂ for refrigeration does not directly contribute to reduction of CO₂ emissions.

There exist some chemical processes for CO₂ conversion in chemical industry, for which synthesis of urea from ammonia and CO₂ (Eq. (1)) and the production of salicylic acid from phenol and CO₂ (Eq. (2)) are representative examples. Urea is used for making various polymer materials, for producing fertilizers and in organic chemical industry. It is a preferred solid nitrogen fertilizer because of its high nitrogen content (46%). As an example of the usefulness of salicylic acid, acetyl salicylic acid is used for making Aspirin, a widely used common medicine.

Supercritical CO₂ can be used as either a solvent for separation or as a medium for chemical reaction, or as both a solvent and a reactant. The use of supercritical CO₂ (SC-CO₂) allows contaminant free supercritical extraction of various substances ranging from beverage materials (such as caffeine from coffee bean), foods (such as excess oil from fried potato chips), and organic and inorganic functional materials, to herbs and pharmaceuticals. It is also possible to use SC-CO₂ to remove pollutants such as PAHs from waste sludge and contaminated soils and toxics on activated carbon adsorbent (Akgerman et al. 1992).

The dissociation of CO₂ on catalyst surface could produce active oxygen species. Some heterogeneous chemical reactions can benefit from using CO₂ as a mild oxidant, or as a selective source of "oxygen" atoms. For example, the use of CO₂ has been found to be beneficial for selective dehydrogenation of ethylbenzene to form styrene, and for dehydrogenation of lower alkanes such as ethane, propane and butane to form ethylene, propylene, and butene, respectively. Some recent studies on heterogeneous catalytic conversion using CO₂ as an oxidant have been discussed in several recent reviews (Song et al, 2002; Park et al, 2001). If renewable sources or waste sources of energy are used, recycling of CO₂ as carbon source for chemicals and fuels should be considered for applications where CO₂ can be used that have desired environmental benefits. CO₂ recycling would also make sense if such an option can indeed lead to less consumption of carbon-based fossil resources without producing more CO₂ from the whole system. Conversion of CO₂ to C1 to C10 hydrocarbon fuels via methanol has also been reported (Nam et al, 1999). There has been

some reported effort on direct synthesis of aromatics from hydrogenation of CO₂ using hybrid catalysts composed of iron catalysts and HZSM-5 zeolite (Kuei and Lee, 1991). Related to the methanol synthesis and Fischer- Tropsch synthesis is the recently proposed tri-reforming process for conversion of CO₂ in flue gas or in CO₂-rich natural gas without CO₂ pre-separation to produce synthesis gas (CO + H₂) with desired H₂/CO ratios of 1.5–2.0 (Song & Pan 2004). For the CO₂ conversion to methanol using H₂, it should be noted that H₂ is currently produced by reforming of hydrocarbons which is an energy-intensive process and accompanied by CO₂ formation both from the conversion process and from the combustion of the fuels which is used to provide the process heat (Armor, 2000). Therefore, methanol synthesis using CO₂ does not contribute to CO₂ reduction unless H₂ is produced by using renewable energy or process waste energy or nuclear energy. BTX hydrocarbons (benzene, toluene, and xylenes) are important sources of petrochemicals for gasoline and other feed-stocks. Aromatization of lower alkanes is an interest in industry, and many efforts have been made in this area. The transformation of CH₄ to aromatics is thermodynamically more favorable than the transformation of CH₄ to C₂H₆, and extensive efforts have also been devoted to the direct conversion along this line in heterogeneous catalysis. To achieve the high activity and stability in methane dehydroaromatization, novel approaches to reduce carbon deposition are being made. The co-feeding of some oxidants (NO, O₂, CO, and CO₂) with CH₄ has been proposed. CO₂ is an acidic oxide, when it is dissolved in water, either as bicarbonate or carbonate (Ayers, 1988), it is slightly acidic. This weak acidity can be used in neutralization processes e.g., in purification of water from swimming pools. Due to its weak acidity, the pH value it can reach is limited (from pH of 12-13 to 6-9). Carbon dioxide can react in different ways with a large variety of compounds. The products that may be obtained are including, e.g., organic carbonates, (amino-) acids, esters, lactones, amino alcohols, carbamates, urea derivatives, and various polymers or copolymers. The limited number of publications in this research area shows that this new territory is still to be exploited. Some of these products are of great technical interest. The major reactions and their products are listed in Table 10. There are both natural and artificial ways to capture or fix the carbon to avoid or delay emission into the atmosphere, such as

reactants	products with CO ₂	reactants	products with CO ₂
alkane	syngas, acids, esters, lactones	Substituted hydrocarbon ^c	acids, esters, lactones, polycarbonates
cycloalkane	acids, esters, lactones	alkyne	lactones, unsaturated organic carbonates
active-H compound	acids, esters, lactones	epoxide	carbonates, (co)polymers (polycarbonates)
monoalkene	acids, esters, lactones	NH ₃ and amine	symmetrical ureas, aminoacids, (co)polymers
diene ^a	acids, esters, lactones ^b	diamine	ureas, carbamates, (co)polymers (polyureas)
cycloalkene	acids, esters, lactones, (co)polymers	imines	carbamates, (co)polymers (urethane)
^a Allenes and 1,3-dienes; ^b With longer C-C chain than the original monomer; ^c Dihalogen substituted			

Table 10. Reactants and their products in CO₂ reactions

forestation, ocean fertilization, photosynthesis, mineral carbonation, *In-situ* CO₂ capture and hydrate. Interested researcher is referred to (Yamasaki A, 2003; Stewart C, Hessami M, 2005; Maroto-Valer et al., 2005; Druckenmiller and Maroto-Valer, 2005; Liu et al., 2005; Stolaroff et al., 2005) for further details in this subject.

7. Conclusion

CO₂ emission along with its global warming is one of the most important and emergency problem threatens the living on the earth. Although some governmental laws and protocols have limited the emissions, but the emission rates are so high that the accumulation of CO₂ have caused the global climate change. Carbon based fossil fuels have the correct energy concentration and most probably will continue to be the main energy source in the short-medium term but it is necessary to control the CO₂ emission to the atmosphere. The future trends for controlling CO₂ emission and accumulation in the atmosphere should forced on:

1. Reducing fossil fuel use or switching to less CO₂ intense fuels such as biofuels and H₂.
2. Using more efficient energy systems.
3. Increasing the contribution of alternative energies such as solar, wind, etc. in processes.
4. Developing and improving the capture and separation technologies that are economically sound and effective under the operating conditions of CO₂-producing processes.
5. Developing and improving CO₂ storage including terrestrial biomass, deep oceans, saline aquifers, and minerals.
6. Utilizing and sequestering CO₂ by emphasis on fostering and chemical processes.

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Understanding greenhouse gas capture, utilization, reduction, and storage is essential for solving issues such as global warming and climate change that result from greenhouse gas. Taking advantage of the authors' experience in greenhouse gases, this book discusses an overview of recently developed techniques, methods, and strategies: - Novel techniques and methods on greenhouse gas capture by physical adsorption and separation, chemical structural reconstruction, and biological utilization. - Systemic discussions on greenhouse gas reduction by policy conduction, mitigation strategies, and alternative energy sources. - A comprehensive review of geological storage monitoring technologies.

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