Carbon Capture – Purpose and Technologies

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Abstract

The paper discusses the sources of carbon dioxide in the atmosphere, both natural and anthropogenic as well as various technologies, both currently in use and under evaluation, for capturing anthropogenic emissions before they enter the atmosphere.

The purpose of this paper is to explore carbon capture in more detail: its purpose, sources for carbon capture, and carbon capture technologies, as well as storage and utilization of the captured carbon. The pros and cons of carbon capture are also discussed briefly but are limited in scope to the technologies and economics.

Keywords:

CO_2 emissions, CCS, carbon capture, carbon storage, carbon utilization.

1. Carbon Cycle

The carbon cycle is a biogeochemical cycle explaining how atoms of carbon are recycled in different parts of the Earth, moving from living things (e.g. plants and animals) to non-living things (e.g. water, air, and minerals) and back. There are five major "reservoirs" of carbon that form the carbon cycle:

- Atmosphere,
- Terrestrial Biosphere,
- Ocean,
- Geosphere (i.e. soil and other sediments), and
- The Earth's interior (also known as the "deep carbon cycle").

The overall carbon cycle, minus the deep carbon cycle, is best illustrated in the Figure 1, a diagram from the U.S. Department of Energy.

1.1 Human Influence on the Carbon Cycle

As shown in Figure 1 (2007 data), man-made CO_2 contributions to the carbon cycle result in a net-positive increase in the amount of atmospheric carbon. As CO_2 is considered a "greenhouse gas" (GHG), an increase in the concentration of CO_2 in the atmosphere can potentially contribute to an increase in average global temperatures. The increase in atmospheric CO_2 absorbed via the air-sea gas exchange process also contributes to acidification of the oceans.

1.2 Anthropogenic Sources of CO_2 Emissions

There are natural and human (or anthropogenic, from anthropo meaning "human being" and genic meaning "formed by") sources of CO_2 emissions. Natural sources include ocean release, decomposition of organic matter and respiration. Human sources come from industrial production (e.g. cement manufacturing, ammonia synthesis, ethylene oxide synthesis), deforestation, and burning of fossil fuels.

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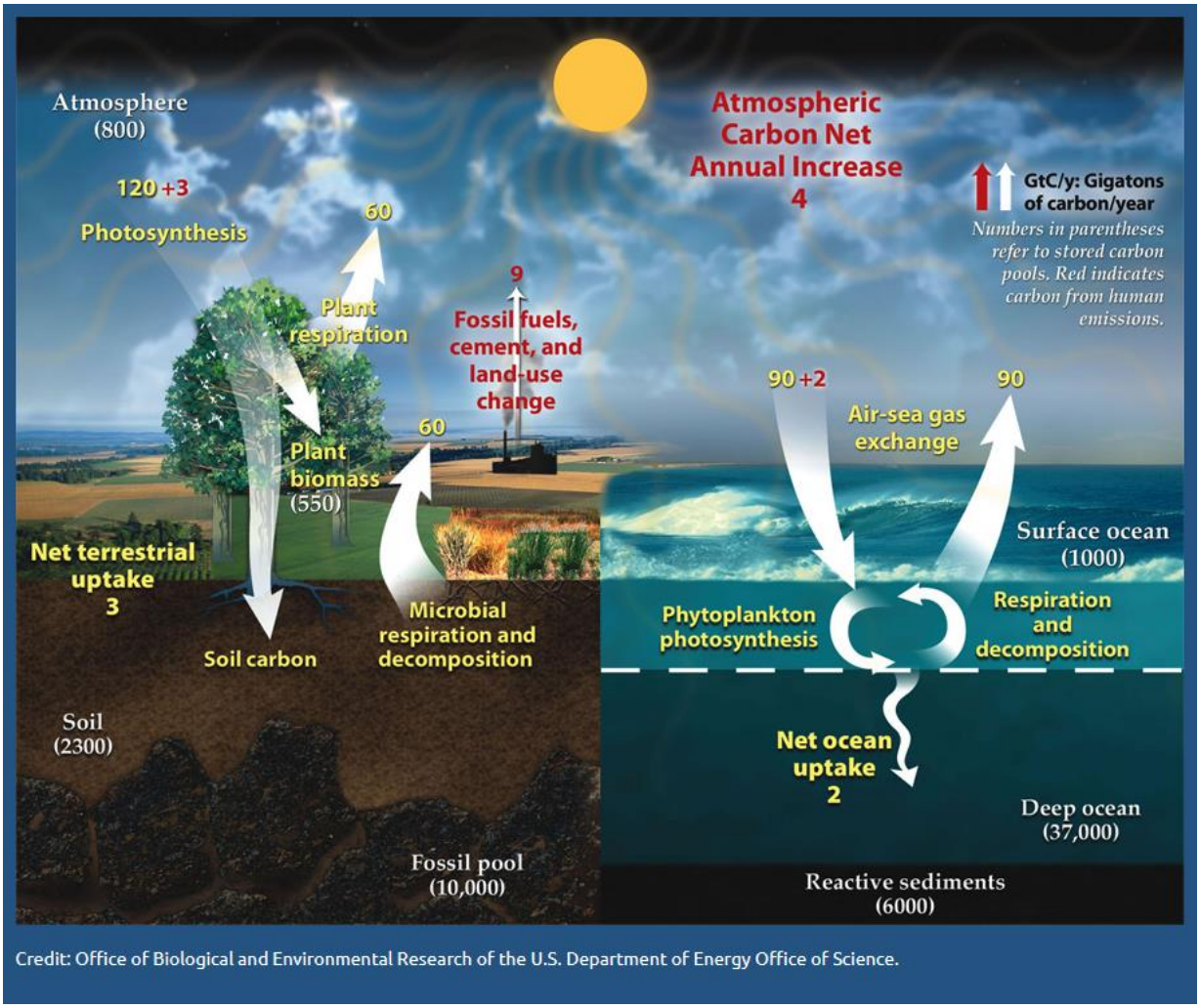


Figure 1 Carbon Cycle Diagram

A United Nations conference was held in Rio de Janeiro in 1992 during which the United Nations Framework Convention on Climate Change (UNFCCC) was formed to help establish strategies that would help stabilize the greenhouse gas levels in the atmosphere.

On 11 December 1997, at the UNFCCC meeting in Kyoto, Japan, the Kyoto Protocol was adopted, and entered into force on 16 February 2005, that commits state parties to reduce greenhouse gas emissions. Currently there are 192 Parties to the Kyoto Protocol. The Kyoto Protocol has legally binding obligations for greenhouse gas emission, reductions and limits. There are penalties for non-compliance. The applicability of the Kyoto Protocol ends in 2020. Since climate change needs to be addressed beyond 2020, the UNFCCC climate conference held in Paris in 2015 adopted the Paris Agreement.

The Paris Agreement was adopted by 196 countries to drastically reduce CO_2 emissions to keep global warming below 2°C above pre-industrial levels and pursuing efforts to limit the temperature increase to 1.5°C above-pre-industrial levels. In order to achieve these long-term temperature goals, parties to the Agreement aim to reach global peaking of greenhouse gas emissions as soon as possible and to undertake rapid reductions thereafter to achieve a balance between anthropogenic emissions by sources and removals by sinks of greenhouse gases in the second half of this century [1].

The difference between the Kyoto Protocol and the Paris Agreement is that the Kyoto Protocol was intended for developed countries only and involved legally binding targets for greenhouse gas emissions reduction. The Paris Agreement was prepared for all countries of the world, both developed and developing. It is a non-binding document without any penalties if signatories fail to meet their targets [2].

The scale of the CO_2 emissions is summarized in Tables 1 and 2 [3]. The Tables shows that CO_2 emissions are still increasing, and no peaking is in sight.

Source	1990 [%]	2015 [%]	Notes
Energy	70	74	* Other includes large-scale biomass burning (excluding CO_2), post-burn decay, peat decay, indirect N_2O emissions from non-agricultural emissions of NO_x and NH_3, waste and solvent use.
Industrial Processes	6	8	
Agriculture	18	13	
Other *	6	5	

Table 1 Anthropogenic Sources of Greenhouse Gas (GHG) Emissions

In 2017, almost 33 billion tonnes of CO_2 was emitted from fuel combustion in the world. Table 2 shows the CO_2 emissions by sector. Around 42% of CO_2 emissions come from power and heat generation. For comparison, the average American car emits around 7 tonnes of CO_2 per year (~365 SCF/d).

Million tonnes of CO_2	Coal	Oil	Natural Gas	Other *	Total	% Change 1990 - 2017
CO_2 from fuel combustion	14,502	11,377	6,743	218	32,840	60
Electricity and heat generation	9,761	715	2,975	152	13,603	78
Other energy industry own use	328	578	676	1.2	1,583	62
Manufacturing and construction	3,811	1,029	1,333	54	6,227	57
Transport	0.3	7,794	246	-	8,040	75
road transport	-	5,855	103	-	5,958	80
Other	601	1,262	1,513	11	3,387	1
residential	299	598	1,035	0	1,932	5
services	132	253	447	7.5	840	8
International marine bunkers	-	697	0.1	-	697	88
International aviation bunkers	-	585	-	-	585	126

* Other includes industrial waste and non-renewable municipal waste.

Table 2 2017 CO_2 Emissions by Sector

The numbers illustrate the enormity of carbon capture work that needs to be done to meet that target. Presently, there are 21 large carbon capture facilities in operation in the world, but they remove only 1% of CO_2 needed to be captured to reach the climate goals.

Greenhouse gas emissions in Canada in 2018 amounted to 729 million tonnes of CO_2e, 37% of which were generated in Alberta [4].

Table 2 showed CO_2 emissions by sector, Table 3 on the other hand shows CO_2 emissions by country. The Table shows only the top 10 CO_2 emitters. The data are for the year 2018 and percent change is shown between 2005, the year of signing the Kyoto Protocol, and 2018 [5].

Country	2018 CO_2 Emissions [Billion Tonnes]	Global Share	Change Since Kyoto Protocol
China	9.43	27.8%	54.6%
U.S.A.	5.15	15.2%	-12.1%
India	2.48	7.3%	105.8%
Russia	1.55	4.6%	5.7%
Japan	1.15	3.4%	-10.1%
Germany	0.73	2.1%	-11.7%
South Korea	0.70	2.1%	34.1%
Iran	0.66	1.9%	57.7%
Saudi Arabia	0.57	1.7%	59.9%
Canada	0.55	1.6%	1.6%

Table 3 Top 10 CO_2 Emitters in 2018

The fossil fuels used for the purposes mentioned in Table 2 contain differing amounts of carbon. They will produce different quantities of CO_2. Table 4 shows those quantities for some of the fuels [6]. It is clear that the fossil fuel that produces the least amount of CO_2 per GJ of energy is natural gas.

Fuel	kg CO_2 per GJ (HHV)
Natural gas	49.9
Gasoline	63.5
Diesel fuel	65.6
Bituminous coal	93.1
Sub-bituminous coal	90.1
Lignite coal	87.1

Table 4 Typical Quantities of CO_2 from Common Fossil Fuels

Note: the source [7] gives the units of pounds of CO_2 per 10^6 Btu. A conversion factor of 1 lb./10^6 Btu = 0.423 kg/GJ was used in the above table.

Other sources give the following comparison of coal to natural gas for electricity generation: coal combustion in a 500 MWe power plant emits 8,000 to 10,000 t/d of CO_2, whereas natural gas in a 500 MWe combined cycle power plant emits ~ 4,000 t/d of CO_2.

2. What is Carbon Capture?

Carbon capture, in its most basic definition, is the removal of carbon dioxide from the atmosphere. This occurs naturally via the growth of biomass (e.g. trees and other forms of vegetation) through the process of photosynthesis represented by Equation (1). For this paper, however, carbon capture will refer solely to the removal of CO_2 from industrial processes using man-made technologies.

$$6CO_2 + 6H_2O \xrightarrow{light} C_6H_{12}O_6 + 6O_2 \quad (1)$$

The acronym CCS is often used for carbon capture and storage. Carbon capture separates (or "captures") CO_2 from industrial exhaust, e.g. at coal power plants, before injecting it in deep underground rock formations. Figure 2 below shows the typical steps in CCS

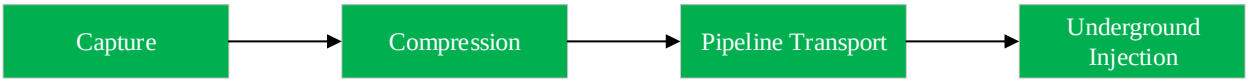


Figure 2 Block Flow Diagram for Carbon Dioxide Handling in CCS

Carbon capture, utilization and storage, for which the acronym CCUS is used, utilizes CO_2 for other purposes, for example enhanced oil recovery (EOR), which is a process of sequestering CO_2 into depleting oil fields to help recover additional trapped oil from reservoirs.

The purpose of carbon capture is to prevent the release of large quantities of CO_2 generated in man-made processes into the atmosphere as a means of lessening CO_2 contribution to global warming and ocean acidification.

2.1 Sources for Carbon Capture

Carbon dioxide can be captured from point sources or directly from the air, referred to as DAC (Direct Air Capture). Point sources are the ones from which CO_2 is released in one location such as cement plants or fossil fuel fired power plants.

Sometimes, bioenergy with carbon capture and storage (BECCS), is categorized as a separate carbon capture process. The source of carbon is biomass used for electricity or heat generation, or biofuels. The biomass can be combusted, fermented, subject to pyrolysis, etc. The CO_2 emitted during these processes is captured in the same manner that carbon emissions generated in industrial processes are handled. It is claimed that BECCS is a carbon capture technology because atmospheric CO_2 is absorbed by the biomass when it grows.

Capturing CO_2 from the air is used to manage CO_2 emissions from distributed sources like exhaust fumes from cars. The challenge of DAC is the low concentration of CO_2 in the air (~400 ppm). It seems that a temperature swing adsorption would be the best technology for DAC, but an adsorbent with high CO_2 to N_2 selectivity would have to be used.

3. Carbon Capture Pathways

There are four pathways for the capture of CO_2 energy conversion systems, as shown in Figure 3 [7]. Those are pre-combustion capture, oxy-fuel combustion, post-combustion capture and industrial processes.

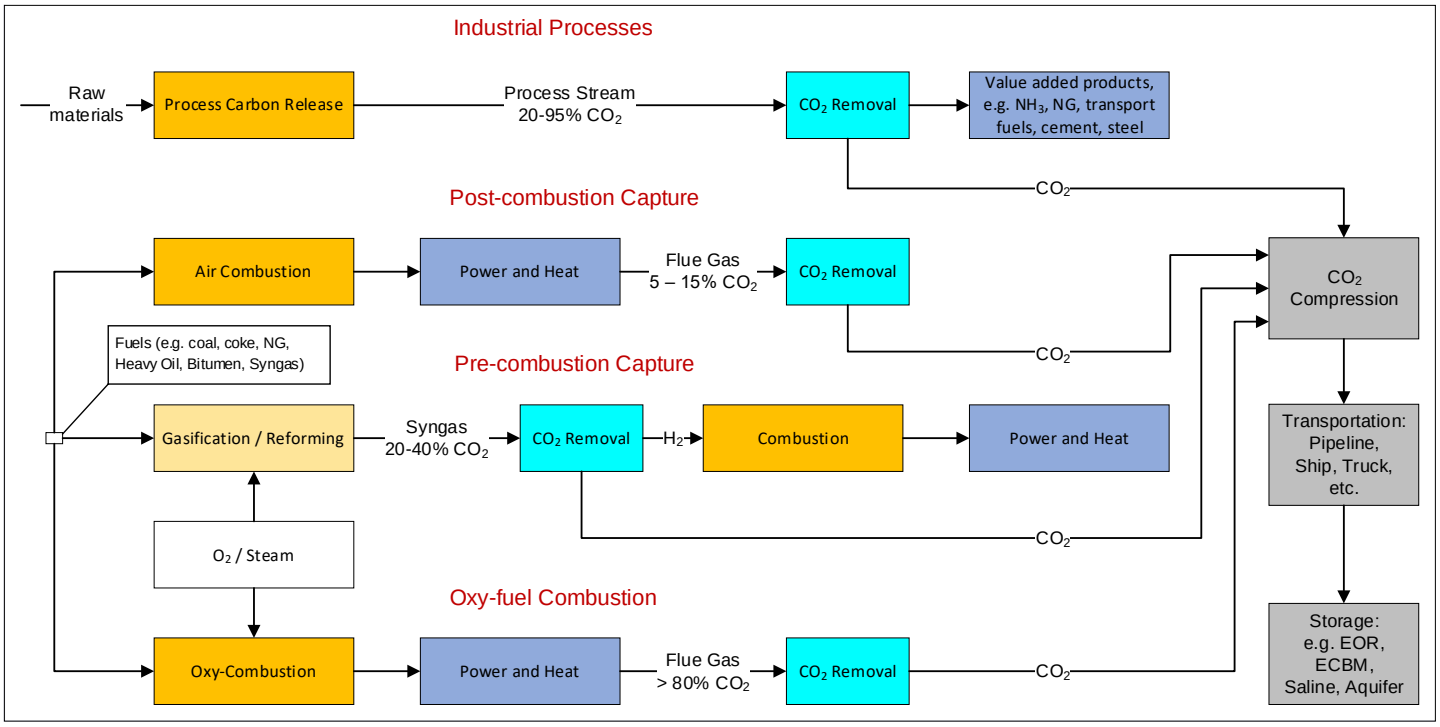


Figure 3 Carbon Capture Pathways

The three carbon capture pathways used in power and heat generation utilize different processes for CO_2 separation. These are summarized in Table 5 [8].

Gas Separation Technology	Pre-Combustion (IGCC with WGS)	Post-Combustion (SPP + IGCC)	Oxy-Combustion (SPP + IGCC)
Absorption	Physical wash	Chemical wash	
Phase separation			Cryogenic air separation
Adsorption	PSA	Sorbents	PSA
Reaction with solids	Carbonate looping + WGS (combined)	Carbonate looping	Chemical looping
Membranes	Polymer + WGS in membrane reactor	Polymer	Mixed conductors

where SPP – Steam Power Plant, WGS – Water Gas Shift, IGCC – Integrated Gasification Combined Cycle

Table 5 Overview of Separation Technologies Used in Power Plant CCS

3.1 Industrial Processes

The largest source of anthropogenic carbon dioxide emissions is electricity and heat generation, while the second is transportation. The industrial sector is the third largest source of man-made carbon dioxide emissions. It consists of manufacturing, construction, mining, and agriculture. Manufacturing is the largest of the four and can be broken down into five main categories: paper, food, petroleum refineries, chemicals, and metal/mineral products [9].

The cement industry accounts for 5% - 7% of total global CO_2 emissions. Cement flue gas itself contains around 18 vol% of CO_2. More than 60% of the CO_2 emissions associated with the production of cement and lime are released directly from the chemical reaction in the process and not from the combustion of fossil fuels.

Fossil fuels are, however, burned to heat the limestone to 900°C (a process of calcination) to turn it into cement, as per Equations (2) and (3):

$$CaCO_3 \xrightarrow{\text{heat}} CaO + CO_2 \qquad (2)$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (3)$$

The calcination takes place in a vessel called a calciner. Fuel is burned in oxygen in the same vessel. It is therefore difficult to separate nitrogen from CO_2. A patented process called LEILAC (Low Emissions Intensity Lime and Cement) uses a technology called Direct Separation. The Direct Separation Reactor (DSR) includes a calciner that has an inner tube where limestone and steam are mixed, and the fuel is burned in the annulus. CO_2 produced in the calcination process contains only steam, which is relatively easy to separate through condensation.

Figure 4 depicts the concept of the LEILAC technology. A pilot plant is in operation at the Heidelberg Cement plant in Lixhe, Belgium. However, the first commercial-scale carbon capture facility for use in cement production will be installed at the Norcem cement plant in Brevik, Norway [10].

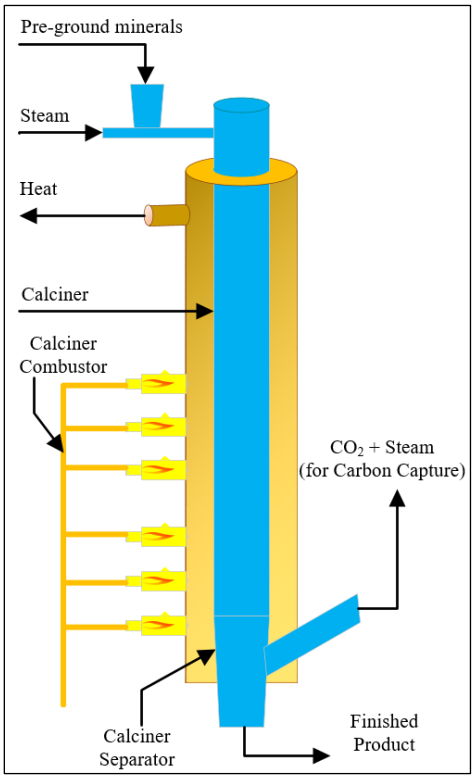


Figure 4 A Design Concept of the LEILAC DSR [11]

The flue gas from the cement plant will be cooled down from 100 – 165°C to 30°C in a direct contact cooler. NaOH will be added to remove SO_2 and HCl from the flue gas. CO_2 will then be removed from the flue gas by an amine solvent. Residual heat from the cement plant will be used to generate steam for the amine reboiler. CO_2 from the amine unit will be compressed and liquefied. The liquid CO_2 will be transported by ship to a transit storage facility in Kollsnes, on the Norwegian West Coast, where it will be injected to a subsea formation.

3.2 Post-Combustion Capture

Post-combustion capture means capturing CO_2 from flue gases. CO_2 is generated by burning various fuels in the air, or oxygen-enriched air. The ratio of carbon to hydrogen of various types of coal is much higher than of fuel oils and even higher than of natural gas. Because of the carbon density, coal produces much more CO_2 than other types of fuel. Furthermore, coal is the most widely used fuel for power generation with 40% of the world's electricity being produced using that resource. The concentration of CO_2 in the power plant flue gases varies from 4 vol% to 14 vol% depending on process configuration and fuel characteristics. Post-combustion capture technologies include absorption, adsorption, membrane, and cryogenic processes.

Capturing CO_2 from power plants is quite different from capturing CO_2 from gases in the oil and gas industry. The differences are presented below:

The temperature of the flue gas is relatively high.

The pressure of the flue gas is very low (nearly atmospheric). The low pressure requires large diameter towers because of large volumetric flowrates. The towers must have packing, usually structured, and not trays, to minimize pressure drop across the tower internals. Additional power may be required for a flue gas blower to drive the flue gas through the tower, increasing the pressure by roughly 25 kPa.

The energy required for solvent regeneration is the dominant operating cost of carbon capture. For that reason, CO_2 recovery seldom exceeds 90% although there are several processes that claim higher recovery levels.

There is no need for deep CO_2 removal. Leaving about 1% of CO_2 in the cleaned gas would be considered normal.

There is no need for low lean solvent loading (not as low as in typical gas plants) because treating is limited by absorber rich-end conditions and not by lean-end pinch created when a high purity gas product is required.

The amine must be as reactive as possible to offset the lack of driving force and to reduce contactor height. Primary amines are often MEA, DGA, and AMP. However, higher reactivity means higher regeneration energy, which in turn increases the cost of carbon capture. As well, solvent losses can be considerable due to high vapor pressures at elevated treating temperatures.

The driving force for CO_2 absorption is its partial pressure. In atmospheric pressure flue gas, the CO_2 partial pressure is very low. Low partial pressure slows down absorption rates which drives the need for longer retention times and higher solvent circulation rates.

In carbon capture from flue gas, MEA is a better choice than activated MDEA containing piperazine, but aqueous concentrated piperazine is a better choice than MEA.

Flue gases almost always contain oxygen which degrades alkanolamines. Consequently, thermal reclamation of the degradation products is required, and product make-up will be higher than gas treating applications.

Flue gas is often contaminated with SO_x, NO_x, heavy metals, ash and other particulates, etc. that cause significant operational issues and expenses. Conventional amines react irreversibly with SO_2.

A consideration should be given to combustion at high pressure – it is then easier to remove CO_2 from the combustion flue gas, but this will require compression of both the fuel gas and the combustion air.

3.3 Pre-Combustion Capture

In pre-combustion processes (like steam methane reforming), the fuel is converted into a gaseous mixture of H_2 and CO_2. H_2 is separated from CO_2 and can be burned without producing CO_2. CO_2 itself is compressed and transported for storage.

In a gasification process, for example, a fuel, e.g. coal, is partially oxidized (sub-stoichiometric combustion) at high pressure and temperature with steam and oxygen to form synthesis gas (syngas):

$$3C + O_2 + H_2O \rightarrow H_2 + 3CO \quad (4)$$

The syngas can be used in a Fischer-Tropsch process to produce liquid hydrocarbons, or it can undergo the water-gas shift reaction to produce more hydrogen (and more CO_2):

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (5)$$

The concentration of CO_2 in the reaction mixture can range from 15% to 30%. The CO_2 can be captured for sequestration using chemical or physical absorbents. The cost of capturing CO_2 generated in an integrated gasification combined cycle (IGCC) power plant is around $60 US per tonne of CO_2 [12].

Coal contains a significant amount of polycyclic aromatic hydrocarbons (PAHs), heavy metals, including mercury, sulfur compounds, and inorganic compounds like ash and particulates. All of these pollutants require additional costs to remove and to keep the carbon capture system operational.

3.4 Oxy-Fuel Combustion

Oxy-fuel combustion is combustion of fuels in a high oxygen environment to produce undiluted CO_2 suitable for direct sequestration. Normally, 95% pure oxygen would be used – higher purity would involve the removal of argon and hence higher cost of producing oxygen. The flue gas contains more than 80% of CO_2 so it is easier to

capture CO_2 than in post-combustion processes. The high concentration of CO_2 in the flue gas allows its purification and condensation in a cryogenic processing unit. Oxy-combustion can be done at high pressure which reduces or eliminates the compression stage.

Burning fuel, like pulverized coal, in pure oxygen, increases the temperature of flue gas which can be used to recover waste heat. For natural gas, the adiabatic combustion temperature (using air, 21% O_2) is 1,900°C. When 95% O_2 is used, that temperature increases to 2,800°C. To protect the metal that contains the flame, some thermal diluent is required. The nitrogen removed from the air must be replaced by another compound, typically water or carbon dioxide. Therefore, some of the flue gas can be recycled and used to control the flame temperature, normally at around 700°C. If waste heat recovery is pursued, the flame temperature can be controlled at 1,900°C. However, the radiant heat transfer is extremely complicated, as changing the combustion gases also impacts the radiant energy which is a significant part of the heat transfer from a flame.

Oxy-fuel combustion products contain CO_2, H_2O, oxygen impurities, and impurities and oxidation products from the fuel, like SO_x, NO_x, HCl or Hg. The main step in treating the flue gas is the condensation of water.

The cost of oxy-fuel combustion is increased by the addition of an air separation unit, purification, and possibly compression of oxygen, although O_2 is seldom compressed unless usage is in small quantities and PSA is used for oxygen purification. Most oxygen plants will be cryogenic, and the oxygen product will be a liquid which is pumped up to application pressure. Compression is mostly limited to the much larger air feed stream.

A variation of oxy-combustion is chemical looping combustion, where oxygen is provided in the form of a metal oxide. Chemical looping combustion is discussed in a separate section of the paper. An added benefit of using oxy-fuel combustion is the lower content of NO_x in the flue gas than in other combustion processes.

Hydrogen enriched fuel could also be considered as a means of reducing the amount of CO_2 in the flue gas.

4. Carbon Capture Technologies

It is difficult to capture and separate carbon dioxide because it is an inert molecule that is thermodynamically stable. However, several carbon capture technologies have been developed, some of them proven and used for years with others in various stages of development.

In general, the technologies can be divided into:

- Absorption
- Adsorption
- Chemical looping
- Carbonate looping
- Membrane
- Cryogenic
- Microbial
- Hybrid

Absorption and cryogenic distillation are already used on industrial scales. Adsorption, chemical looping combustion and membrane separation are technologies that are still under development.

The dominant technology for carbon capture is absorption with amines.

Future or emerging technologies for CO_2 capture include [13]:

- Metal-organic frameworks. Highly absorbent nanoporous materials with incredibly high surface area that can hold significant volumes of gas.

- Nano sponges. Highly effective CO_2 trapping powder that consists of a silica scaffold, a sorbent support, with nanoscale pores. The scaffold is dipped into liquid amine which soaks into the support and partially hardens.
- Hybrid membranes. A hybrid membrane that is part polymer and part metal organic framework, developed at the Lawrence Berkeley National Laboratory. CO_2 molecules can travel through it via two different channels: through the polymer component of the membrane, or through "CO_2 highways" created by metal organic frames. This makes the hybrid membrane eight-times more CO_2 permeable than polymer membranes.
- Crystals. A copper silicate crystal that is a recyclable material that has different adsorption sites for water and CO_2. It can be used for capturing CO_2 from the atmosphere.
- Turning carbon to rock. Atmosphere CO_2 can be injected into volcanic bedrock. CO_2 reacts with the rock forming environmentally harmless products. CO_2 is mineralized in less than two years.
- Turning carbon into fuel. Converting CO_2 from the air into methanol by bubbling air through an aqueous solution of pentaethylenehexamine at an elevated temperature in the presence of a catalyst.
- Turning carbon into fibers. Converting atmospheric CO_2 directly into carbon nanofibers through electrolytic syntheses in a bath of molten carbonates at 750°C with nickel and steel electrodes. To power the syntheses, heat and electricity are produced through an extremely efficient hybrid solar-energy system.
- Biochar-based adsorbents [14]. Biochar is a porous carbonaceous material produced through the thermochemical conversion of organic materials in oxygen-depleted conditions. It can be used as a cost-effective and sustainable material for CO_2 adsorption.
- Turning CO_2 from the air into carbon black powder. The NECOC (Negative Carbon diOxide to Carbon) research project, conducted at Karlsruhe Institute of Technology, in which CO_2 is adsorbed from the air (direct air capture, DAC) and reacted with renewable hydrogen to form methane in a micro-structured reactor. The methane produced is then passed into a bubble reactor filled with liquid tin at 1200°C, where a pyrolysis reaction takes place and methane is decomposed into carbon and hydrogen, which is re-used. Due to the difference in density between tin and carbon, the latter floats at the top and can be discharged in powder form from the reactor. The major advantage of this method over CCS is that carbon is far less difficult to handle than CO_2 [10].

4.1. Absorption

Absorption technologies can in turn be divided into chemical (reactive) and physical (solubility). Chemical absorption technologies utilize solvents that react with CO_2, like aqueous ammonia or MEA, a primary amine, or provide an alkaline environment that enables the hydrolysis of CO_2 to carbonate and bicarbonate ions. Examples of such solvents are MDEA, a tertiary amine, and AMP (2-amino-2-methyl-1-propanol), a primary hindered amine. Amine capacity for CO_2 absorption is limited by stoichiometry of chemical reactions. Physical solvents do not react with CO_2. Examples of physical solvents are dimethyl ether of poly(ethylene glycol) (DEPG), cold methanol (Rectisol®) and N-formyl morpholine (Morphysorb®). It is, however, rather difficult for physical solvents to remove more than 90% of the CO_2 in the flue gas at atmospheric pressure, which is a typical target, because physical absorption depends on the partial pressure of CO_2.

4.1.1 Chemical Absorption

Chemical absorption is the most mature post-combustion carbon capture technology. The most common solvents used in various industries are amine based, like MEA, DEA and MDEA, alkaline solvents like $Ca(OH)_2$ and NaOH, and aqueous ammonia.

Solvent regeneration reboiler energy is one of the highest operating costs associated with carbon capture using amines. MEA and ammonia react very fast with CO_2 to form a carbamate and the heat of absorption is high, so

the required heat of regeneration is also high. This is the reason that the CO_2 recovery is not pursued above around 90%. Above 90%, the energy consumption escalates rapidly [15].

The benchmark amine for post-combustion carbon capture is MEA. It was the first solvent developed for carbon capture. Other alkaline solvents of interest are aqueous ammonia and AMP (2-amino-2-methyl-1-propanol), a sterically hindered amine. Caustic-neutralized amino acids are another class of amine-type solvents.

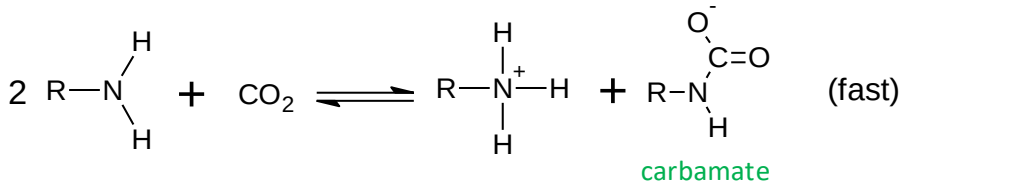
Reaction rates of solvents like AMP, ammonia, potassium carbonate, MDEA (a tertiary amine), are slow relative to MEA. A promoter or a catalyst is required for these solvents to increase the absorption rate of carbon dioxide. Such promoters or catalysts are piperazine, amino acids and carbonic anhydrase.

There are a number of proprietary, amine based processes for lowering CO_2 emissions, like HiPACT (High Pressure Acid Gas Capture Technology, offered by JGC Corporation and BASF SE [16], [17], KM CDR Process developed by Mitsubishi Heavy Industries Engineering and Kansai Electric Power Company that utilizes a hindered amine solvent called KS-1, AdvaCap developed jointly by IFP and Prosernat and licensed by Prosernat, or OASE® sulfexx™, offered by BASF SE and ExxonMobil. Each of these solvents has distinct advantages.

4.1.1.1 Amine-Based Technologies

Amines are weak organic bases that react with CO_2 and H_2S (acid gases) to form unstable salts at moderate temperatures, like carbamates, carbonates and bicarbonates.

The reaction of amines with CO_2 can be described by equations (6) to (8):



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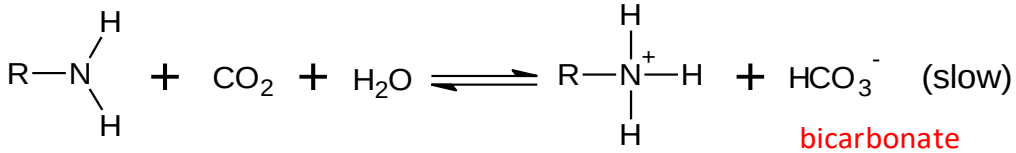

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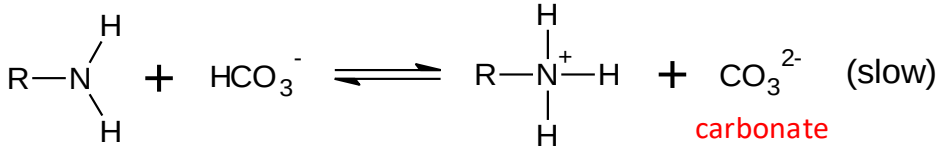


(8)

As can be seen from the above equations, two moles of amine are needed to absorb one mole of CO_2 when carbamate is formed. One mole of amine is needed to absorb one mole of CO_2 when bicarbonate is formed. Below is a description of some of the solvents that are used in carbon capture.

A simplified diagram of amine-based CO_2 capture is presented in Figure 5. The images of equipment in this and some other Figures are taken from Symmetry process software platform. Symmetry is trademark of Schlumberger.

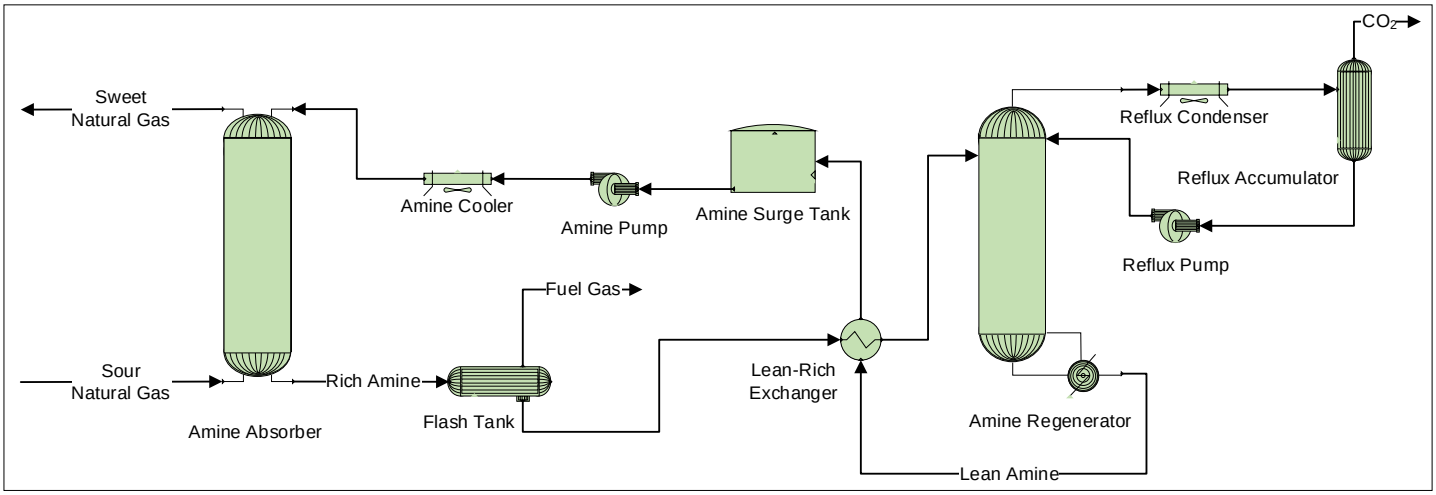


Figure 5 Amine Based Carbon Capture

- **MEA**

Post-combustion CO_2 capture using monoethanolamine (MEA), $H_2N\text{-}CH_2\text{-}CH_2\text{-}OH$, is the most mature and widely used process. MEA has been used for over 60 years for sour gas sweetening. Most carbon dioxide capture facilities use aqueous MEA for the removal of CO_2 from flue gas because of its high reactivity and high absorption. MEA is often used at a concentration of 15-30 wt.%. The drawbacks of using MEA for post-combustion capture is that, due to its high reactivity, MEA reacts irreversibly with acid impurities contained in flue gases, like SO_2 or nitrogen oxides. It should be noted that NO_x in flue gas is not a major problem since the predominant form of nitrogen is NO (constituting 90 to 95% of total NO_x in the flue gas), which does not react with inhibited amines. Untreated flue gases of coal-fired power plants contain 700-2500 ppm SO_2 [18], so desulfurization of flue gas is required to a desired level of 10 ppm SO_2. MEA also reacts with oxygen present in flue gases to form heat stable salts.

The most economical way to operate MEA absorbers is when they are severely rich end pinched (high rich amine loading), around 0.5 mol/mol. This causes the temperature in the absorber to be the highest close to the top of the column, which increases the water and amine losses. A water wash on top of the column can be used to lower the losses. The lean amine loading is normally above 0.1 mol/mol.

Structured packing is normally used, with large surface area to minimize the height of the packing in the absorber. The absorption of CO_2 is usually conducted at temperatures between 30 and 50°C and at a pressure just a few kPa above atmospheric. Corrosion inhibitors can be used in the MEA service to minimize the corrosive effect of the CO_2. MEA is readily degraded by oxygen which is always present in flue gases.

As much as 30% of the power plant output may have to be used just for the amine regeneration, although using the power plant steam will lower that number. Around 80% of operating costs of an MEA unit is used for amine regeneration. The European Union recommends that the energy required for solvent regeneration be around 2 MJ/kg CO_2 but presently it is around 3 to 4.5 MJ/kg CO_2 [27].

The oldest commercial MEA process, offered by Kerr-McGee/ABB Lummus Crest, used 20 wt.% MEA. Econamine, offered by Fluor Daniel, used 30 wt.% MEA. The HiCapt+ process was developed by IFP Energies nouvelles in France. It uses 40% MEA and oxidative inhibitors that prevent corrosion and degradation problems typical to conventional MEA solvents [19].

- **AMP**

AMP, 2-amino-2-methyl-1-propanol, is a sterically hindered amine. It is a primary amine, but the amino group is hindered, preventing the formation of a carbamate, so the reaction product is carbonate. The reaction is exothermic. AMP is much more resistant to degradation by oxygen and much more resistant to thermal degradation than MEA. AMP is also more volatile than MEA. It requires less energy for regeneration and has a higher CO_2 absorption capacity because 1 mole of AMP reacts with 1 mole of CO_2, potentially doubling the capacity of the solvent.

- **Promoted MDEA**

Methyldiethanolamine is a tertiary amine and does not react directly with CO_2 – it is unable to form a carbamate. In fact, MDEA is intended for high H_2S removal and rejection (slippage) of CO_2. But it can be promoted with a primary amine like MEA or a secondary amine like piperazine to increase its ability to absorb carbon dioxide. Promoted MDEA has a lower heat of absorption and consequently requires lower energy of regeneration than some other solvents, like MEA. But the benefit of using MDEA is that it serves as a large sink for protons produced by slow CO_2 hydrolysis:

$$CO_2 + H_2O \leftrightarrow H^+ + HCO_3^- \quad (9)$$

$$H^+ + CH_3(CH_2CH_2OH)_2N \leftrightarrow CH_3(CH_2CH_2OH)_2NH^+ \quad (10)$$

Usually, the highest concentration of MDEA used in gas sweetening is 50 wt.%. CO_2 absorbs into the solution physically and chemically. The physical solubility of CO_2 in water, which constitutes the majority of the MDEA solution, is low, but it is much more soluble in MDEA. The chemical solubility of CO_2 in MDEA solutions is very high because the protonation of MDEA allows the bicarbonate and carbonate ions to be produced. However, the limiting step in CO_2 solubility is the diffusion of CO_2 from the gas into the gas-liquid interface.

- **Piperazine**

Aqueous piperazine may become a new standard for carbon capture technology. The standard solvent to date is 30 wt.% MEA. A new standard process was proposed that uses 40 wt.% piperazine with regeneration at 150°C by a two-stage flash [20]. Piperazine solvent is resistant to degradation by oxygen and is less volatile than MEA, even though the boiling point of MEA is 170°C and that of piperazine is 146°C. Piperazine is not corrosive to stainless steel. Also, it is not subject to much thermal degradation at temperatures up to 150°C. Any degradation products can be removed by distillation.

The expected energy requirement for an aqueous piperazine scrubbing process is around 220 kWh/tonne CO_2. The heat requirement is 2.6 MJ/tonne CO_2.

- **Cansolv**

The Cansolv™ technology was developed by Union Carbide Corporation and commercialized by Cansolv Technologies Inc. as CANSOLV® SO_2 Scrubbing System. The regenerative process uses an aqueous diamine of the form R_1-R_2-N-R_3-N-R_4-R_5. The amine is resistant to oxidative environments and is highly selective to SO_2. The process is used for flue gas treating, as well as tail gas from sulfur recovery units (SRU). The tail gas containing H_2S is thermally oxidized to SO_2 in the incinerator. After cooling, the Cansolv solution selectively absorbs SO_2 from the incinerator tail gas and is regenerated using steam. The product is water-saturated SO_2 that can be recycled to the Claus SRU and converted to sulfur or it can be used to produce sulfuric acid.

An integrated Cansolv process for SO_2 and CO_2 capture uses the Cansolv SO_2 absorber, where SO_2 is removed. Then the treated gas is introduced to the CO_2 capture absorber, where CO_2 is removed.

In 2008 Cansolv Technologies Inc. was acquired by Shell Global Solutions. Shell Catalysts & Technologies now offers a technology for post-combustion CO_2 removal called Shell Cansolv® CO_2 Capture System, that employs a regenerable proprietary amine.

- **Chilled Ammonia**

This is a process patented by Alstom Power. The solvent is a cold, aqueous mixture of ammonia and ammonium carbonate. Carbon dioxide reacts with the solvent components and converts them to ammonium carbamate and ammonium bicarbonate, which precipitates from the solution. Removal of the bicarbonate enables the solution to absorb more CO_2. The issues associated with the process are handling the suspended bicarbonate, keeping the solution cold and losses of volatile ammonia.

- **Biphasic Solvents**

Biphasic solvents (phase-change solvents) are amine blends made up of a primary or secondary amine as a CO_2 absorption accelerator and a tertiary amine as a CO_2 sink. Once CO_2 has been absorbed, the CO_2-rich solvent undergoes liquid-liquid phase transition and more than 90% of the absorbed CO_2 is concentrated in one phase. The liquid-liquid stream leaves the absorber and the two liquid phases are separated in a liquid-liquid phase separator. Only the CO_2-rich phase is sent to the desorber (CO_2 stripper). The concept of the technology (still in development) is presented in Figure 6. Depending on the blend, the phase transition may occur with the temperature change. In that case, the liquid-liquid phase separator is placed between the heat exchanger and the desorber.

Biphasic solvents require about 50% less regeneration energy and have four times the cyclic loading capacity compared to MEA (cyclic loading capacity is the difference between rich and lean loading multiplied by the amine concentration and expressed in moles of CO_2 per liter of amine solution. It determines the maximum amount of CO_2 that can be produced per cycle.) [21].

A phase change solvent called DMX-1 is used in the DMX™ Process developed by IFP Energies nouvelles and is licensed by AXENS. It has a high cyclic capacity, up to 1 mol CO_2 per mole of solvent. The solvent is not corrosive and does not degrade up to 160°C, so the regeneration can be operated at 6-7 bara. OPEX is reduced by 30% compared to traditional amine-based solvents. A DMX industrial pilot plant located in Dunkirk, France will start its operation in 2020. More details of the DMX process can be found in [22].

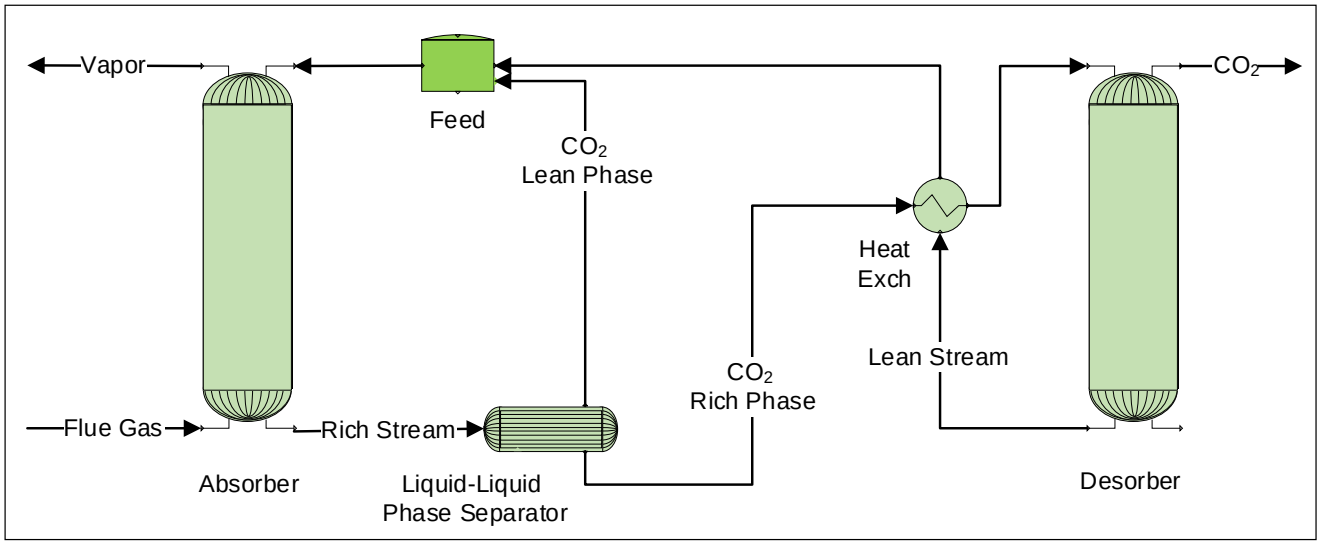


Figure 6 Concept of a Biphasic Solvent Process

4.1.1.2 Other Chemical Absorption Solvents

- **Promoted Potassium Carbonate**

Conventional amine processes for carbon capture require the formation of high temperature steam to regenerate the solvent. To reduce the cost of CO_2 capture, other aqueous solvents have been proposed, one of them being potassium carbonate solutions (K_2CO_3). The potassium carbonate process was developed by the U.S. Bureau of Mines for removing CO_2 from manufactured gas [23]. The operating temperature in the K_2CO_3 contactor is 90-110°C and for that reason the process is also called "hot pot". The energy required for regenerating the solution is lower than for MEA. The "hot pot process" is known under different commercial names like Benfield™, licensed by UOP LLC, Catacarb®, offered by Eickmeier & Associates, Inc., and Giammarco-Vetrocoke developed by Giammarco-Vetrocoke.

The potassium carbonate process is based on a reversible reaction represented by equation (11)

$$K_2CO_3 + H_2O + CO_2 \leftrightarrow 2KHCO_3 \quad (11)$$

K_2CO_3 solutions are good solvents for CO_2 capture because they have low regeneration energy, low degradation rates and low corrosivity. One limitation of K_2CO_3 is that it has slow reaction kinetics with CO_2. This limitation can be overcome by the addition of promoters to K_2CO_3 solutions, for example a reactive amine like piperazine. Piperazine promoted K_2CO_3 can have rates and capacities comparable to MEA, with one significant advantage: the heat of desorption of CO_2 is 50% to 75% of that for MEA. Addition of enzyme catalyst promoters to K_2CO_3 ,such as carbonic anhydrase, glycine (Giammarco-Vetrocoke) or DEA (Benfield), increases the reaction kinetics with carbon dioxide.

- **Amino Acids (Sodium Glycinate)**

Amino acids are also being considered as post-combustion carbon capture solvents. The simplest amino acid is glycine of the formula NH_2-CH_2-COOH. These chemicals are both acids and bases and when the carboxyl group is neutralized with a base like NaOH or KOH, the amino group is activated. Sodium glycinate (NH_2-CH_2-COONa) is more reactive towards CO_2 than MEA. It also requires lower regeneration energy than MEA. In addition, it is completely non-volatile so the vaporization losses would be essentially none. Sodium glycinate is partially oxidized which makes it resistant to further oxidation by O_2 in the flue gas. Potassium dimethylglycinate $(CH_3)_2$N-CH_2-COOK is a tertiary amine and can be used as a carbon capture solvent when promoted with piperazine or an enzyme catalyst.

- **Enzymatic Technology - Human Carbonic Anhydrase**

Carbonic anhydrase (CA) is a naturally occurring enzyme that regulates CO_2 in all living organisms. CA catalyzes the conversion of CO_2 to bicarbonate. CO2 Solutions Inc. (CSI) developed a technology that does not use or emit toxic products but lowers the cost of carbon capture. In 2020, Saipem acquired that technology from CSI.

Carbonic anhydrase can be used as a catalyst in potassium carbonate solutions, improving the CO_2 absorption kinetics similar to amine solutions. Low-grade heat sources can be used to strip the solvent of CO_2. A temperature below 80°C in the reboiler is usually sufficient for stripping the solvent to release the CO_2.

The primary purpose of an enzyme is to provide a catalytic reaction site in which increased reaction rates occur. Enzymes are typically paired with an amine in an amine-based solvent or some other alkaline solvent, such as potassium carbonate. While the enzyme provides an enhanced reaction, the alkaline base is needed to provide a means of holding the CO_2 in solution. The molecular weights of enzymes are very high. For example, Human Carbonic Anhydrase C (HCAC) has the molecular weight of approximately 29,000 g/mol. For that reason, they are used at very low concentrations, ranging from 2-6 kg of enzyme per m^3 of solution. They are thermally

degraded at around 70°C. For this reason, regenerators are run under vacuum to keep the temperature low enough to avoid degradation.

A demonstration plant commissioned in Quebec was able to capture up to 95% of CO_2 and produced a carbon dioxide stream with a purity of 99.95%. A techno-economic analysis determined the cost to be $28 per tonne of CO_2 captured [24].

Carbon capture using human carbonic anhydrase C, K_2CO_3 and potassium dimethyl glycinate can be modeled using Pro-Treat®, a software developed by Optimized Gas Treating. An example of such a simulation is presented in Figure 7 below.

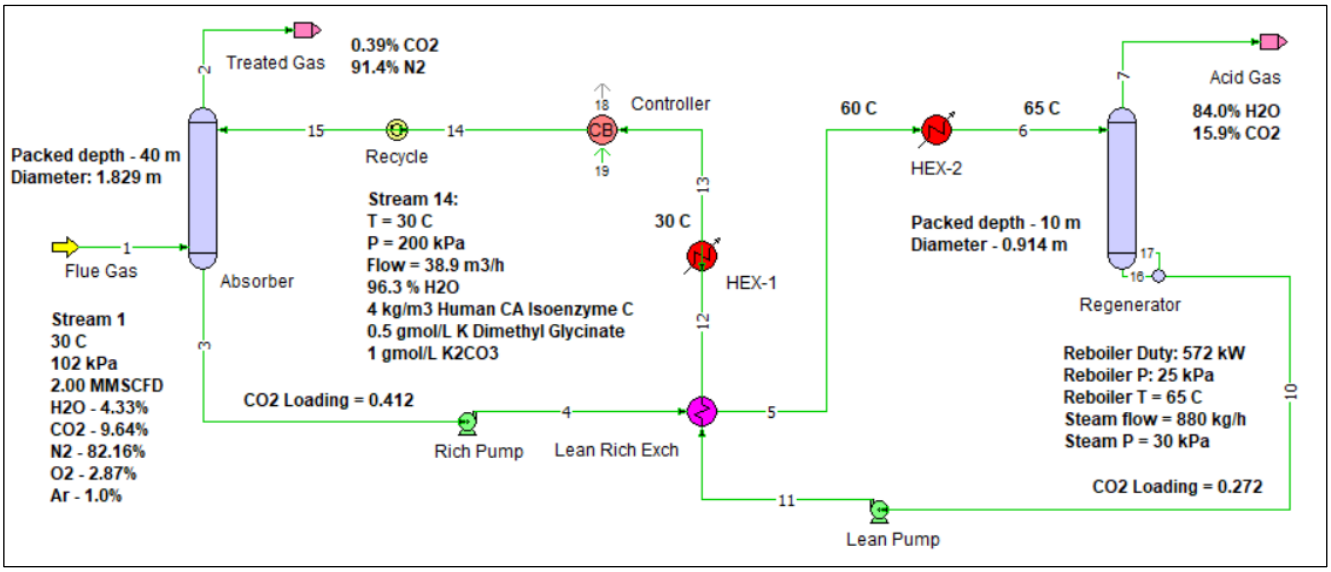


Figure 7 Pro-Treat® Simulation of Post-Combustion CO_2 Capture Using Human Carbonic Anhydrase

4.1.2 Physical Absorption

Physical absorption generates only heat of dissolution of CO_2 into the solvent because there is no heat of reaction between CO_2 and the solvent. The lower the temperature and the higher the CO_2 partial pressure in the gas to be treated, the higher the volume of CO_2 that can be captured. The partial pressure of CO_2 in pre-combustion processes is already high, which makes physical solvents good candidates for pre-combustion carbon capture solvents. Typical physical solvents in carbon capture include DEPG, methanol, propylene carbonate, NMP (N-methyl-pyrrolidone), NFP and NAM (derivatives of morpholine). Other physical solvents are being developed, like ionic liquids. Physical solvents used on commercial scale in pre-combustion capture are SELEXOL™, Rectisol®, Fluor Solvent™ and Purisol®. Ionic liquids are close to industrial scale.

- **DEPG**

  Dimethyl ether of polyethylene glycol (DEPG), known by the trade names of SELEXOL™ (Dow Chemical), Genosorb® 1753 (Clariant) and Coastal AGR or AGR Solvent (Coastal Chemical) has a general formula $H_3CO(CH_2CH_2O)_nCH_3$, with n varying from 3 to 9. It is a good solvent for the removal of H_2S and CO_2, and because of its polar nature also for COS, CS_2 and mercaptans. The heat of absorption of CO_2 in DEPG is low compared to amines so the energy required for regeneration is also low. It has been used to remove CO_2 from landfill gas at atmospheric pressure. DEPG regeneration can be done with inert gas (no need for a reboiler).

  DEPG is usually used at concentrations above 94 wt.%, with the rest being water. When processing wet gas, DEPG absorbs more water so eventually excess water will have to be purged from the system.

A simplified diagram of a SELEXOL™ unit is shown in Figure 8. The solvent is regenerated by pressure reduction and gas stripping.

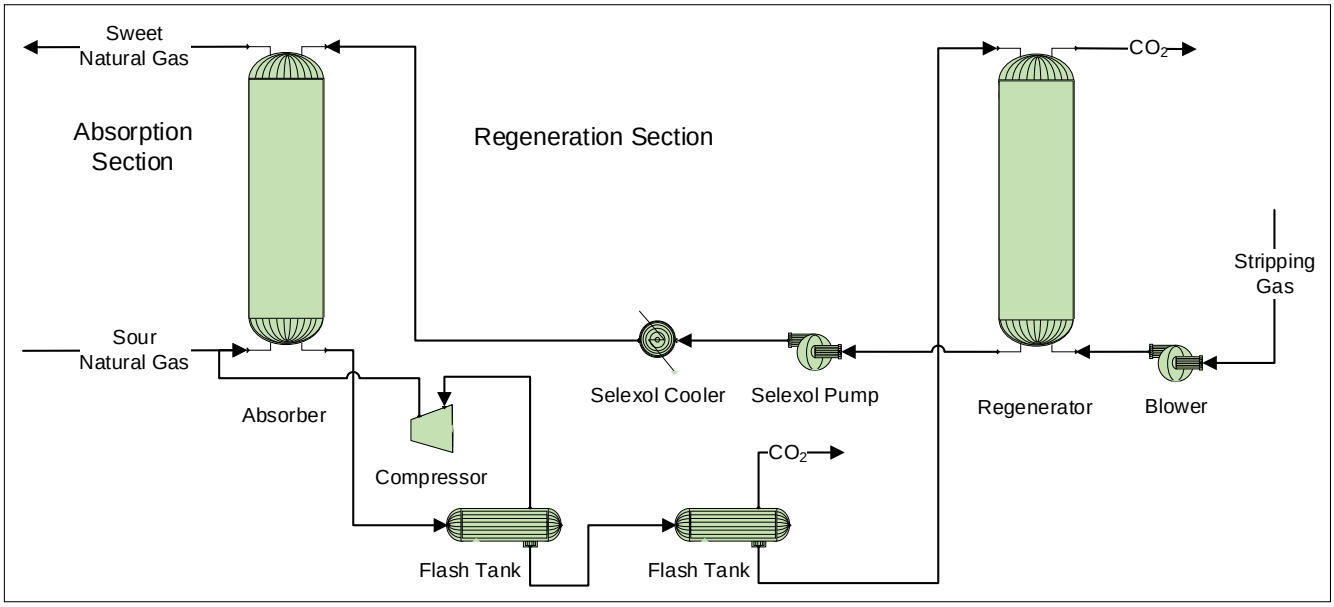


Figure 8 Carbon Capture by Physical Absorption Using SELEXOL™

- **Methanol (Rectisol, Ifpexol)**

The benefits of using methanol are its availability, low cost, and chemical and thermal stability. Depending on operating conditions, methanol also dehydrates the gas to be treated thus preventing hydrate formation.

There are a couple of carbon capture processes involving methanol as the physical solvent, namely Rectisol and Ifpexol.

Rectisol™ was the first physical organic solvent process. It was independently developed by Linde and Lurgi. It uses methanol as a wash solvent to purify gasification-based syngas. The process removes CO_2, H_2S and COS. It also removes other impurities produced in the gasification of coal or heavy oil, like HCN, BTEX and mercaptans. Similar to other physical solvents, the performance of the solvent is subject to partial pressure.

Rectisol operates at pressures of 2750 kPag to 6880 kPag and temperatures as low as -60 to -70°C. At these low temperatures, methanol has still a low viscosity and its CO_2 carrying capacity at these temperatures is much higher than that of other physical solvents at their typical operating temperatures [25]. The Rectisol process is used in the Sturgeon Refinery in Alberta to capture 3,500 t/d of CO_2 from the bitumen gasifier unit.

The process can remove CO_2 to ppmv levels and capture up to 99% of CO_2. However, it is a complex process, requiring methanol refrigeration, and the costs of a carbon capture plant can be high. For this reason, Rectisol is used in applications where other treating processes may not be suitable, like the purification of gas streams in heavy oil partial oxidation and coal gasification.

Rectisol is an example of a pre-combustion carbon capture process. The process is licensed by Linde AG and Lurgi, a division of Air Liquide.

Ifpexol, a two-step process, uses methanol to achieve simultaneous water and hydrocarbon dew point control (Ifpex-1), and removal of acid gases and sulfur compounds (Ifpex-2).

In the Ifpex-2 process, the gas is contacted with refrigerated methanol in a counter-current contactor, where CO_2, H_2S, mercaptans and COS are absorbed. The solvent, loaded with these gases, is regenerated by flashing at around 1000 kPag, which makes the process suitable for acid gas injection.

The licensor of the process is Prosernat (on January 1, 2019 Prosernat merged into Axens. Now Axens offers Ifpexol as a proprietary technology for simultaneous dehydration and hydrocarbon dewpoint control).

- **Propylene Carbonate (Fluor Solvent)**

  Propylene carbonate is used in the Fluor Solvent Process, which can remove CO_2 to below 1 mol%. The process was developed in the late 1950s by The Fluor Corporation. It is suited for feed gases with a CO_2 partial pressure above 480 kPa, H_2S concentration below 50 ppm and C_{5+} components concentration less than 0.5 mol%. CO_2 is desorbed from the solvent without heat. The solvent loading increases with decreasing temperature, so to reduce the circulation rate, the absorber is operated below -18°C. The licensor of the Fluor Solvent Process is Fluor.

- **NMP (Purisol)**

  N-methyl-2-pyrrolidone is used in the Purisol process for the removal of acid gases from natural gas, fuel gas and syngas. It is an inexpensive and non-corrosive solvent. It can remove CO_2 from gas streams to less than 0.1 mol%. The licensor of the Purisol process are Lurgi and Air Liquide.

- **Morpholine (Morphysorb)**

  Morphysorb is a mixture of N-formyl morpholine and N-acetyl-morpholine. It is used for the removal of H_2S, CO_2, COS and RSH from natural gas or syngas. Bulk acid gas removal, down to 2% CO_2, can be achieved with simple flash regeneration. Additional thermal regeneration is required for CO_2 removal to 50 ppm. The process simultaneously dehydrates the gas and removes BTEX. The typical pressure of the feed gas for the Morphysorb process is from 27 bar to 90 bar and the composition of the acid components from 5% to 70%. The Morphysorb solvent has high acid gas capacity, is non-corrosive, and non-toxic. Because of its low vapor pressure, the losses of the solvent to the product and acid gas are low. Morphysorb is licensed by Thyssenkrupp Uhde.

- **Ionic Liquids**

  Ionic liquids (Ils) are salts in a liquid state at room temperature. There are a large variety of them, comprised of various cations and anions. The advantages of ionic liquids are low volatility (negligible vapor pressure), good thermal stability (decomposition above 300°C), low degradation, low corrosivity, relative low flammability and low regeneration energy. An important advantage of ionic liquids is that CO_2 is absorbed physically and a chemical reaction does not occur. Yet another advantage of a number of Ils is a selectivity towards CO_2 in the presence of nitrogen and methane.

  Various ions have been tested in CO_2 capture like hexafluorophosphate PF_6^- (1-butyl-3-methylimidazolium hexafluorophosphate) and tetrafluoroborate BF_4^- (1-*n*-butyl-3-methylimidazolium tetrafluoroborate), in which CO_2 dissolves very well. Other ionic liquids included imidazolium,

pyridinium, pyrrolidinium, guanidinium, carboxylate, azolate, phenoxide, thionate, halide. The number of available ionic liquids allows the designer to select the one that achieves the best carbon dioxide solubility.

The solubility of CO_2 in all the ionic liquids increases with increasing CO_2 pressure and decreases with increasing temperature. A disadvantage of ionic liquids is their viscosity, which increases with increasing CO_2 capture. The viscosity of ionic liquids can be lowered in different ways, including the addition of an amine solvent.Despite the interest in ionic liquids, there are problems with applying them on an industrial scale because of their availability, price, impact on the environment (biodegradability), toxicity and long-term stability.

4.2 Adsorption

Adsorption is a process whereby gas or liquid molecules are retained on a solid surface. Carbon capture processes use regenerable adsorbents that have high affinity for CO_2, such as activated carbon or zeolites, e.g. 13X (naturally occurring or synthesized silico-aluminates). Metal organic frameworks, like Mg-MOF-74, are also being considered. Similar to physical solvents, the lower the temperature and the higher the CO_2 partial pressure in the gas to be treated the higher the volume of CO_2 that can be captured. Adsorption requires clean feed gas, so it is not the best technology for coal or cement applications.

Depending on the method of regeneration, adsorption processes can be divided into pressure swing adsorption (PSA) or temperature swing adsorption (TSA). PSA is more is more suited for pre-combustion processes. For post-combustion carbon capture, TSA or VSA (Vacuum Swing Adsorption) is more appropriate.

A schematic diagram of a TSA system is shown in Figure 9 [26]. The adsorbers could be fixed bed, fluidized bed, or moving bed.

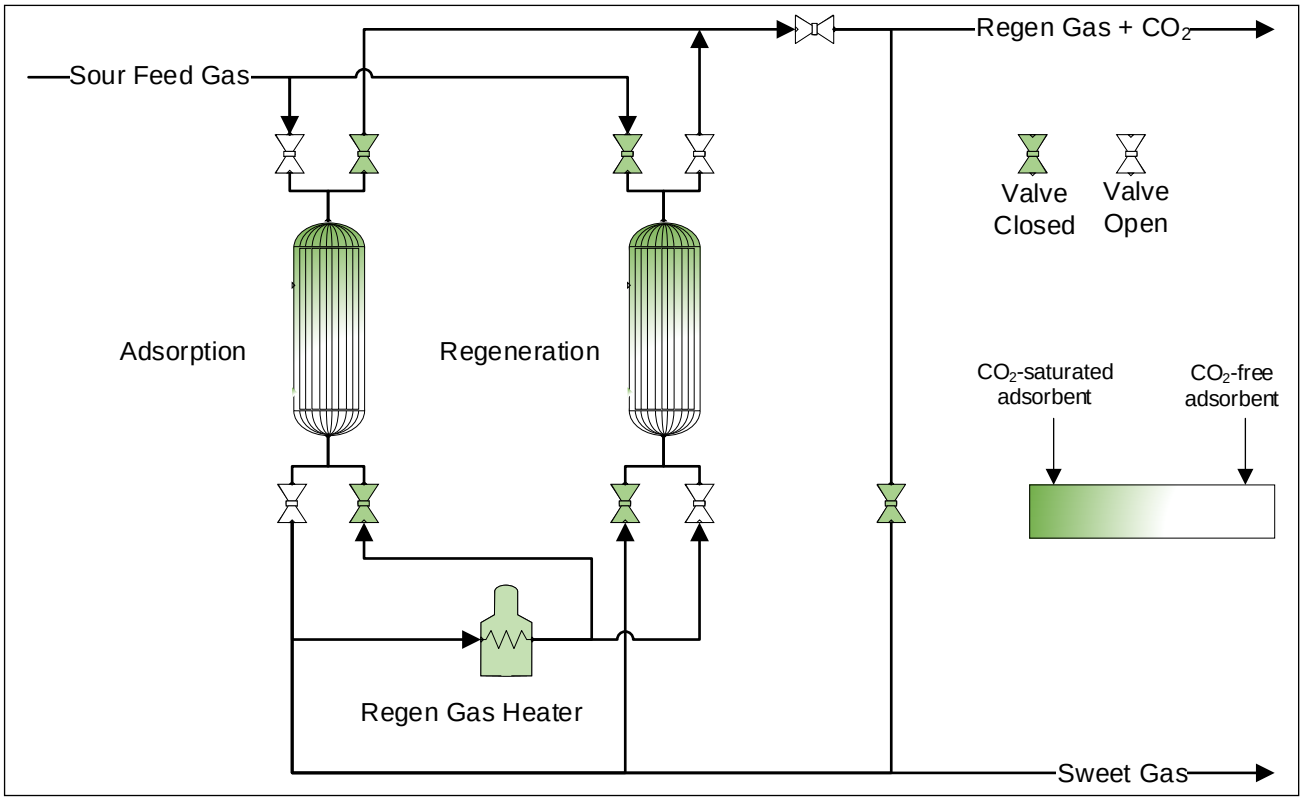


Figure 9 TSA Type Adsorption Unit for Carbon Capture

No commercial scale adsorption type carbon capture project has been implemented yet.

An adsorption process with chemical reaction was developed by RTI International. It is called the dry carbonate process and can be used for CO_2 recovery from power plant flue gas. The technology is still under development, but field testing demonstrated that the process can capture more than 90% of CO_2 from the flue gas.

Carbon dioxide reacts with dry sodium carbonate (soda ash) in a CO_2 adsorber to produce sodium bicarbonate (baking soda). The reaction is reversed in the regenerator at 120 – 140°C.

$$Na_2CO_3\ (s) + CO_2\ (g) + H_2O\ (g) \leftrightarrow 2NaHCO_3\ (s) \quad (12)$$

The vapor leaving the regenerator contains CO_2 and H_2O. Condensation of H_2O produces a pure CO_2 stream that can be used as a value-added commodity (concrete curing, conversion into biomass etc.), or it can be compressed and sequestered.

4.3 Chemical Looping Combustion

Chemical looping combustion (CLC) is a carbon capture process for power generation. Oxygen stored in an oxygen carrier in the form of a metal oxide like Fe_2O_3, NiO, CuO, Mn_2O_3, is used to combust the fuel, either by releasing the oxygen into the gas phase, or by direct contact with the fuel. Combustion is divided into oxidation and reduction reactions that take place separately in an air reactor and a fuel reactor. In the fuel reactor, the metal oxide is reduced by the fuel:

$CH_x + MeO \rightarrow CO_2 + H_2O + Me$ (exothermic or endothermic reaction, depending on the metal)

The fuel itself is oxidized to CO_2 and H_2O. In the air reactor, the reduced carrier is oxidized back to metal oxide:

$Me + ½\ O_2 \rightarrow MeO$ (exothermic reaction)

A process flow diagram of chemical looping combustion is shown in Figure 10.

The advantages of chemical looping combustions:

- The exhaust gas from the air reactor is mainly nitrogen.
- The exhaust gas from the fuel reactor is carbon dioxide and water.
- NO_x formation is minimized.
- Carbon dioxide can be separated from water in a condenser, that requires much less energy than energy needed in absorption processes.

The disadvantages of chemical looping combustion:

- Sulfur must be removed from the fuel to prevent sulfidation of the oxygen carrier
- Slow redox kinetics (slow rate of redox reactions) which limits the capacity of the chemical looping combustion reactors.

Most chemical looping combustion processes have been tested on the laboratory scale. There are a few large-scale demonstration facilities of this technology [27].

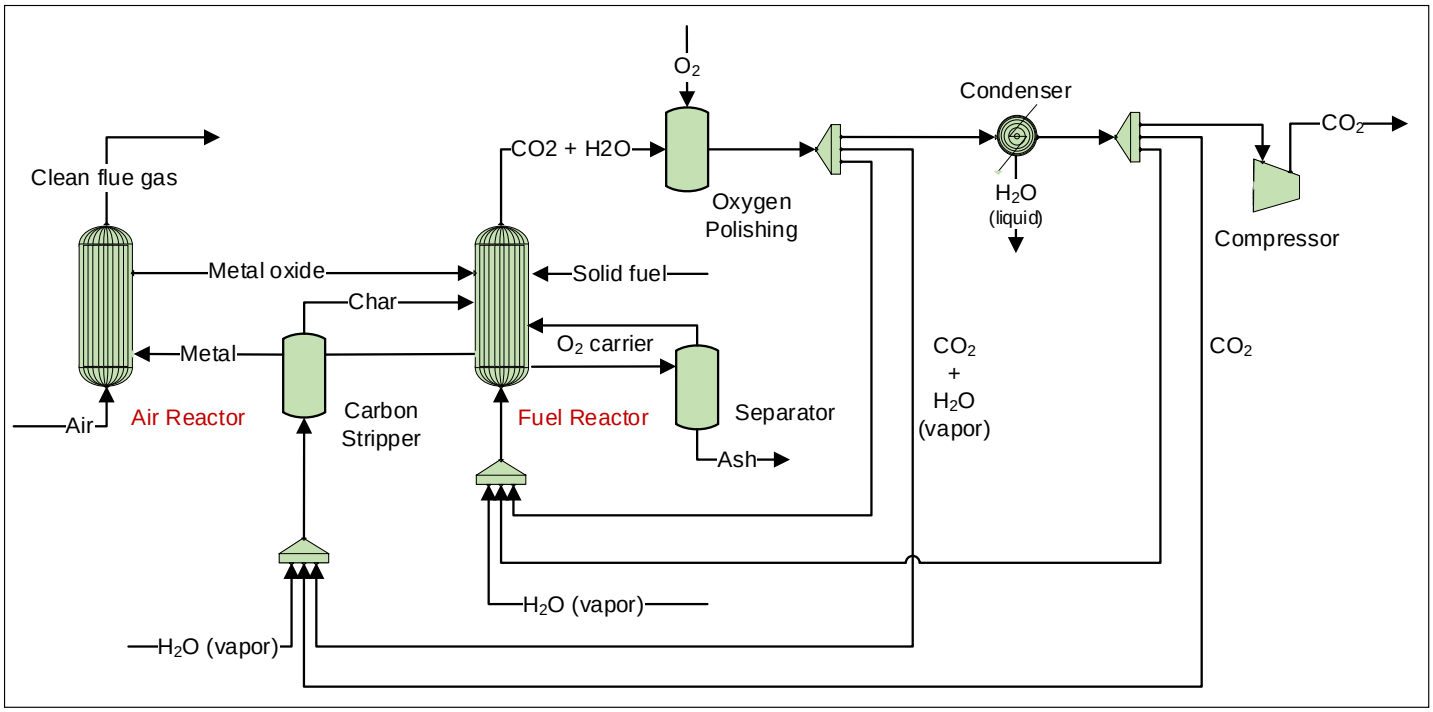
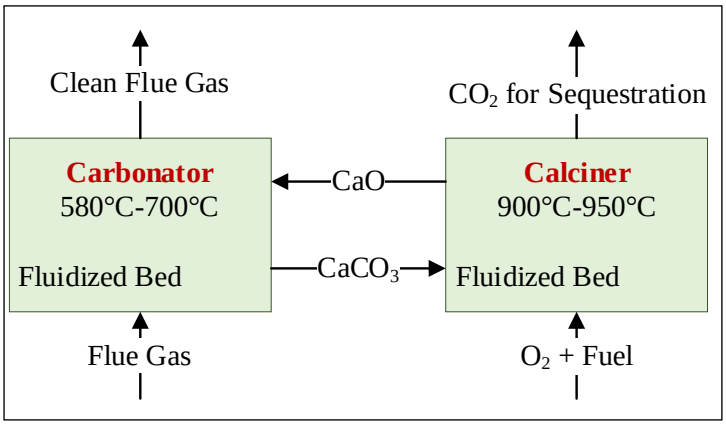


Figure 10 Process Flow Diagram for the CO_2 Capture from Flue Gas by Chemical Looping Combustion Process

4.4. Calcium Looping

The calcium looping technology is a post-combustion carbon capture based on the reversible carbonation of lime (CaO). The schematic diagram of the process is illustrated in Figure 11 [28].



The solid sorbent is circulated between two fluidized beds. The flue gas is fed to the Carbonator. Calcium oxide undergoes a carbonation reaction with the CO_2 contained in the flue gas, forming calcium carbonate. $CaCO_3$ is then transferred to the Calciner where the carbonate is decomposed to CaO and CO_2. The calcination reaction is endothermic. The heat is provided by burning fuel in pure oxygen to obtain a concentrated stream of CO_2.

Figure 11 Schematic Diagram of Calcium Looping

Calcium looping has some advantages over amine scrubbing:

- Lower efficiency penalty (efficiency penalty refers to power generation loss by installing CCS on a power plant).
- Cost of CO_2 avoided between \$30 – \$50 per tonne of CO2, roughly 50% less than for amine scrubbing.
- Limestone, the source of CaO, is inexpensive, widely available, and environmentally benign.

A disadvantage of the calcium looping technology is diminishing sorbent reactivity after 20 to 30 cycles due to sorbent sintering during calcination.

4.5 Membrane Separation

The essence of the membrane process is the fact that, under the effect of a driving force (which could be the difference in partial pressure of the components of the gas on both sides of the membrane) various components of the gas diffuse through a membrane at different rates. Membrane processes require a high operating pressure; therefore, they may be better suited to pre-combustion capture. They can be used for CO_2 capture in coal fired power plants, natural gas fired power plants, cement plants, steel plants, separation of CO_2 from biogases.

Of the various membranes being considered for carbon capture, such as polymeric, inorganic, facilitated transport (liquid, ion-exchange, fixed carrier) and mixed matrix, only polymeric membranes have been used on a commercial scale. Membranes are more suitable for pre-combustion carbon capture (e.g. IGCC, Integrated Gasification Combined Cycle) because of the high pressure of the gas from pre-combustion processes.

A schematic diagram of CO_2 separation using a membrane is shown in Figure 12.

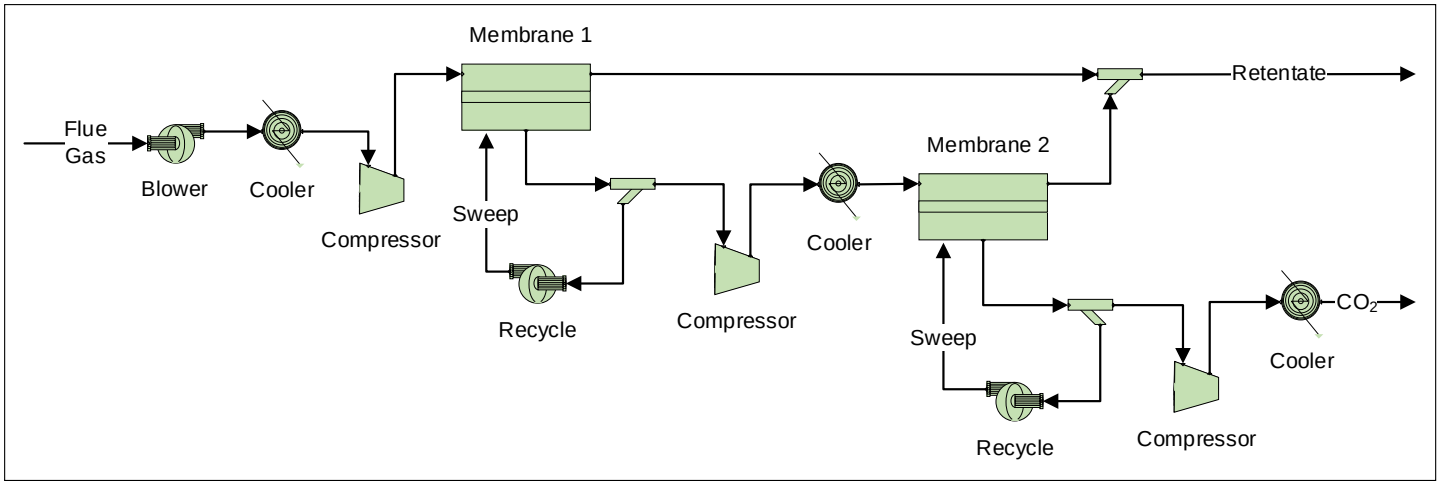


Figure 12 CO_2 Separation Using a Two-Stage Membrane [27]

Membrane Technology and Research (MTR) offers Polaris™ membranes for separation of CO_2 from syngas. The membranes can typically separate 80% of the feed CO_2 and produce up to 95 vol% pure CO_2. Figure 13 depicts CO_2 removal from syngas using a Polaris membrane [29]: This membrane is used in MTR's PolarCap™ process, specifically developed for CO2 capture, among others in coal fired power plants.

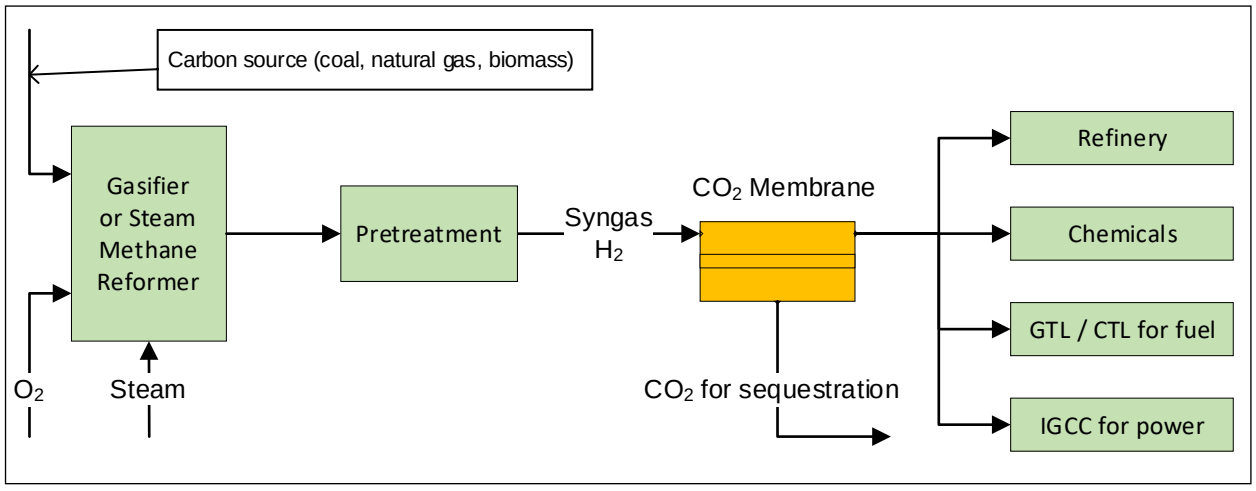


Figure 13 CO_2 Removal from Syngas Using MTR's Polaris™ Membrane

Pretreatment shown in Figure 13 is needed because coal fired power plants and cement plants are a challenging service for porous media. Heavy metals and particulate matter will "contaminate" membranes, not to mention CO, SO_x, NO_x and PAHs (Polycyclic Aromatic Hydrocarbons).

4.6 Cryogenic

Carbon dioxide can be separated from the gas by lowering its temperature and changing its phase into liquid or solid. The liquid CO_2 can then be separated from the mixture by cryogenic distillation. One such technology is the Ryan/Holmes process for the separation CO_2 from natural gas. The formation of solid CO_2 makes it easy to separate the gas from the solid.

Cryogenic distillation of CO_2 can be used in pre-combustion processes which produce high concentration of carbon dioxide.

Conventional cryogenic processes like distillation are not suitable for post-combustion carbon capture because of low concentration of CO_2 in the flue gas. However, other low-temperature processes can be used for CO_2 separation like anti-sublimation (reverse sublimation) of carbon dioxide or hydrate formation of CO_2.

A process-based on reverse sublimation was developed by École des Mines de Paris and Alstom. The flue gas is first dehydrated and then cooled to low temperature (around -120°C) at which the CO_2 changes its state from gaseous to solid. The temperature at which CO_2 solidifies depends on the concentration of the CO_2 in the flue gas. The flue gas can be separated from CO_2 in that manner. CO_2 is then re-melted and recovered as a separate stream.

An improvement of that process, called Cryogenic Carbon Capture™ is offered by SES Innovation [30]. Figure 14 shows the concept of the process.

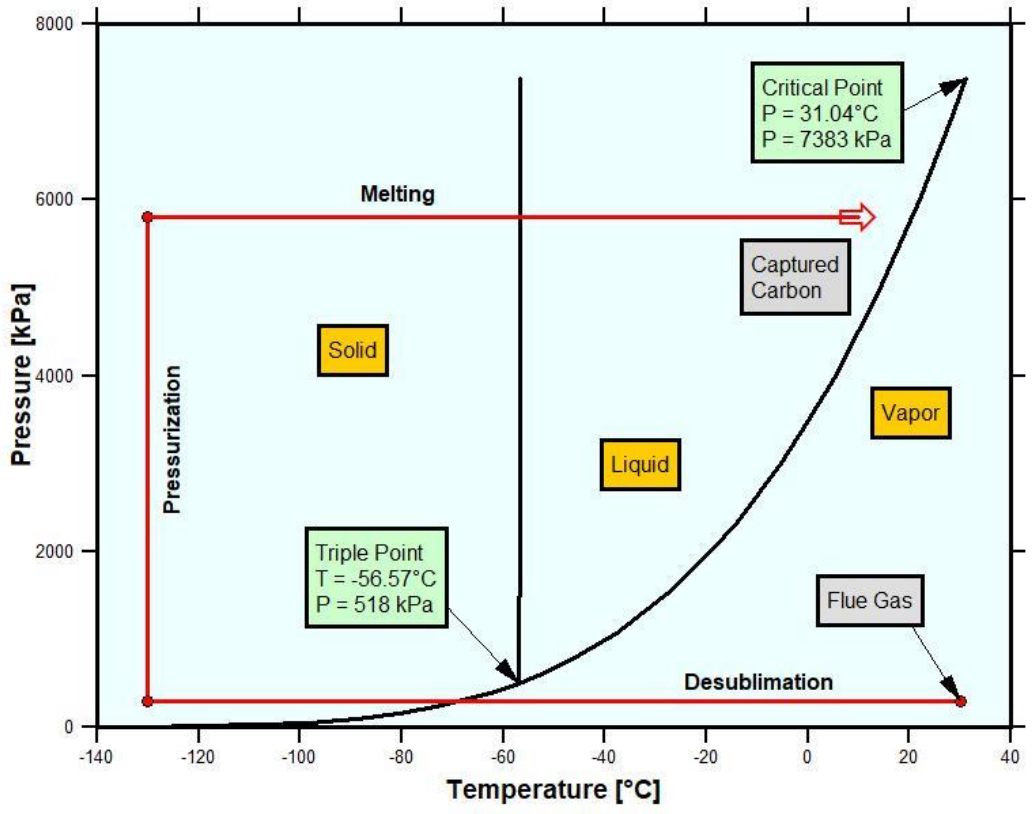


Figure 14 Cryogenic Carbon Capture™ Concept

The temperatures and pressures of the process shown on the graph only visualize the process and do not reflect the actual conditions. Flue gas is cooled down to a temperature, at which reverse sublimation of CO_2 takes place (around -140°C), which means that CO_2 changes its phase from vapor directly to solid. Then the gas is separated from the solid and the solid is pressurized and melted. The CO_2 is delivered to a pipeline for sequestration or utilization. Since the triple point of carbon dioxide lies at -56.6°C and 518 kPa on the CO_2 phase diagram, the final state of CO_2 has to be above and to the right of the triple point, in the range of the operating pressure of the pipeline.

According to SES Innovation, the cost of Cryogenic Carbon Capture is less than $30 per tonne of captured CO_2.

4.7 Microbial

Soil Carbon Co., an Australian company, is working on a microbial process that would enable the capture of CO_2 from the atmosphere into the agricultural soil to increase its fertility. The technology uses fungi and bacteria to extract CO_2 from the atmosphere. The advantage of this technology is that no additional equipment or energy is required.

Some microbes like melanized endophytic fungi (endophytic – living within a plant) feed on the plant root exuded matter containing labile (unstable) carbon compounds and produce melanin, a polyaromatic carbon compound resistant to hydrolysis in the soil, deposited in tiny, compressed balls of soil. Carbon captured in such a manner can be stored in the soil long term [31].

Soil Carbon Co. would like to lower the cost of carbon capture to below $20 per tonne of CO_2, compared to $80 - $100 per tonne of CO_2 offered by other technologies.

4.8 Hybrid

Hybrid technologies can enhance separation efficiency and decrease the cost of separation. Examples would include membrane-PSA or membrane-distillation processes. To date, these hybrid processes have not proceeded beyond feasibility studies.

5. Carbon Capture and Storage in the Oil and Gas Industry

Compared to power production and transportation fuels, oil and gas processing results in a relatively small fraction of CO_2 emissions. However, the oil and gas industry is doing its share in reducing carbon dioxide emissions. In 2014, the Oil and Gas Climate Initiative (OGCI) was established by CEO's of twelve of the world's largest energy companies, with a mandate to work together to accelerate the reduction of greenhouse gas emissions. The actions to reduce CO_2 emissions include improving energy efficiency, minimizing flaring, upgrading facilities and co-generating electricity and heat. The Spanish oil company Repsol became the first to give a date by which it will become carbon neutral, pledging to achieve this goal by 2050. Since that time, a number of energy companies have made similar pledges.

The world's first commercial CO_2 capture storage project was started by Statoil in the North Sea Sleipner field in 1996 to avoid a large tax liability (NOK 1 million/day, around CAD $ 130,000/day). The capture and storage rate is 0.9 million tonnes of CO_2 per year. The producing field contains approximately 9% CO_2. An amine process is used to lower carbon dioxide concentration in the sales gas to 2.5%. The extracted CO_2 is stored in the Utsira Formation, a deep saline reservoir 800 – 1000 m below the sea floor.

Canada is a leader in CCS, Carbon Capture and Storage and CCUS, Carbon Capture, Utilization and Storage. In 2014, the SaskPower Boundary Dam power station became the world's first power plant with CCS. It uses a chemical absorption process based on Shell Cansolv solvents. In 2015, the largest CCS project in Canada, Shell's Quest CSS project began capturing CO_2 from a bitumen upgrader near Edmonton and injecting it into an

underground reservoir for storage – a deep saline aquifer [32]. This was the world's first commercial-scale CCS facility installed for oil sands operations.

The 240-kilometer long, $320 million CAD Alberta Carbon Trunk Line (ACTL) is the world's largest capacity pipeline for anthropogenic carbon dioxide, with the capacity of 14.6 million tonnes per year of CO_2. ACTL is owned by Wolf Midstream. It presently transports CO_2 captured at the North West Redwater Partnership Sturgeon Refinery and Nutrien's Redwater Fertilizer Plant, both located north of Fort Saskatchewan, Alberta, to an EOR application owned by Enhance Energy, near Clive, Alberta. The CO_2 from ACTL is used for enhanced oil recovery. The pipeline is expected to connect more CO_2 generating facilities and storage reservoirs in the future.

Gas Liquids Engineering Ltd. was involved in multiple segments of the ACTL system. GLE designed the Wolf Midstream main CO_2 Compressor Station located just south of the Sturgeon Refinery. The Compressor Station compresses up to 4,400 t/d of dry CO_2 from the Refinery and sends the compressed gas to the Alberta Carbon Trunk Line. GLE also designed the AG9 CO_2 Compressor / Pump Station with the capacity of 800 t/d of wet CO_2 from the Fertilizer Plant. CO_2 is compressed, dehydrated, liquefied using ammonia refrigeration and pumped into the Alberta Carbon Trunk Line. At the downstream end of the trunk line, GLE designed the Clive Oil Battery for Enhance Energy, which included multiple compressors for sequestration of the ACTL carbon dioxide into a geological formation for EOR purposes.

According to the Global CCS Institute, as of June 26, 2020, the total number of CCS facilities in various stages of development was 59, with a capture capacity of more than 127 million tonnes per annum. Combined with the newly operational Alberta Carbon Trunk Line, there are now 21 facilities in operation, 3 under construction, and 35 in various stages of development. The 21 facilities operating today capture only 1% of CO_2 needed to be captured to reach climate goals.

Out of the 21 facilities that are operating, 1 is in iron and steel production (UAE), 2 in hydrogen production (US and Canada), 1 in oil refining (Canada), 3 in fertilizer production (2 in US, one in Canada), 2 in power generation (US and Canada), 10 in natural gas processing (4 in US, 2 in Norway, 1 in Australia, Brazil, China and Saudi Arabia), 1 in synthetic fuels production (US) and 1 in ethanol production (US). Ten of the operating facilities are located in the United States, four in Canada, one in China, two in Norway, and one each in Australia, Brazil, Saudi Arabia and United Arab Emirates. [33].

Table 6 summarizes large-scale CCS facilities by country:

	Early Development	Advanced Development	Construction	Operating	Total
United States	5	12	1	10	28
Canada	-	-	-	4	4
China	3	-	2	1	6
Great Britain	7	-	-	-	7
Norway	-	1	-	2	3
Australia	1	1	-	1	3
UAE	-	1	-	1	2
Netherlands	1	1	-	-	2
Brazil	-	-	-	1	1
Saudi Arabia	-	-	-	1	1
Ireland	1	-	-	-	1
South Korea	1	-	-	-	1
Total	**19**	**16**	**3**	**21**	**59**

Table 6 Large-Scale CCS Facilities by Country

The Canadian large-scale CCS operating facilities include:

- North West Redwater Partnership's Sturgeon Refinery (since 2020)
- Nutrien's Fertilizer Plant (since 2020)
- Boundary Dam Carbon Capture and Storage – coal-fired power generation (since 2014)
- Quest – three SMR's at the Scotford Upgrader (since 2015)

The US National Energy Technology Laboratory (NETL) reported that North America has enough storage capacity for more than 900 years' worth of carbon dioxide at its current production rates. Figure 15 lists all 21 large scale carbon capture and storage facilities and the year of startup [33], [34].

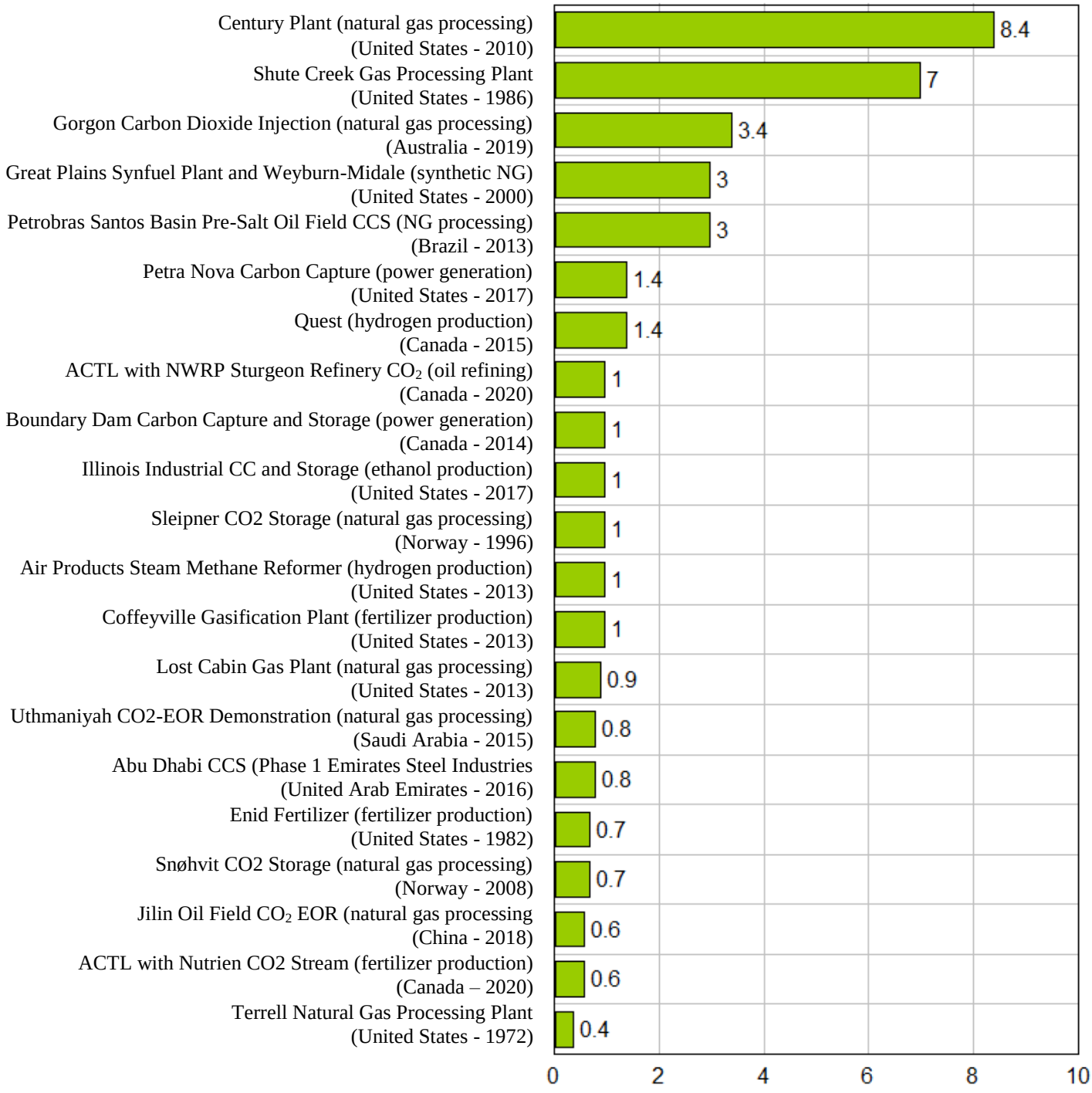


Figure 15 Capacity of Operational Large-Scale Carbon Capture and Storage Facilities Worldwide in Million Tonnes CO_2 per Year

The following technologies in the oil and gas industry contribute to CO_2 recovering or reducing CO_2 emissions, or both:

- Two-stage physical solvent treating
- Bulk fractionation
- Acid gas enrichment
- Sulfur plant tail gas incinerators
- Acid gas injection

5.1 Two-Stage Physical Solvent Treating

Physical solvent treating is most effective for treating gas with CO_2 concentration above10 mol% and below 5% of hydrocarbons higher than ethane (C_{3+}) because of inherently high solubility of heavy hydrocarbons in physical solvents. Two stage physical solvent units are used for acid gas treating, recovery of CO_2 for EOR and enriching acid gas quality feedstock to sulfur plants [35]. A two-stage physical solvent treating is shown in Figure 16.

For CO_2 removal only, the second stage design is required. The largest facility using a two-stage SELEXOL™ solvent is the Shute Creek Gas Processing Plant in La Barge, Wyoming, in operation since 1986. It treats 700 MMSCF/d of natural gas containing 66% CO_2 and 5% H_2S. The volume of CO_2 captured in this facility is 7 million tonnes per year, which is used in enhanced oil recovery in Wyoming and Colorado.

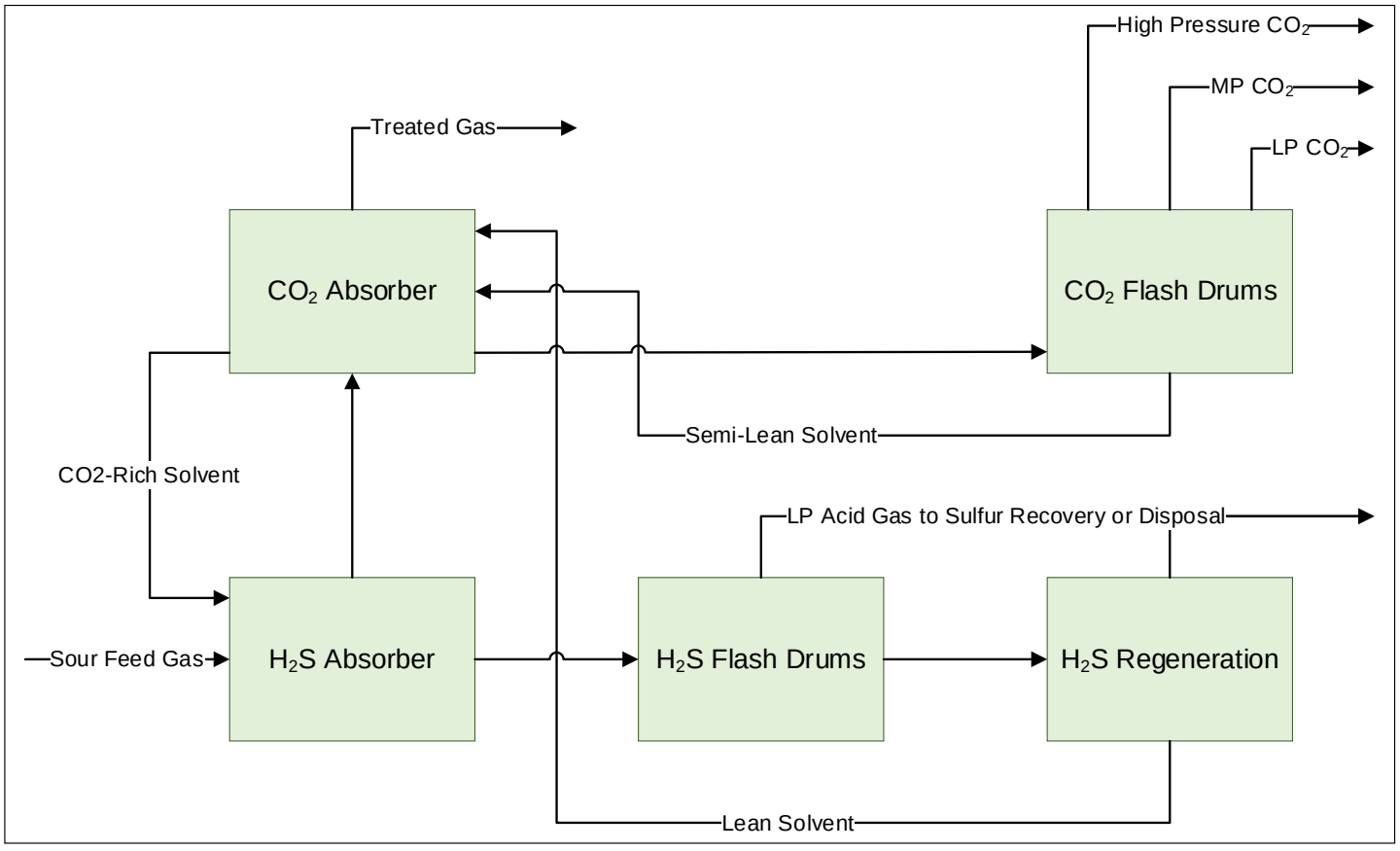


Figure 16 A Block Flow Diagram of a Two-Stage Physical Solvent Treating System

5.2 Bulk Fractionation

Bulk fractionation or distillation can be used for a feed gas with high concentration of CO_2 and H_2S. This process can reduce the emissions of CO_2 by at least 80%.

Bulk fractionation columns operate between 3450 kPag and 5500 kPag and between -35°C and -60°C at the top of the column and between -5°C and 50°C at the bottom of the column. Distillation of CO_2 from feed gas is limited to about 15% CO_2 in the fractionation column overhead vapor because of CO_2 solidification in the column. The overhead vapor is further processed to separate the rest of CO_2 and H_2S from methane, usually using a physical solvent.

Bulk fractionation has an advantage over solvent processes when the acid gas is injected into a reservoir. In bulk fractionation, acid gas is already liquid at 3450 – 5500 kPag and requires less energy to pump it underground. Solvent processes produce acid gas at a pressure close to atmospheric and much more energy is needed for injection.

Since heavier hydrocarbons are soluble in physical solvents, bulk fractionation should be used for lean feed gas, otherwise it may become necessary to recover natural gas liquids upstream of bulk fractionation.

A block flow diagram of the bulk fractionation process is shown in Figure 17.

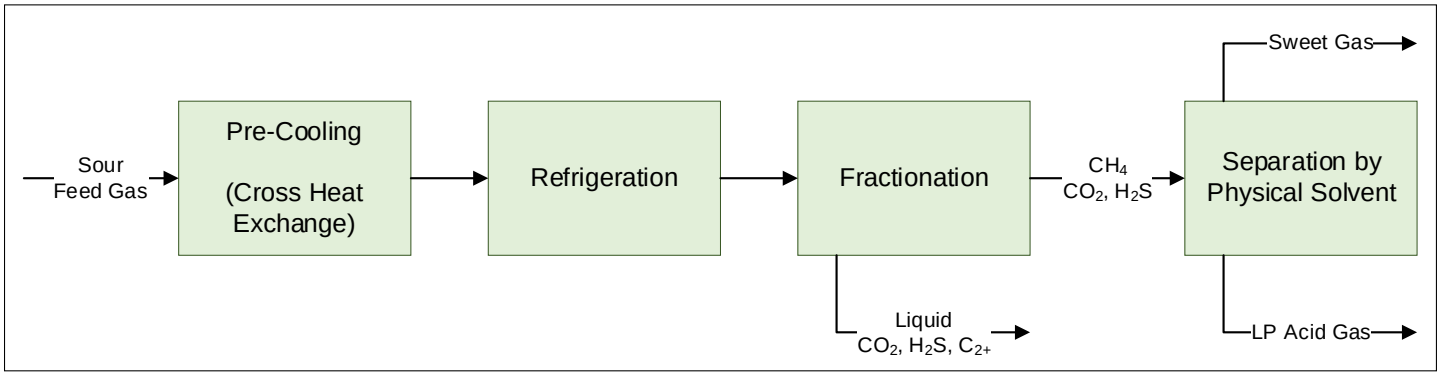


Figure 17 A Block Flow Diagram of a Bulk Fractionation Followed by Physical Solvent Process.

5.3 Acid Gas Enrichment

Acid gas enrichment is a process of increasing the concentration of H_2S in the feed to a Claus furnace for the purpose of increasing the Claus thermal reactor temperature and stabilizing the burner flame. The feed to the Claus sulfur recovery plant is treated with a solvent selective for H_2S, like MDEA or Flexsorb. The enriched regeneration offgas is the feed to the Claus furnace and the treated gas containing CO_2 is vented to the atmosphere. Even if the treated gas is further treated in a tail gas unit, CO_2 is released to the atmosphere through the incinerator which often requires fuel gas (thus generating additional CO_2) to ensure sufficient destruction temperatures. Instead of venting CO_2 to the atmosphere, it can be captured for sequestration.

5.4 Sulfur Plant Tail Gas Incinerators

Incinerators oxidize residual H_2S from the sulfur plants. They are located downstream of tail gas cleanup units and are of thermal type. They operate at 650°C - 850°C to ensure complete oxidation and destruction of sulfur compounds. The residence time of the tail gas in the thermal incinerator is approximately 1 s. A waste heat boiler recovers some of the heat of combustion. The feed to the thermal incinerator is composed mostly of nitrogen and carbon dioxide which have zero heating value, so to incinerate sulfur species, fuel gas is required. However, fuel gas also contributes to CO_2 emissions when burned.

To lower the fuel gas consumption and reduce CO_2 emissions, catalytic oxidation of sulfur compounds is used, which takes place at 300°C to 400°C. The catalyst is usually made of a mixture of platinum and palladium. The residence time for the tail gas in the catalytic incinerator is less than 0.5 s. This is an advantage of catalytic

incinerators over thermal incinerators because the combustion reaction equipment is smaller. A disadvantage of this process is that these temperatures are too low to recover the waste heat for steam generation. If steam is needed at the plant where the catalytic incinerator is installed, fuel may have to be burned to generate steam and the overall CO_2 emission reduction may be reduced or counteracted entirely. Yet another disadvantage of catalytic incinerators is that CS_2 (carbon disulfide) and COS (carbonyl sulfide) are only partially oxidized and CO is not oxidized to CO_2.

A simplified catalytic incineration of tail gas is depicted in Figure 18.

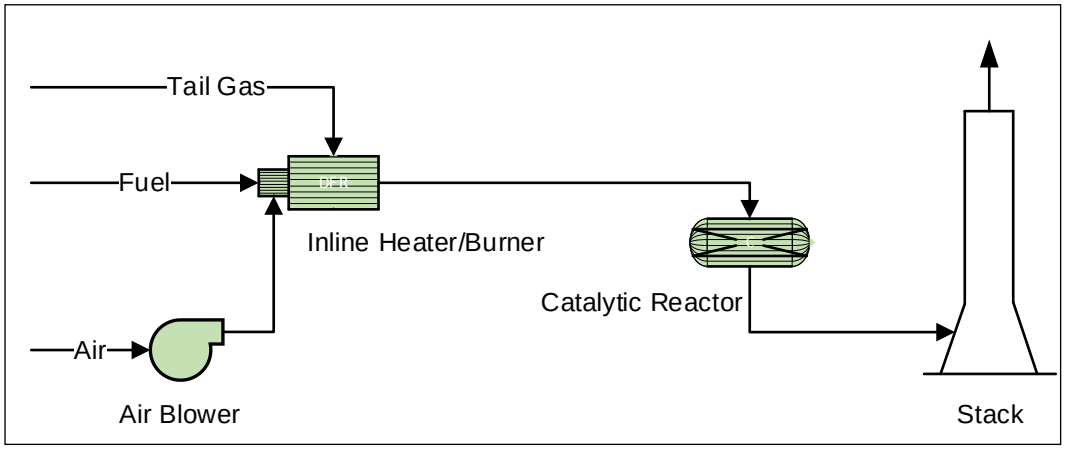


Figure 18 Catalytic Incineration of Tail Gas from a Sulfur Recovery Unit

5.5 Acid Gas Injection

Acid gas injection (AGI) is a method of disposing of unwanted mixtures of CO_2 and H_2S into a subsurface formation such as a depleted reservoir or an aquifer. The process involves compressing and, if need be, also pumping the compressed dense phase acid gas into a disposal well. The acid gas often contains small amounts of other contaminant like mercaptans and lower molecular weight hydrocarbons, predominantly methane. It is usually saturated with water, which is the byproduct of the sweetening of sour gas.

The acid gas is usually compressed from 50 – 100 kPag to 7,000 – 18,000 kPag, using three-stage to five-stage compressors, but the actual compressor discharge pressure depends on the required wellhead injection pressure. The wellhead injection pressure in turn depends on the reservoir pressure and the depth of the reservoir. A computer program for the calculation of the wellhead injection pressure was developed by Dr. John J. Carrol of Gas Liquids Engineering called GLEWPro. The program estimates the phase, property, and flowing profiles along the wellbore. GLEWPro can handle the phase changes in the wellbore, the heat transfer between the stream and the formation, and the flowing behavior from the wellhead to the reservoir.

A 5-stage acid gas compression scheme is shown in Figure 19. It is an example simulation using ProMax, a software offered by Bryan Research and Engineering, Bryan, Texas. The compressed gas after the third stage of compression is sent to a TEG dehydration unit and the dehydrated gas is fed to the suction of the fourth stage. The dense phase fluid after the fifth stage of compression is pumped to the required wellhead injection pressure.

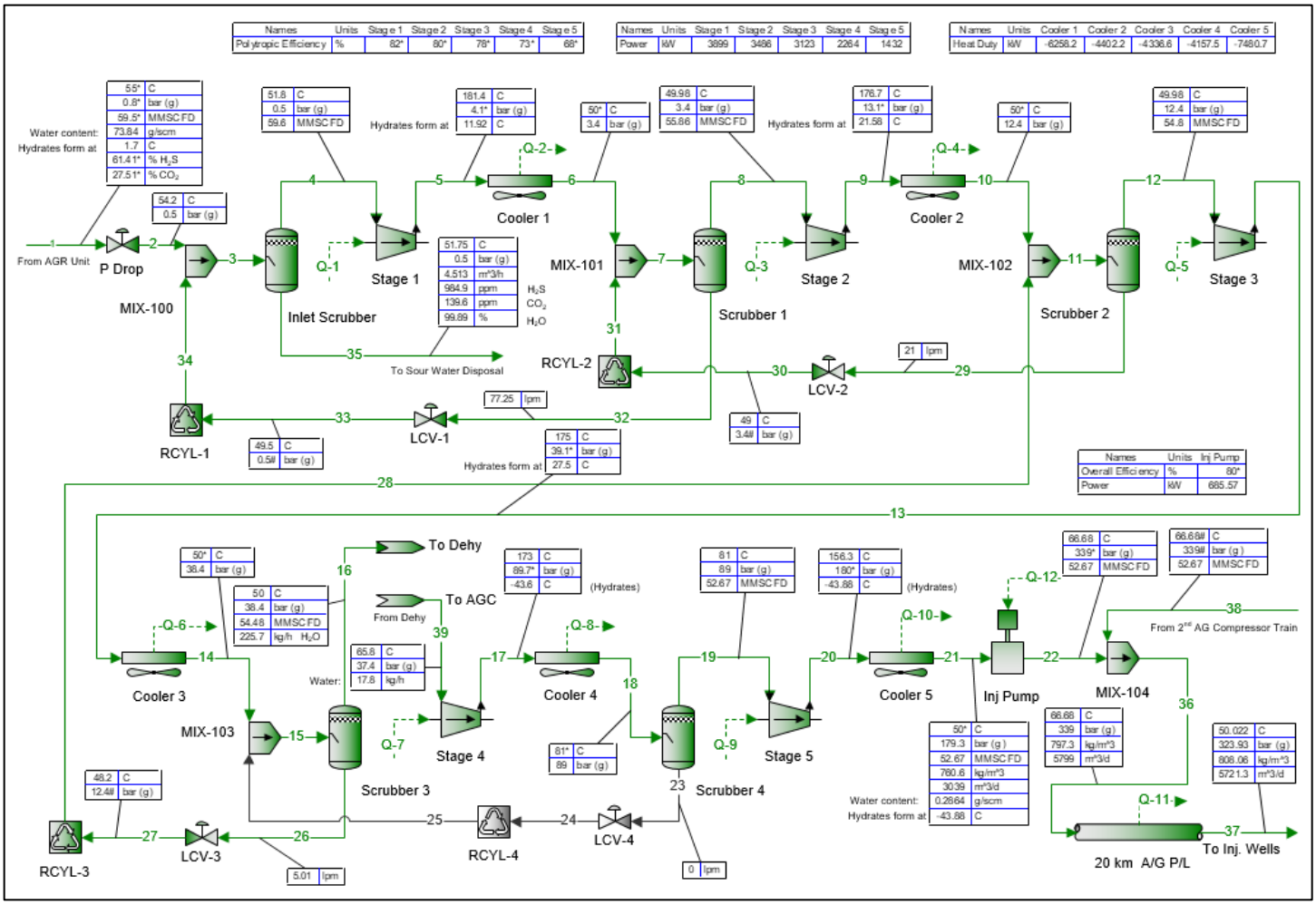


Figure 19 A Five-Stage Acid Gas Compression with Dehydration by Compression and Cooling Only

The acid gas may have to be dehydrated prior to injection to prevent corrosion of the injection pipeline and hydrate formation or to meet a spec outlined by a 3rd party custody transfer pipeline such as the ACTL in Alberta. Dehydration may be achieved by compression and cooling alone, or by using TEG dehydration, refrigeration, mole sieves or the DexPro™ technology, a thermodynamic phase separation, offered by DexPro Canada. Dehydration of acid gas is usually done after the second to last compressor stage but this requires optimization and can vary depending on composition, pressures and system requirements.

DexPro is fully integrated with the compressor for optimal water removal. The advantages of DexPro over TEG dehydration is lower capital cost, lower operating cost, small physical footprint, no chemicals, no emissions, and high turndown [36].

A knowledge of the water content of carbon dioxide and acid gas in general is essential for the proper design of an acid gas injection scheme. There are a number of methods for estimating the water content of acid gas, but the one universally recognized by the industry as being amongst the most accurate software for equilibrium water content of sour and acid gas is Aqualibrium, developed by Dr. John J. Carroll [37].

6. Carbon Utilization and Storage

Once carbon dioxide has been captured (separated), it can be either utilized, a combined process known as CCU, Carbon Capture and Utilization, or it can be stored, for which the acronym CCS, Carbon Capture and Storage, is used.

6.1 Carbon Utilization

The captured CO_2 can be used for enhanced oil recovery or it can be turned into useful products, although it can be challenging because CO_2 is thermodynamically stable (not very reactive). Captured CO_2 as a feedstock can be used in the production of carbonated drinks, fire retardants, urea, polymers, and other chemicals. CO_2 can also be used in water treatment or can be used as a technological fluid in air-conditioning or dry washing. However, these industries utilize only 1% of the CO_2 emitted to the atmosphere. In addition, turning captured CO_2 into fuels and chemicals are largely technologies on a laboratory scale, far from being commercialized. Figure 20 depicts the carbon utilization pathways.

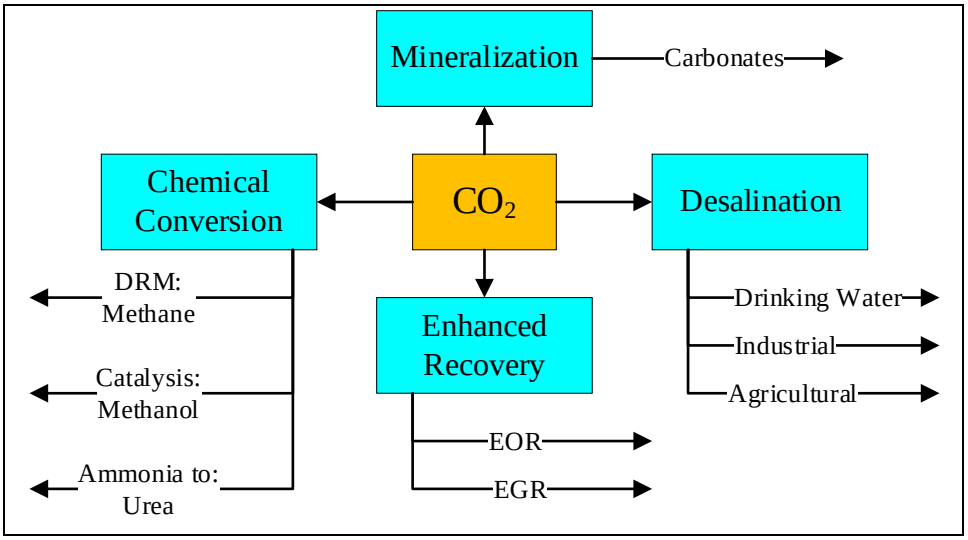


Figure 20 CO_2 Utilization pathways [38]

- **Enhanced Oil Recovery**

  Enhanced oil recovery (EOR), also known as improved oil recovery (IOR), is a process of injecting carbon dioxide into a depleted oil bearing reservoir to increase the pressure in the reservoir and decrease the oil viscosity, thus making it easier to pump the oil to the surface.

  CO_2 is very soluble in crude oils at reservoir pressures. CO_2 is also much more soluble in water than hydrocarbons are. CO_2 diffuses through water in the reservoir and swells the bypassed oil until the oil becomes mobile. CO_2 is then produced together with the oil, separated and re-injected into the reservoir to repeat the process.

  Typically, EOR increases oil production by 10 – 15% and extends the life of an oil field by 20 to 40 years. Most of the CO_2 for EOR come from natural sources but CO_2 captured from flue gas or industrial effluents is also used. CO_2 can also be used for enhanced gas recovery (EGR). Still, EOR constitutes only 3% of CO_2 utilization.

  There are many benefits of EOR. It is a proven and safe technology, it reduces the greenhouse gas emissions, it revitalizes and extends the life of mature oil reservoirs, and it turns a waste CO_2 into a value-adding commodity.

- **Production of Fuels**

CO_2 can be converted into syngas, hydrocarbons, and methanol. Since carbon dioxide is thermodynamically stable (standard Gibbs free energy of formation = -394.4 kJ/mol; see the Annex - chemical thermodynamics refresher at the end of the paper), most conversion reactions are endothermic and require a lot of energy (heat) and reactants with high Gibbs free energy, like methane or hydrogen, as well as the use of catalysts. The two most important methods of CO_2 conversion to fuels are DRM (dry reforming of methane) and hydrogenation.

Dry reforming of methane to syngas can be represented by equation (13). The development of the active catalyst for large scale industrial applications is still ongoing. At lower reaction temperatures, carbon deposits on the surface of the catalysts and deactivates it.

$$CO_2 + CH_4 \overset{Ni}{\rightarrow} 2H_2 + 2CO \quad \Delta_R^0 = +247.38\ kJ/\text{mol } CO_2 \tag{13}$$

The above reaction provides building blocks for the production of hydrocarbons by the Fischer-Tropsch process, operated at elevated temperatures and pressures, in presence of a catalyst:

$$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \tag{14}$$

where n = 10 to 20 and most of the alkanes produced are straight chain.

Methanol is commercially produced from synthesis gas (CO + CO_2 + H_2) using $CuO/ZnO/Al_2O_3$ catalysts. Methanol can also be produced by direct hydrogenation of CO_2, represented by equation (15). The conversion takes place at moderate temperatures and pressures and the presence of a catalyst, e.g. Cu-Zn, or In_2O_3.

$$CO_2 + 3H_2 \xrightarrow{In_2O_3} CH_3OH + H_2O \tag{15}$$

The challenge of this technology is the production of hydrogen and clean CO_2 from waste gas. Hydrogen can be produced by electrolysis of water, pyrolysis of biomass, or steam/oxygen gasification processes and reforming of biomass derived products [39]. CO_2 can be captured from any industrial source or from air.

- **Production of Chemicals**

Carbon dioxide can be used as a feedstock for the production of chemicals like urea, carbonates (inorganic and organic), polyurethane, acrylic acid, formic acid, salicylic acid etc. [8].

By far, the largest production of chemicals from CO_2 is urea.

$$CO_2 + 2NH_3 \rightarrow (NH_2)_2CO + H_2O \tag{16}$$

Most of the CO_2 used to produce urea comes from the steam reforming process to produce the required hydrogen for ammonia synthesis. For that reason, urea manufacturing is usually directly coupled to the ammonia synthesis facility.

However, urea production cannot be called carbon capture because, when urea is applied to the soil, an equal amount of CO_2 is emitted to the atmosphere [40].

A schematic representation of an ammonia plant, showing the two products that become feedstocks for the production of urea (CO_2 and ammonia) is shown in Figure 21.

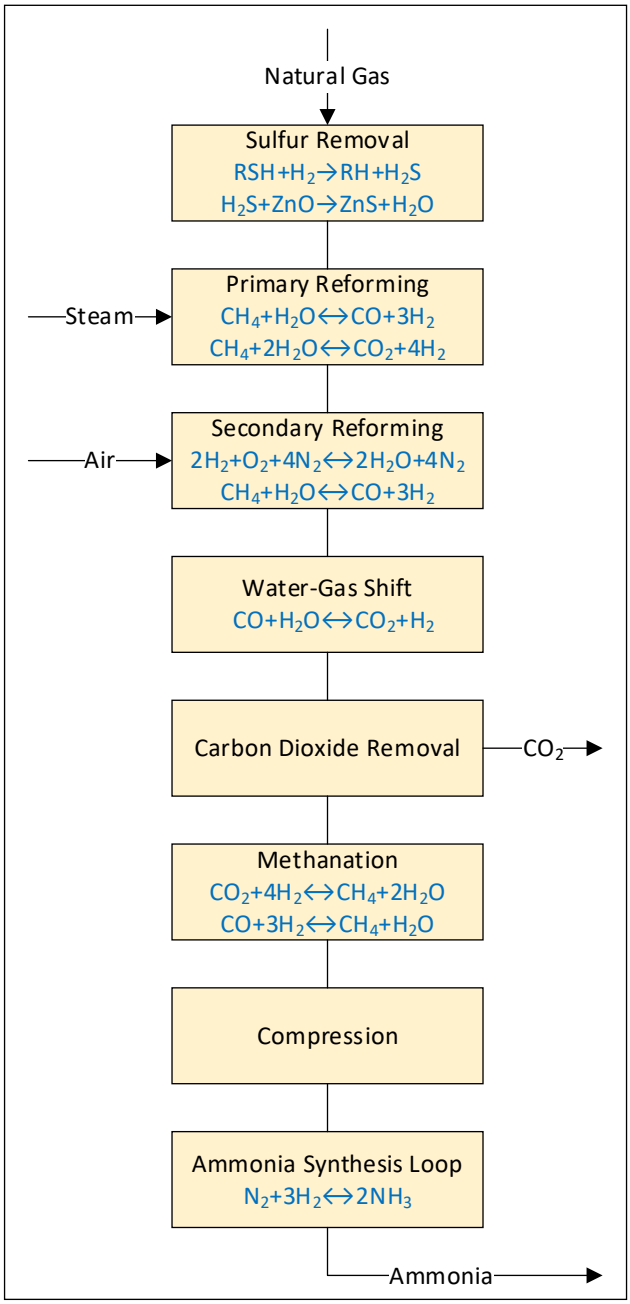


Figure 21 Schematic Representation of an Ammonia Plant [8]

- **Desalination**

  Captured CO_2 can be used to remove total dissolved solids (TDS) from brackish water like sea water or brine. There are different processes under investigation. One of them uses ammonia and carbon dioxide in forward osmosis. Another technique is the formation of CO_2 hydrates at low temperature and high pressure to separate water from salt and then decomposing the hydrates by returning the pressure and pressure to ambient thus separating CO_2 from water. CO_2 can then be recycled and re-used. These technologies require further refinements to be competitive with the established technologies like distillation or reverse osmosis.

- **Electrolysis of CO_2**

  CO_2 can be converted to carbon monoxide (CO) by means of electrolysis. CO is an important building block for the chemical industry (production of acetic acid, formic acid, acrylic acid, phosgene etc.). There are many electrolytic technologies being pursued. The three most mature are solid oxide electrolysis, molten carbonate electrolysis and low-temperature electrolysis [41].

6.2 Carbon Storage

Capture carbon dioxide can be stored in geological location like depleted oil and natural gas fields, aquifers, or un-minable coal seams. It can also be stored in enclosed basins on the deep ocean floor.

- **Government Regulations Regarding Carbon Storage**

  In Alberta, existing oil and gas regulations cover many parts of carbon capture and storage (CCS). However, a few acts and regulations have been introduced specifically for CCS, along with some amendments to the *Mining and Minerals Act*. The *Carbon Capture and Storage Statutes Amendment Act*, passed in 2010, makes it mandatory for CCS operators to contribute to the Post-Closure Stewardship Fund, which will be used for ongoing monitoring of sites and maintenance/remediation where required. Money from this fund will only be used after the provincial government takes over the leases for CCS sites where CO_2 injection operations have ceased. The *Carbon Sequestration Tenure Regulation*, passed in 2011, created the process through which CCS operators can acquire permits for evaluations of potential CO_2 sequestration sites, as well as obtain leases for suitable storage sites. However, the regulation also specifies the criteria required for MMV (Monitoring, Measurement, and Verification) and closure plan approval, and stipulates that pore space tenure can only be granted for CO_2 sequestration depths greater than 1 km.

  A *Regulatory Framework Assessment* was undertaken by the Government of Alberta from 2011 to 2013, with the purpose being to review the existing carbon capture and storage (CCS) regulations, identify any issues or gaps, and implement any findings or recommendations for improvement from the review. Topics covered in the review included site selection; monitoring, measurement, and verification (MMV); CO_2 transportation and composition; well construction, and CO_2 classification. The assessment ultimately identified more than 70 conclusions and recommendations for improvement in the CCS regulations, including development of CCS-specific emergency planning zones (EPZs), continuous tracking of the CO_2 stream composition, and research into leak detection methods for CO_2 pipelines.

  In British Columbia, the Ministry of Natural Gas Development undertook a similar regulatory framework assessment. A draft of the CCS regulatory policy was submitted for public consultation and comments in the spring of 2014. The comments received led to the creation and passage of the *Natural Gas Development Statutes Amendment Act* in the fall of 2015, which included a round of amendments to both the Petroleum and Natural Gas Act and the Oil and Gas Activities Act. Both the ministry and the BC Oil and Gas Commission (OGC) undertake implementation of the CCS regulatory policy.

- **Geologic Storage of CO_2**

  Depleted oil and natural gas fields are preferred locations for storing captured CO_2 because of known geology that ensures fluid retention. Such locations have impermeable cap rocks that prevent CO_2 from migrating to the surface.

Aquifers are underground layers of rock filled with saline water. Their CO_2 retention capacity and suitability has to be determined through geologic survey. What is required of a good candidate for CO_2 storage is the presence of a low permeability geological cap rock that will prevent CO_2 from leaking to the strata above and possibly to the atmosphere.

Injection of CO_2 into a coal seam, known as ERCBM – Enhanced Recovery of Coal Bed Methane, displaces methane from the coal surface. A beneficial side effect of CO_2 storage could be methane production and the revenue from methane can partially offset the cost of CO_2 capture and storage.

To store CO_2 in deep ocean waters, it would have to be pumped to a depth where the density of the CO_2 is higher than that of ocean water. At 2°C, liquid CO_2 and ocean water have the same density at 2,715 m, At 2°C and the depth of 6,500 m, the density of CO_2 is 1.13 kg/L and ocean water has the density of 1.06 kg/L – the liquid CO_2 would sink to the bottom of the ocean. The good locations are enclosed basins like [42]:

- The Indonesian Sunda Trench, which has a length of 3,200 km and a maximum depth of 7,290 m. The trench has the capacity to store 19,000 gigatonnes of liquid CO_2, equivalent to 575 years of global CO_2 production from burning fuel (33 gigatonnes in 2017).
- The Puerto Rico Trench, 800 km long and 8,376 m deep (maximum). The trench has the capacity to store 24,000 gigatonnes of liquid CO_2.
- The Japanese Ryukyu Trench, with a length of 1398 km and a maximum depth of 7460 m. The trench has the capacity to store all the CO_2 captured in China at 3 gigatonnes per year for over 200 years.

Table 7 provides estimates for global CO_2 storage capacity. The estimates are collected from different sources.

Storage Option	**Capacity [gigatonnes CO_2]**
Depleted oil and gas fields	675 - 920
Aquifers (deep saline formations)	1,000 - 10,000
Un-minable coal seams	15 - 200
Deep ocean	> 4,000

Table 7 Global CO_2 storage capacity

According to a new study published by Energy & Environmental Science, a capacity of 2,700 gigatonnes should be sufficient to sustain peak injection rates of 40 – Gt of CO_2 per year to meet the climate targets. The estimates of prospective storage capacity available is 10,000 Gt [43].

A few international examples of CCS and CO_2 EOR projects:

- Gorgon CO_2 Injection Project, the site of the world's largest commercial CO_2 injection undertaking, is operated by Chevron Australia in joint venture with ExxonMobil. This project is part of the Gorgon Project situated on the Barrow Island in the Indian Ocean, off the coast of Western Australia. Natural gas from the Gorgon field containing 14% CO_2, and from the Jans-Io field, containing less than 1% CO_2, is used for LNG production. Carbon dioxide is removed by a proprietary activated MDEA solvent, compressed, and injected into the Dupuy Formation at a depth of 2300 m beneath Barrow Island. The formation is a sandstone saturated with brackish water. The injection project started in August 2019. The project plans to inject 3.4 to 4 million tonnes of CO_2 per year.

- Shute Creek Gas Processing Plant near La Barge, Wyoming, owned by ExxonMobil, in operation since 1986. It treats 700 MMSCF/d of natural gas containing 66% CO_2 and 5% H_2S. The volume of CO_2 captured in this facility is 7 million tonnes per year (365 MMSCF/d), which is used in enhanced oil recovery in Wyoming and Colorado. The carbon capture technology used at Shute Creek is the Controlled Freeze Zone (CFZ), a single step cryogenic separation process that freezes out CO_2 and then melts it.
- Sleipner CO_2 Storage, the world's first commercial CO_2 capture storage project, started by Statoil in the North Sea Sleipner field in 1996 to minimize taxes (NOK 1 million/day, around CAD $ 130,000/day). The capture and storage rate is 0.85 million tonnes of CO_2 per year. The field contains 9% CO_2. An amine process is used (original design: aMDEA) to lower carbon dioxide concentration in the sales gas to 2.5%. The CO_2 is stored in Utsira Formation, a deep saline reservoir, 800 – 1100 m below the sea floor. The injected gas is 98% CO_2.

Examples of CCS in Canada:

- Boundary Dam Power Station Unit 3 (BD3) Project. It is a SaskPower's coal-fired power station near Estevan, Saskatchewan producing 115 MW of power. A refurbishment program to retrofit CO_2 capture facility with a capture capacity of 1 million tonnes/year was finished in October 2014. Most of the captured CO_2 is transported via pipeline and used for EOR at the Weyburn Oil Unit. A portion of the captured CO_2 is also transported via pipeline to the Aquistore Project for geological storage in a 3.4 km deep saline reservoir. This power station became the first in the world to successfully use CCS technology. It is capable of reducing CO_2 emissions by 90%. Shell's Cansolv amine capture system consisting of Cansolv DS® solvent (an aqueous diamine) and Cansolv DC-103® solvent (an activated tertiary amine) was installed at SaskPower's BD3 for the removal of SO_2 and CO_2 from the flue gas. SO_2 is a feedstock for the production of sulfuric acid.
- Quest CCS Project, located in Scotford near Fort Saskatchewan, Alberta, started in November 2015. CO_2 is captured from three steam methane reformers at the Scotford Upgrader which processes extra-heavy crude oil from oil sands into synthetic crude oils. The upgrader is owned by Athabasca Oil Sands Project. Quest has the capacity to capture approximately 1 million tonnes/year of CO_2 (52 MMSCF/d). The captured CO_2 is transported through a pipeline for geological storage.
- Weyburn-Midale CO_2 Project, located in Midale, Saskatchewan. In 2008 it was the largest capture and storage project in the world (now, it is the Century Plant in the United States, with the capacity of 8.4 million tonnes/y of CO_2. The Great Plains Synfuels Plant in Beulah, North Dakota, produces synthetic natural gas (SNG) from lignite coal, the only coal-to-SNG facility in the United States. Rectisol is used in pre-combustion capture of CO_2 generated during the gasification of the coal. The capture capacity of the Rectisol unit is approximately 3 million tonnes of CO_2 per year. The captured CO_2 (95.5% pure) is then transported via a 330-km long pipeline to the Weyburn Oil Unit and the Midale Oil Unit in Saskatchewan for use in EOR.

- **<u>Non-Geologic Storage of CO_2</u>**

CO_2 can be stored by mineral carbonation, i.e. by producing carbonates. It can be done in situ (in underground formations) or ex situ (CO_2 reacting with mineral feedstock above ground, near the source of emission and far from potential geologic storage sites).

Mineral carbonation in situ enables the storage of CO_2 in areas not considered feasible previously, like injecting CO_2 into reactive rock, such as mafic rock, igneous rock rich in magnesium and iron, like basalt or peridotite (from **ma**gnesium + **f**errum, Latin for iron). There is enough basalt rock to store more CO_2 than generated by human activity. This type of storage is safer than geological storage (in sedimentary rock) because CO_2 is permanently (chemically) bound to the rock.

Equations (16) and (17) are the overall reactions of the components of mafic rocks with CO_2.

$$Mg_2SiO_4 + 2CO_2 + 2H_2O \rightarrow 2MgCO_3 + H_4SiO_4 \quad (16)$$

$$Fe_2SiO_4 + 2CO_2 + 2H_2O \rightarrow 2FeCO_3 + H_4SiO_4 \quad (17)$$

Ex situ mineralization is an above ground operation that involves the reaction of CO_2 with miscellaneous feedstock like steel slug, fly ash, mine tailings, or ground reactive rock [44]. Ex situ mineral carbonation is being explored in many parts of the world. For example, Mineral Carbonation International operates a mineral carbonation pilot plant in Newcastle, New South Wales, Australia. They mine serpentinite, a metamorphic rock rich in magnesium (an alkaline earth silicate mineral), grind it, activate thermally, and contact with waste CO_2 in a reactor. The product is magnesium carbonate that could be used to manufacture cement, plasterboard and other building products.

7. Pros and Cons of Carbon Capture

- **Pros**

Use in EOR: the captured CO_2 can be used for EOR to increase oil production from mature field.

Tax credits: governments offer tax credits for carbon capture projects. For example, Section 45Q of the US tax code provides a tax credit for carbon capture projects that securely store the captured CO_2 in geological formations such as oil fields or saline formations or beneficially use captured CO_2 as a feedstock to produce fuels, chemicals and products such as concrete in a way that results in emissions reductions. A paper was presented at the 2020 Laurance Reid Gas Conditioning Conference discussing the current U.S. regulatory environment for CO_2 emissions and economic factors to be considered when deciding whether it is economically justifiable to capture CO_2 emissions [45].

Reduction of greenhouse gas emissions.

Reformation into “carbon neutral” or “net zero” fuels.

- **Cons**

One of the main reasons that carbon capture and storage has not been widely adopted yet is due to the complexity of the technology and high costs of operating the equipment required to capture the carbon dioxide. A typical cost of carbon capture is 80 – 100 USD per tonne of CO_2.

Most anthropogenic CO_2 is produced at a pressure close to atmospheric, like acid gas recovery unit regenerators or ethanol fermenters, so inlet compression is required to send the CO_2 containing gas to a capture facility. In most cases the capture facility uses an amine solvent for CO_2 recovery and energy is required to regenerate the amine. Then the purified CO_2 stream needs to be compressed and dehydrated to send it to a disposal well or for enhanced oil recovery. A significant amount of energy is required for carbon capture.

On the other hand, the CCS technologies can compete with renewable power generation on the basis of Levelized Cost of Electricity (LCoE), being defined as:

$$LCoE = \frac{\sum_t^T \left((Investment_t + O\&M_t + Fuel_t + Decommissioning_t) \cdot (1+r)^{-t} \right)}{\sum_t (Electricity_t \cdot (1+r)^{-t})} \quad (18)$$

where: r – interest rate
t – year
T – power plant economic lifetime

8. GLE Experience with Carbon Capture and Storage Technologies

Gas Liquids Engineering is an industry leader in carbon capture and sequestration, with more acid gas sequestration projects than any other engineering firm. GLE has a thorough understanding of the unique properties of carbon dioxide.

With over 30 years of successful CO_2 projects, GLE's experience in the specialized requirements of CO_2 systems has made us uniquely skilled in the processes, equipment selection, and specifications related to these projects. This experience also led to the development of the lowest cost dehydration process available for CO_2, now used globally in both enhanced oil recovery (EOR) and CO_2 pipeline operations.

GLE has additionally carried out CO_2 purification projects and some of the largest carbon sequestration projects in Canada, including all facilities connected to the Alberta Carbon Trunk Line (ACTL), Alberta's primary pipeline system for CO_2 sequestration. In early 2020, GLE completed engineering on the largest CO_2 EOR project carried out in Canada since 2005, which is currently in operation.

Some areas of CO_2 projects for which GLE has comprehensive capabilities include:

- CO_2 thermodynamics and phase behaviour
- CO_2 injection, disposal, or sequestration
- CO_2 distillation and purification
- CO_2 dehydration
- Removal of CO_2 from natural gas
- Removal of CO_2 from flue gas
- EOR projects using CO_2
- CO_2 compression facilities
- CO_2 pumping facilities
- CO_2 truck-in / truck-out terminals
- CO_2 Storage
- CO_2 pipeline design
- Supercritical CO_2 equipment specifications
- Metallurgy requirements for CO_2 / water acid forming systems

Glossary of Acronyms

ACTL	Aberta Carbon Trunk Line
AGI	Acid Gas Injection
BECCS	Bio-energy with Carbon Capture and Storage

CLC	Chemical Looping Combustion
CCS	Carbon Capture and Storage
CCUS	Carbon Capture, Utilization and Storage
DAC	Direct Air Capture
DSR	Direct Separation Reactor
EOR	Enhanced Oil Recovery
EPZ	Emergency Planning Zone
ERCBM	Enhanced Recovery of Coal Bed Methane
GHG	Greenhouse Gas
IGCC	Integrated Gasification Combined Cycle
Ils	Ionic Liquids
LEILAC	Low Emissions Intensity Lime and Cement
MMV	Monitoring, Measurement, and Verification
MTR	Membrane Technology and Research
NETL	National Energy Technology Laboratory
OGC	Oil and Gas Commission (in British Columbia)
OGCI	Oil and Gas Climate Initiative
PAH	Polycyclic Aromatic Hydrocarbons
PSA	Pressure Swing Adsorption
SMR	Steam Methane Reforming
SPP	Steam Power Plant
TDS	Total Dissolved Solids
TSA	Temperature Swing Adsorption
VSA	Vacuum Swing Adsorption
WGS	Water Gas Shift
UNFCCC	United Nations Framework Convention on Climate Change

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Skeptical Science, https://skepticalscience.com/

Technology Centre Mongstad, https://tcmda.com

The Carbon Sense Coalition, http://carbon-sense.com/

The Intergovernmental Panel on Climate Change (IPCC), https://www.ipcc.ch/

United States Department of Energy Carbon Storage Program, http://www.netl.doe.gov/coal/carbon-storage

Conferences related to Carbon Capture and Storage:

International Conference on Carbon Dioxide Capture and Storage Technologies

International Conference on Carbon Dioxide Utilization and Reduction

International Conference on Carbon Dioxide Utilization and Sustainability (ICCDUS)

International Conference on Carbon Dioxide Utilization and Sustainable Development (CCDUSD)

International Conference on Fossil and Renewable Energy

International Conference on Geological Sequestration of Carbon Dioxide

International Conference on Greenhouse Gas Control Technologies

Annex

Why is CO_2 a stable molecule?

A compound with a negative free energy of formation is stable – a chemical thermodynamics refresher

When a chemical reaction occurs, heat is either evolved or absorbed from the surroundings – the enthalpy of the system changes.

The enthalpy change for any reaction is equal to the enthalpies of formation of the substances on the right side of the chemical equations minus the enthalpy of formation of the substances on the left side of the chemical equation.

A criterion for spontaneous change is that energy should decrease (negative ΔH, an exothermic reaction). Systems tend to go to the most probable state (most disordered molecular arrangement – highest entropy). Natural processes resulting in a decrease of energy and processes resulting in an increase in entropy are favored.

Total energy of a system = free energy G + unavailable energy (T·S). Free energy G = H – T·S (due to the disordering influence of temperature, not all the energy H in a system is available for extraction)

For changes in free energy:

$\Delta G = \Delta H - \Delta(T \cdot S)$

For an isothermal change, $\Delta G = \Delta H - T \cdot \Delta S$ (at constant temperature and pressure a chemical reaction or some physical change can occur spontaneously only if it is accompanied by a decrease of free energy; for a spontaneous process ΔG should be negative. A system at equilibrium has no tendency to change, it represents a state where the free energy has reached a minimum.

Now let's take a look at the combustion of methane:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H_R^0 = -890.24\ kJ/mol\ ;\ \Delta G_R^0 = -817.8\ kJ/mol \tag{17}$$

This is an exothermic reaction (negative ΔH) and a spontaneous reaction (negative ΔG). The reaction in the opposite direction (reaction of CO_2 with water) would have the same values of ΔH and ΔG but with an opposite sign – the reaction would be endothermic and non-spontaneous.

The enthalpy and free energy changes for the above reactions were calculated using the values from Table 5:

Another example, carbon dioxide methanation, also known as the Sabatier reaction, for which Paul Sabatier, a French chemist, received the Nobel prize in chemistry in 1912, can be represented by the following equation:

$$CO_2 + 4H_2 \xrightarrow{Ni,\ 400°C} CH_4 + 2H_2O \quad \Delta H_R^0 = -252.96\ kJ/mol\ ;\ \Delta G_R^0 = -130.6\ kJ/mol \tag{18}$$

Molecule	ΔH_f^0 standard enthalpy of formation at 25°C [kJ/mol]	ΔG_f^0 standard free energy of formation at 25°C [kJ/mol]
CO_2 (g)	-393.51	-394.4
CO (g)	-110.5	-137.2
O_2	0	0
H_2	0	0
CH_4 (g)	-74.87	-50.8
H_2O (g)	-241.8	-228.6
H_2O (l)	-285.8	-237.1
CH_3OH (l)	-238.7	-166.4

Table 5 Standard enthalpies and free energies of formation for some simple compounds

The carbon dioxide methanation is thermodynamically favorable (negative ΔG) but kinetically limited (activation energy is required), therefore the reaction takes place at an elevated temperature and pressure in the presence of a Ni or Ru catalyst.

As was mentioned in the paper, most conversion reactions involving CO_2 are endothermic and require a lot of energy (heat) and reactants with high Gibbs free energy, like methane or hydrogen, as well as the use of catalysts to lower the high kinetic barrier of many reactions. This is because the carbon-oxygen bonds are very strong, and a lot of energy is required to break them.

The enthalpy and free energy changes for the two example reactions were calculated as follows:

The enthalpy change for methane combustion ΔH_R^0: (-393.51+2·(-285.8)) – (-74.87+2·0) = -890.24 kJ
The Gibbs free energy change for methane combustion ΔG_R^0: (-394.4+2·(-237.1)) – (-50.8+2·0) = -817.8 kJ
The enthalpy change for the Sabatier reaction ΔH_R^0: (-74.87+2·(-285.8)) – (393.51+4·0) = -252.96 kJ.
The free energy change for this reaction ΔG_R^0: (-50.8+2·(-237.1)) – (-394.4+4·0) = -130.6 kJ.

As a side note, the Sabatier reaction will be used by NASA in the cabin Atmosphere Revitalization System for low-earth orbit and long-term manned space missions. Precision Combustion, Inc. (PCI) has developed a Sabatier (CO_2 methanation) reactor that can recycle carbon dioxide from cabin air to generate oxygen or use Martian atmosphere CO_2 to generate oxygen.

Hydrogen for the Sabatier reaction is produced from electrolysis of water using power from solar cells. CO_2 from human exhalation is removed from the atmosphere by sorbent beds. Hydrogen is then mixed with CO_2 over a nickel catalyst at high temperature and water is produced together with methane. Water can be used to produce more hydrogen through electrolysis and methane can be used for heating or as a rocket propellant.