

CO₂ capture – New challenge in refinery industry

Artur Thernesz (44)

MEng in Chemical Engineering
Refining & Marketing Division, DS
Development, Százhalombatta
E-mail: AThernesz@mol.hu

Gabriella Szalmás PhD (57)

MEng in Chemical Engineering
MOL Plc., Refining & Marketing Division,
DS Development, Százhalombatta
E-mail: PGSzalmasne@mol.hu

Peter Dinka (40)

MEng in Chemical Engineering
Refining & Marketing Division, DS
Development, Bratislava
E-mail: peter.dinka@slovnaft.sk,

Tibor Simon (65)

MEng in Chemical Engineering
Consulting engineer
E-mail: simontibor@externet.hu

Abstract

Emission of CO₂ globally has been brought into attention in recent years through declarations such as the Kyoto and recent Bali conventions, and also by industry leaders committing themselves to substantial reductions. One approach to limiting CO₂ emissions from combusting of carbon-based fuels is to capture the CO₂. The purpose of CO₂ capture is to produce a concentrated stream that can be readily transported to a CO₂ storage site. The CO₂ capture and sequestration processes are in the development phase. First of all, it is necessary to become acquainted with the current practice and to identify the results achieved in the leading industrialized countries. MOL Group refinery installations, power generation facilities and chemical industry installations are subject to ETS (Emission Trading Scheme) and imposed to growing reduction requirements on GHG emission.

With the currently available technologies the removal of CO₂ from the flue gases is a capital and energy intensive process due to the low pressure, low CO₂ concentration and the presence of undesired components in the flue gases.

This paper provides an overview of the existing and developing methods and technologies for carbon capture and summarizes the Danube Refinery opportunities to achieve substantial reduction in CO₂ release in refinery by capturing CO₂ from Hydrogen plant process gas.

Összefoglalás

CO₂ kinyerés – új kihívás a kőolajiparban

A Kiotói és a közelmúltban tartott Bali klímaváltozási konferencia megállapodásai, továbbá a vezető ipari hatalmak elkötelezettsége a károsanyag kibocsátás csökkentés mellett egyre inkább a figyelem középpontjába helyezték a globális CO₂ kibocsátást. A szén alapú fűtőanyagok eltüzelése révén jelentkező CO₂ emisszió csökkentésének egyik lehetséges módja a széndioxid kinyerése. A kinyerési technológia célja, hogy olyan koncentrált formában állítsa elő a széndioxidot, amely könnyen a tárolási helyre szállítható. A széndioxid kinyerési és tárolási technológiák döntően fejlesztési stádiumban vannak, ezért szükséges, hogy áttekintsük a jelenlegi gyakorlatot, azonosítsuk a vezető ipari országokban elért eredményeket.

A MOL-csoport finomítói, erőművei, vegyipari létesítményei az EU ETS (Emisszió Kereskedelmi Rendszer) hatálya alá tartoznak, elvárás az üvegházhatást okozó gázok emissziójának növekvő mértékű csökkentése.

A füstgázokban a CO₂ alacsony nyomáson, kis koncentrációban, más egyéb nem kívánt komponensekkel együtt van jelen, az ismert rendelkezésre álló technológiákkal a CO₂ eltávolítása rendkívül beruházás és energia igényes folyamat.

Jelen cikk áttekintést nyújt a már megvalósított és a fejlesztési stádiumban lévő CO₂ kinyerési technológiákról, a Dunai Finomító esetében bemutatja a CO₂ csökkentési lehetőségeket a hidrogén gyártás folyamatában keletkező CO₂ kinyerése révén.

1. Introduction

Climate change is recognized by many observers as a potential threat to the global environment. Predicted impacts include increasing global average temperatures, rising sea levels, and changes in precipitation, with consequences for low-lying inhabited areas, agriculture, biodiversity, and human health [1]. The cause of these changes is the increased levels of greenhouse gases in the atmosphere, due to human activities. Global anthropogenic emissions are emitted from industrial, residential, transportation, commercial and agricultural sources.

The major greenhouse gas is carbon dioxide (CO₂) and the major source of anthropogenic CO₂ is the combustion of fossil fuels. The volume of emitted CO₂ is estimated to 26 billion metric tons in 2004 and the quantity is increasing in the foreseeable future [2].

1.1 INDUSTRIAL EMISSIONS

Industry sectors combined dominate current global CO₂ emissions, accounting for about



Figure 1. World carbon dioxide emissions by region, 2003 – 2030

70% of total CO₂ emissions. CO₂ emissions from industry sector arise from a number of different sources, but mainly from the combustion of fossil fuels. Carbon dioxide not related to combustion is emitted from a variety of industrial production processes which transform materials chemically or physically. Fossil fuels currently supply over 80% of the world's energy needs and will remain in abundant supply well into the 21st century [3].

A database of 8049 industrial facilities around the world has been compiled. Each of the facilities emits more than 100 kt CO₂ annually [4]. Together these facilities account for 13-14 Mt/year CO₂ in Y 2006, mainly from industrialized countries (Figure 2.).

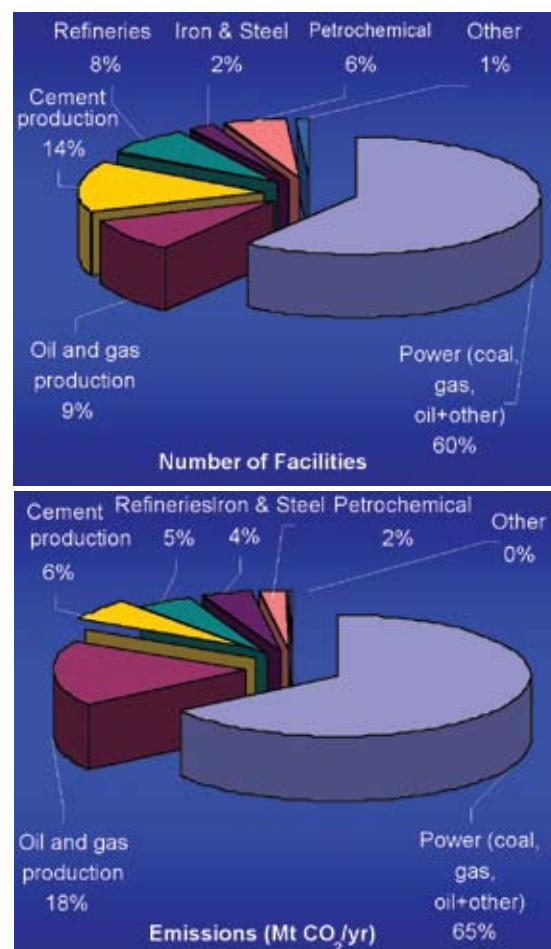


Figure 2. Database of 8049 industrial facilities: CO₂ emissions from large stationary sources

The main large stationary sources of CO₂ in industry can be sorted:

- Power plants emit more than one-third of the CO₂ emissions worldwide. Power plants are usually built in large centralized units, typically delivering 500-1000 MW of electrical power.
- Heat generation to cover own process

heat requirement of different industries (oil refining, cement production, metallurgy, etc.)

- Several industrial processes produce highly concentrated streams of CO₂ as a byproduct. Industrial processes that lend themselves to carbon capture are ammonia manufacturing, fermentation and hydrogen production.
- Natural gas coming out from the wells often contains a significant fraction of CO₂ that could be captured and stored.

1.2 REFINERY EMISSIONS

Refinery emissions account for about 5% of industrial emissions worldwide. Most emissions from the refinery itself originate from the feedstock used. These feedstock are the main crude oil(s) to be processed, plus other imported feedstock, such as condensates or VGOs, and supplementary natural gas for fuel or hydrogen plants. Whilst most carbon emissions from the refinery will be in the form of CO₂, there are other emissions, such as VOCs, coke on catalysts (which could be landfilled) and other minor emissions. Shadow emissions from energy import (CO₂ emissions derived from production of energy offsite), whilst not emitted from the refinery itself, are still important when considering the impact of the refinery operations.

The main emission sources in oil refinery are:

- Fuel for process heating, steam raising and incinerators
- Hydrogen production
- Coke burn-off from the FCC
- Flaring
- Power generation if it is part of the refinery

1.3 CO₂ MITIGATION

The climate carbon wedge concept was introduced by two Princeton professors, Rob Socolow and Stephen Pacala. [5] These wedges describe a portfolio of energy technologies and choices about how we live, that when taken together form wedges against increasing carbon emissions.

The 50-year emissions reductions are idealized as a perfect triangle in Fig. 3. Stabilization is represented by a "flat" trajectory of fossil fuel emissions at 7 GtC/year, and BAU is represented by a straight-line "ramp" trajectory rising to 14 GtC/year in 2054. A wedge



Figure 3. Possible emissions scenarios (Carbon tons equivalent of CO₂ tons: ~ 3,7)

represents an activity that reduces emissions to the atmosphere that starts at zero today and increases linearly until it accounts for 1 GtC/year of reduced carbon emissions in 50 years. Areas recommended to achieve the reductions are:

- Energy efficiency and Conservation
- Fuel Shift
- CO₂ Capture and Storage
- Nuclear Fission
- Forests and Agricultural Soils

In addressing refinery CO₂ management Capture and Storage can be one of the solutions belonging to the CO₂ mitigation concept.

The purpose of this paper to show the possibilities, methods, reality of CO₂ capture in MOL Group refineries.

2. Summary of CO₂ capture

The purpose of CO₂ capture is to produce a concentrated stream that can be readily transported to a CO₂ storage site. It should be noted that storing the flue gas stack without primarily separating the CO₂ would even be more expensive. Indeed, beside CO₂, the flue gas stack consists of water and nitrogen. The latter needs to be compressed before being stored which is a very expensive process requiring a lot of compressing. CO₂ capture and storage is most applicable to large, centralized sources like power plants, refineries etc.

Capture of CO₂ from industrial process streams has been used for about 80 years, although most the captured CO₂ is vented to the atmosphere because there was not incentive or requirement to store it. Current

examples of CO₂ capture from process streams are purification of natural gas and production of hydrogen-containing synthesis gas for the manufacture of ammonia, alcohols and synthetic liquid fuels [6].

All elements of CCS technology (CO₂ capture from anthropogenic sources, including transportation, storage and monitoring) exist today and have been commercially deployed in various industries, specifically oil and gas production such as Sleipner, Weyburn-Midale and In Salah. However, these technology elements have not been integrated into large-scale CCS projects such as coal-fired power plants and similar low-purity streams. Some technology risks may arise from that integration process; however, the most significant risks are commercial and policy related. At this time, CCS is not commercially viable, due to the high cost of CCS and the currently weak carbon price signals. Moreover, there is no legal/regulatory regime in place that would allow potential developers and investors to adequately assess and manage their risks and liabilities in respect of CO₂ sequestration. The CO₂ capture and sequestration processes are in development phase. The first step in the actual preparation work is to become acquainted with the current practice and to identify the results achieved in the leading industrialized countries. [7]

There are three basic systems for capturing CO₂ from use of fossil fuels and/or biomass:

- Post-combustion capture
- Oxy-fuel combustion capture
- Pre-combustion capture

Post-combustion capture

Capture of CO₂ from flue gases produced by combustion of fossil fuels and biomass in air is referred to as post-combustion capture. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates most of the CO₂. The CO₂ is fed to a storage reservoir and the remaining flue gas is discharged to the atmosphere. A chemical sorbent process would normally be used for CO₂ separation. Other techniques are also being considered but these are not at such an advanced stage of development.

Oxy-fuel combustion capture

In oxy-fuel combustion, nearly pure oxygen is used for combustion instead of air, resulting in a flue gas which contains mainly CO₂ and H₂O. If fuel is burnt in pure oxygen, the flame

temperature is excessively high, but CO₂ and/or H₂O-rich flue gas can be recycled to the combustor to moderate this. Oxygen is usually produced by low temperature (cryogenic) air separation and novel techniques to supply oxygen to the fuel, such as membranes and chemical looping cycles are being developed.

Pre-combustion capture

Pre-combustion capture involves reacting a fuel with oxygen or air and/or steam to give mainly a 'synthesis gas (syngas)' or 'fuel gas' composed of carbon monoxide and hydrogen. The carbon monoxide is reacted with steam in a catalytic reactor called a shift converter, to give CO₂ and more hydrogen. CO₂ is then separated, usually by a physical or chemical absorption process, resulting in a hydrogen-rich fuel which can be used in many applications, such as boilers, furnaces, gas turbines, engines and fuel cells. This process is well known also in petroleum refineries, and its use in power generation is being seriously considered. These systems are considered to be strategically important but the power plant systems of reference today are 4 GW of both oil and coal-based, integrated gasification combined cycles (IGCC) which are around 0.1% of total installed capacity worldwide.

2.1 TYPES OF CO₂ CAPTURE TECHNOLOGIES

Post-combustion systems

CO₂ capture systems use many of the known technologies for gas separation which are integrated into the basic systems for CO₂ capture. A summary of these separation methods is given below.

2.1.1 Separation with sorbents/solvents

The separation is achieved by passing the CO₂-containing gas in intimate contact with a liquid absorbent or solid sorbent that is capable of capturing the CO₂. In the general scheme of, the sorbent loaded with the captured CO₂ is transported to a different vessel, where it releases the CO₂ (regeneration) after being heated, after a pressure decrease or after any other change in the conditions around the sorbent. After the regeneration step is the sorbent is sent back to capture more CO₂ in a cyclic process. In some variants of this scheme the sorbent is a solid and does not circulate between vessels because the sorption and regeneration are achieved by cyclic changes (in pressure or temperature) in the vessel where the sorbent is contained. A make-up flow of

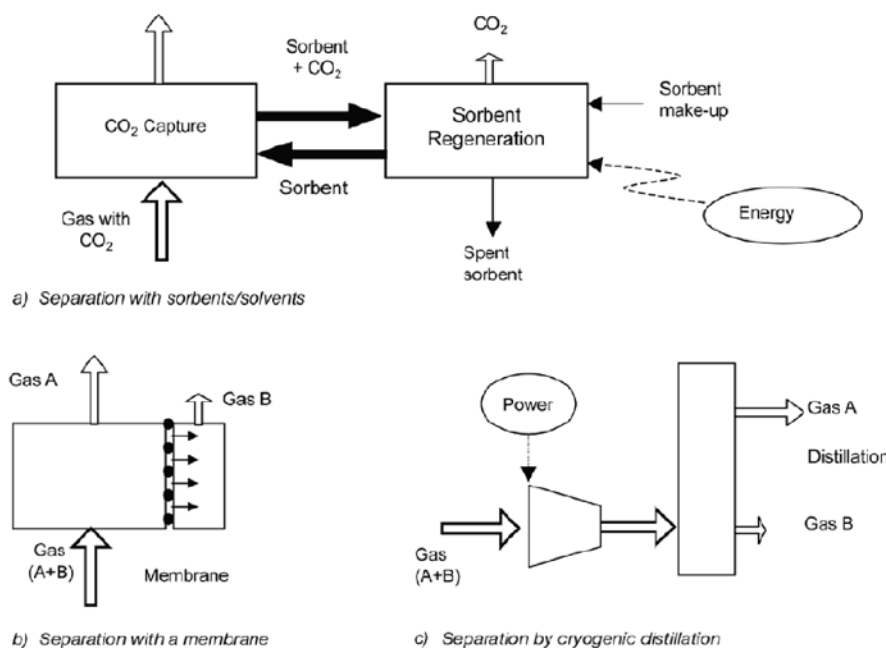


Figure 4. General schemes of the main separation processes relevant for CO₂ capture. The gas removed in the separation may be CO₂, H₂ or O₂.

fresh sorbent is always required to compensate for the natural decay of activity and/or sorbent losses. The general scheme of Figure 4 governs many important CO₂ capture systems, including leading commercial options like chemical absorption and physical absorption and adsorption. Other emerging processes based on new liquid sorbents, or new solid regenerable sorbents are being developed with the aim of overcoming the limitations of the existing systems.

In Figures 4b and 4c one of the separated gas streams (A and B) is a concentrated stream of CO₂, H₂ or O₂ and the other is a gas stream with all the remaining gases in the original gas (A+B).

2.1.2 Separation with membranes

Membranes (Figure 4b) are specially manufactured materials that allow the selective permeation of a gas through them. The selectivity of the membrane to different gases is intimately related to the nature of the material, but the flow of gas through the membrane is usually driven by the pressure difference across the membrane. Therefore, high-pressure streams are usually preferred for membrane separation. There are many different types of membrane materials (polymeric, metallic, ceramic) that may find application in CO₂ capture systems to preferentially separate H₂ from a fuel gas stream, CO₂ from a range of process streams or O₂ from air with the

separated O₂ subsequently aiding the production of a highly concentrated CO₂ stream. Although membrane separation finds many current commercial applications in industry (CO₂ separation from natural gas) they have not yet been applied for the large scale and demanding conditions in terms of reliability and low-cost required for CO₂ capture systems. A large worldwide R&D effort is in progress aimed at the manufacture of more suitable membrane materials for CO₂ capture in large-scale applications.

2.1.3 Distillation of a liquefied gas stream and refrigerated separation

A gas can be made liquid by a series of compression, cooling and expansion steps. Once in liquid form, the components of the gas can be separated in a distillation column. In the case of air, this operation is currently carried out commercially on a large scale. Oxygen can be separated from air following the scheme of Figure 4.c and be used in a range of CO₂ capture systems (oxy-fuel combustion and pre-combustion capture). As in the previous paragraphs, the key issue for these systems is the large flow of oxygen required. Refrigerated separation can also be used to separate CO₂ from other gases. It can be used to separate impurities from relatively high purity CO₂ streams, for example, from oxy-fuel combustion and for CO₂ removal from natural gas or synthesis gas that has undergone a shift conversion of CO to CO₂.

2.2 EXISTING TECHNOLOGIES

There are several commercially available process technologies which can in principle be used for CO₂ capture from flue gases. However, the absorption processes based on chemical solvents are currently the preferred option for post-combustion CO₂ capture. At this point in time, they offer high capture efficiency and selectivity, and the lowest energy use and costs when compared with other existing post-combustion capture processes. Absorption processes have reached the commercial stage of operation for post-combustion CO₂ capture systems, albeit not on the scale required for power plant flue gases.

Absorption processes

Absorption processes in post-combustion capture make use of the reversible nature of the chemical reaction of an aqueous alkaline solvent, usually an amine with an acid or sour gas. The process flow diagram of a commercial absorption system is presented in Figure 5. After cooling the flue gas, it is brought into contact with the solvent in the absorber. A blower is required to overcome the pressure drop through the absorber. At absorber temperatures typically between 40 and 60°C, CO₂ is bound by the chemical solvent in the absorber.

The 'rich' solvent, which contains the chemically bound CO₂ is then pumped to the top of a regeneration vessel (stripper), via a heat exchanger. The regeneration of the chemical solvent is carried out in the regeneration vessel at elevated temperatures (100°C-140°C). This leads to a thermal energy penalty as a result of heating up the solvent [8], providing the required desorption heat for removing the chemically bound CO₂. The 'lean' solvent, containing far less CO₂ is then pumped back to the absorber.

The key parameters determining the technical and economic operation of a CO₂ absorption system are:

- *Flue gas flow rate* – The flue gas flow rate will determine the size of the absorber and the absorber represents a sizeable contribution to the overall cost.
- *CO₂ content in flue gas* – Since flue gas is usually at atmospheric pressure, the partial pressure of CO₂ will be as low as 3-15 kPa. Under these low CO₂ partial pressure conditions, aqueous amines (chemical solvents) are the most suitable absorption solvents.

- *CO₂ removal* – In practice, typical CO₂ recoveries are between 80% and 95%. The exact recovery choice is an economic trade-off, a higher recovery will lead to a taller absorption column, higher energy penalties and hence increased costs.
- *Solvent flow rate* – The solvent flow rate will determine the size of most equipment apart from the absorber. For a given solvent, the flow rate will be fixed by the previous parameters and also the chosen CO₂ concentrations within the lean and the rich solutions.
- *Energy requirement* – The energy consumption of the process is the sum of the thermal energy needed to regenerate the solvents and the electrical energy required to operate liquid pumps and the flue gas blower or fan. Energy is also required to compress the CO₂ recovered to the final pressure required for transport and storage.
- *Cooling requirement* – Cooling is needed to bring the flue gas and solvent temperatures down to temperature levels required for efficient absorption of CO₂. Also, the product from the stripper will require cooling to recover steam from the stripping process.

The purity and pressure of CO₂ typically recovered from an amine-based chemical absorption process are as follows:

- CO₂ purity: 99.9% by volume or more (water saturated conditions)
- CO₂ pressure: 50 kPa (gauge)

A further CO₂ purification step makes it possible to bring the CO₂ – quality up to food – grade standard. Since the flue gas contains oxygen and other impurities, an important characteristic of an absorption process is in the proper choice of solvent for the given process duty. High CO₂ loading and low heat of desorption energy are essential for atmospheric flue gas CO₂ recovery.

Flue gas pretreatment

The temperatures of the flue gases are usually above 100°C, which means that they need to be cooled down to the temperature levels required for the absorption process. This can be done in a cooler with direct water contact, which also acts as a flue gas wash with additional removal of fine particulates. In addition, flue gas from fuel combustion will contain other acid gas components such as NO_x and SO_x. These acidic gas components will, similar to CO₂, have

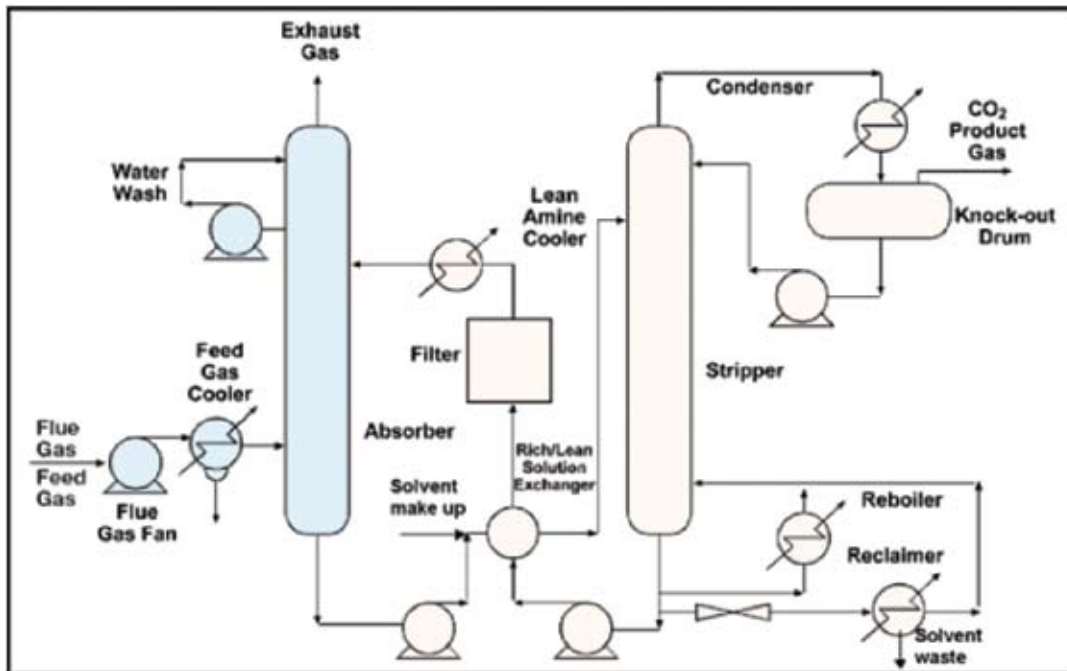


Figure 5. Process flow diagram for CO₂ recovery from flue gas by chemical absorption.

a chemical interaction with the alkaline solvent. This is not desirable as the irreversible nature of this interaction leads to the formation of heat stable salts and hence a loss in absorption capacity of the solvent and the risk of formation of solids in the solution. It also results in an extra consumption of chemicals to regenerate the solvent and the production of a waste stream such as sodium sulphate or sodium nitrate. Therefore, the pre-removal of NO_x and SO_x to very low values before CO₂ recovery becomes essential. The optimal SO₂ content, before the CO₂ absorption process is a cost trade-off between CO₂ – solvent consumption and SO₂ – removal costs. Careful attention must also be paid to fly ash and soot present in the flue gas, as they might plug the absorber if contaminants levels are too high.

2.3 EMERGING TECHNOLOGIES

Other absorption process

Various novel approaches are being investigated, with the object of achieving a reduction of energy consumption and lowering the cost of the process. These new research directions include:

- Searching for new solvents to achieve reduction of energy consumption during of solvent regeneration.
- Novel process designs are also currently becoming available.
- Improving the existing practices and packing types.
- Another area of research is to

increase the concentration levels of aqueous MEA solution used in absorption systems as this tends to reduce the size of equipment used in capture plants.

- Methods to prevent oxidative degradation of MEA by de-oxygenation of the solvent solutions are also being investigated.
- Catalytic removal of oxygen in flue gases from coal firing has been suggested to enable operation with promising solvents sensitive to oxygen.

Adsorption process

In the adsorption process for flue gas CO₂ recovery, molecular sieves or activated carbons are used in adsorbing CO₂. Desorbing CO₂ is then done by the pressure swing operation (PSA) or temperature swing operation (TSA) [9]. Less attention has been focused on CO₂ removal via temperature swing adsorption, as this technique is less attractive compared to PSA due to the longer cycle times needed to heat up the bed of solid particles during sorbent regeneration. For bulk separations at large scales, it is also essential to limit the length of the unused bed and therefore optimize for faster cycle times.

It can be concluded that based on mathematical models and data from pilot-scale experimental installations, the design of a full-scale industrial adsorption process might be feasible. A serious drawback of all adsorptive methods is the necessity to treat the gaseous feed before CO₂ separation in an adsorber. Operation

at high temperature with other sorbents can circumvent this requirement. In many cases gases have to be also cooled and dried, which limits the attractiveness of PSA, TSA or ESA (electric swing adsorption) vis-à-vis capture by chemical absorption.

Membranes

Currently available membrane materials include porous inorganics, nonporous metals (e.g. palladium), polymers and zeolites [10]. Many membranes cannot achieve the high degrees of separation needed in a single pass, so multiple stages and/or recycle of one of the streams are necessary. This leads to increased complexity, energy consumption and costs. Suitable membranes could be used to separate CO₂ at various locations in technological processes.

Membrane processes are used commercially for CO₂ removal from natural gas at high pressure and at high CO₂ concentration. In flue gases, the low CO₂ partial pressure difference provides a low driving force for gas separation. The removal of carbon dioxide using nowadays commercially available polymeric gas separation membranes results in higher energy penalties compared to a standard chemical absorption process. Also, the maximum percentage of CO₂ removed is lower.

The membrane option currently receiving the most attention is a hybrid membrane – absorbent (or solvent) system. Membrane/solvent systems employ membranes to provide a very high surface area to volume ratio for mass exchange between a gas stream and a solvent resulting in a very compact system. This results in a membrane contactor system in which the membrane forms a gas permeable barrier between a liquid and a gaseous phase. In the case of porous membranes, gaseous components diffuse through the pores and are absorbed by the liquid. The contact surface area between gas and liquid phase is maintained by the membrane and is independent of the gas and liquid flow rate.

Solid sorbents

There are post-combustion systems being proposed that make use of regenerable solid sorbents to remove CO₂ at relatively high temperatures. The use of high temperatures in the CO₂ separation step has the potential to reduce efficiency penalties with respect to wet-absorption methods. In principle, they all follow the scheme shown in Figure 7, where

the combustion flue gas is put in contact with the sorbent in a suitable reactor to allow the gas-solid reaction of CO₂ with the sorbent (usually the carbonation of a metal oxide). The solid can be easily separated from the gas stream and sent for regeneration in a different reactor. Instead of moving the solids, the reactor can also be switched between sorption and regeneration modes of operation in a batch wise, cyclic operation.

Solid sorbents being investigated for large-scale CO₂ capture purposes are sodium and potassium oxides and also Li-based and CaO-based sorbents, usually supported on a solid substrate. The Li-based sorbents showed good performance in a wide range of temperatures below 700°C, rapid regeneration at higher temperatures and durability in repeated capture-regeneration cycles. The use of CaO as a regenerable CO₂ sorbent has been proposed in several processes dating back to the 19th century. The carbonation reaction of CaO to separate CO₂ from hot gases (T > 600°C) is very fast and the regeneration of the sorbent by calcining the CaCO₃ into CaO and pure CO₂ is favoured at T > 900°C (at a partial pressure of CO₂ of 0.1 MPa).

The basic separation principle using this carbonation-calcination cycle was successfully tested in a pilot plant (40 tons d⁻¹) for the development of the Acceptor Coal Gasification Process using two interconnected fluidized beds. The use of the above cycle involved regeneration of the sorbent in a fluidized bed, firing part of the fuel with O₂/CO₂ mixtures. The effective capture of CO₂ by CaO has been demonstrated already in a small pilot fluidized bed. One weak point in all these processes is that natural sorbents (limestones and dolomites) deactivate rapidly.

Oxy-fuel combustion capture systems

The oxy-fuel combustion process eliminates nitrogen from the flue gas by combusting a hydrocarbon or carbonaceous fuel in either pure oxygen or a mixture of pure oxygen and a CO₂-rich recycled flue gas (carbonaceous fuels include biomass). Combustion of a fuel with pure oxygen has a combustion temperature of about 3500°C which is far too high for typical power plant materials. The combustion temperature is controlled by the proportion of flue gas and gaseous or liquid-water recycled back to the combustion chamber.

The combustion products (or flue gas) consist mainly of carbon dioxide and water vapour together with excess oxygen required to ensure complete combustion of the fuel. It will also contain others components, originated in the fuel and any diluents in the oxygen stream supplied (SO_x, NO_x, HCl, Hg, N₂, Ar). The net flue gas, after cooling to condense water vapour, contains from about 80-98% CO₂ depending on the fuel used. The CO₂ capture efficiency is very close to 100% in oxy-fuel combustion capture systems.

Current methods of oxygen production by air separation comprise cryogenic distillation, adsorption using multi-bed pressure swing units and polymeric membranes. For oxy-fuel conversions requiring less than 200 tO₂ d⁻¹, the adsorption system will be economic. For all the larger applications, which include power station boilers, cryogenic air separation is the economic solution.

As for pulverized coal, oil, natural gas and biomass combustion, fluidized beds could also be fired with O₂ instead of air to supply heat for the steam cycle. The intense solid mixing in a fluidized bed combustion system can provide very good temperature control even in highly exothermic conditions, thereby minimizing the need for flue gas recycling.

Chemical looping combustion

The main idea of chemical looping combustion is to split combustion of a hydrocarbon or carbonaceous fuel into separate oxidation and reduction reactions by introducing a suitable metal oxide as an oxygen carrier to circulate between two reactors (Figure 6.). Separation of oxygen from air is accomplished by fixing the oxygen as a metal oxide [11]. No air separation plant is required. The reaction between fuel and oxygen is accomplished in a second reactor by the release of oxygen from the metal oxide in a reducing atmosphere caused by the presence of a hydrocarbon or carbonaceous fuel. The recycle rate of the solid material between the two reactors and the average solids residence time in each reactor, control the heat balance and the temperature levels in each reactor. The effect of having combustion in two reactors compared to conventional combustion in a single stage is that the CO₂ is not diluted with nitrogen gas, but is almost pure after separation from water, without requiring any extra energy demand and costly external equipment for CO₂ separation.

In order to move particles between the two reactors, the particles are fluidized. This method also ensures efficient heat and mass transfer between the gases and the particles. A critical issue is the long-term mechanical and chemical stability of the particles that have to undergo repeated cycles of oxidation and reduction, to minimize the make-up requirement.

The temperature in the reactors may be in range of 800°C - 200°C. NO_x formation at these typical operating temperatures will always be low.

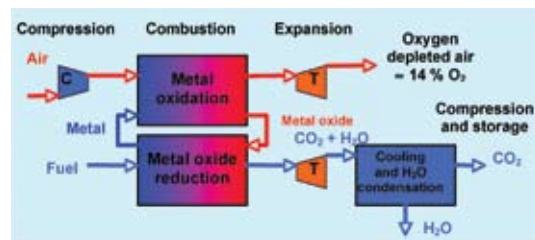


Figure 6. The chemical looping combustion principle in a gas turbine cycle.

Oxy-fuel combustion applied to furnaces, process heaters, boilers and power generation systems is feasible since no technical barriers for its implementation have been identified. As for Chemical Looping Combustion, it is currently still at an early stage of development.

3. Examples of existing CO₂ capture technologies

CO₂ capture and reinjection at the Sleipner field
In the Sleipner gas field in the North Sea, the natural gas contains 9% of CO₂, which must be reduced to 2,5% before export. The extracted 1 million tonnes CO₂ per year would, if released to the atmosphere, have increased Norway's CO₂ emissions by nearly 3%. In order to help meet national emissions targets – and avoid high CO₂ taxes – Statoil decided to adopt an aquifer storage strategy for Sleipner, starting in 1996.

The CO₂ is absorbed in an amine contact tower at a pressure of 100 bars. The amine is then stripped for CO₂ in another tower. The module for the CO₂ extraction process weighs 8200 tonnes – the heaviest module ever lifted offshore –, measures 50x20x35 metres and costs over 350 million ECU. Capture of CO₂ from the smoke stack of gas turbines is not done on Sleipner (it would require larger facilities not well suited for offshore installations and will cost far more than the CO₂ capture from a pressurised natural gas). The CO₂ extracted on Sleipner is injected into a deep

saline aquifer, called "Utsira Sand", some 1000 metres below the sea through a separate injection well. This sand is not connected to the hydrocarbon reservoirs at 3500 metres. It is the first time that CO₂ is injected into an aquifer for environmental reasons. The project will provide valuable information on the feasibility of this technology. To learn the maximum of this ongoing "pilot project", Statoil, and its license partners Elf, Exxon and Norsk Hydro, has invited interested parties to run a 3 years monitoring and verification project.

CO₂ RECOVERY AND SEQUESTRATION AT DAKOTA GASIFICATION COMPANY

The Great Plains Synfuels Plant, located near Beulah, North Dakota, is a gasification plant that produces Synthetic Natural Gas (SNG) from coal. Today upwards of 150 million standard cubic feet per day of SNG are produced together with numerous by-products, including anhydrous ammonia, ammonium sulfate fertilizer, phenol, cresylic acid, krypton/xenon, naphtha and carbon dioxide (CO₂). Since the conception of the plant, the idea was envisioned of adding CO₂ for enhanced oil recovery (EOR) to the list of by-products. In 2000, this became a reality when the company began exporting up to 95 million standard cubic feet per day of high-pressure CO₂. The CO₂ is delivered through a 205-mile pipeline to Weyburn Oil Fields in Saskatchewan, Canada, where it is injected into depleting oil formations to increase production and lengthen the life of the field.

4. Current commercial practice

The Kerr-McGee/ABB Lummus Crest Process – This process recovers CO₂ from coke and coal-fired boilers, delivering CO₂ for soda ash and liquid CO₂ preparations. It uses a 15-20% by weight aqueous MEA (Mono-Ethanolamine) solution. The largest capacity experienced for this process is 800 tCO₂ d-1 utilizing two parallel trains.

The Fluor Daniel ® ECONAMINE™ Process - This process was acquired by Fluor Daniel Inc. from Dow Chemical Company in 1989. It is a MEA-based process (30% by weight aqueous solution) with an inhibitor to resist carbon steel corrosion and is specifically tailored for oxygen-containing gas streams. It has been used in many plants worldwide recovering up to 320

tCO₂ d-1 in a single train for use in beverage and urea production.

The Kansai Electric Power Co., Mitsubishi Heavy Industries, Ltd., KEPCO/MHI Process - The process is based upon sterically-hindered amines and already three solvents (KS-1, KS-2 and KS-3) have been developed. KS-1 was commercialized in a urea production application. In this process, low amine losses and low solvent degradation have been noted without the use of inhibitors or additives. The first commercial plant at 200 tCO₂ d-1 recovery from a flue gas stream has been operating in Malaysia since 1999 for urea production (equivalent to the emissions from a 10 MWT coal-fired power plant).

The Econamine FGSM technology has been implemented at 23 commercial plants worldwide. One of these plants is a 327 t/d CO₂ recovery plant in the Florida Power and Light power plant in Bellingham, MA, USA. The Econamine FGSM plant was designed and constructed by Fluor, and has been in continuous operation since 1991. This facility is operating on gas turbine flue gas. This is notable for three reasons:

1. The CO₂ concentration in the flue gas is low, being only 2.8 to 3.1 vol%.
2. The oxygen concentration in the flue gas is high, being approximately 13 vol%.
3. Neither a backpressure nor a pressure fluctuation in the flue gas line can be tolerated.

The quality of the carbon dioxide product is suitable for use in the food and beverage industry. Fluor is the technology vendor with experience with CO₂ recovery from flue gas with a very high oxygen concentration. Large-scale carbon dioxide sequestration projects are currently being planned by Econamine FGSM. With absorber diameters of 40 to 50 feet considered feasible, CO₂ recovery plant capacities of up to 8,000 t/d are achievable, depending on the inlet flue gas CO₂ concentration. Even larger plants can be realized by employing multiple absorbers sharing a common stripper.

5. CO₂ capture in refinery

The refineries have a large number of process heaters scattered around the site. This makes CO₂ capture difficult, very expensive and impractical. However, about 60% of the CO₂ is

emitted from 4-5 process units in the refinery – AVD distillation. FCC, Hydrogen manufacturing, and steam generation (Figure 7.). Some characteristics of flue gas at leaving point are shown in Table 1.

UNIT	P [bar]	T, [°C]	CO ₂ V/V%
FCC	0,991	260	7,07
AV-2	1,004	177	3,87
BEK-5	1,002	142	6,18
HGY-2	1,004	167	16,71
DCU	1,016	244	8,56

Table 1. Pressure and Temperature data at stack leaving point.

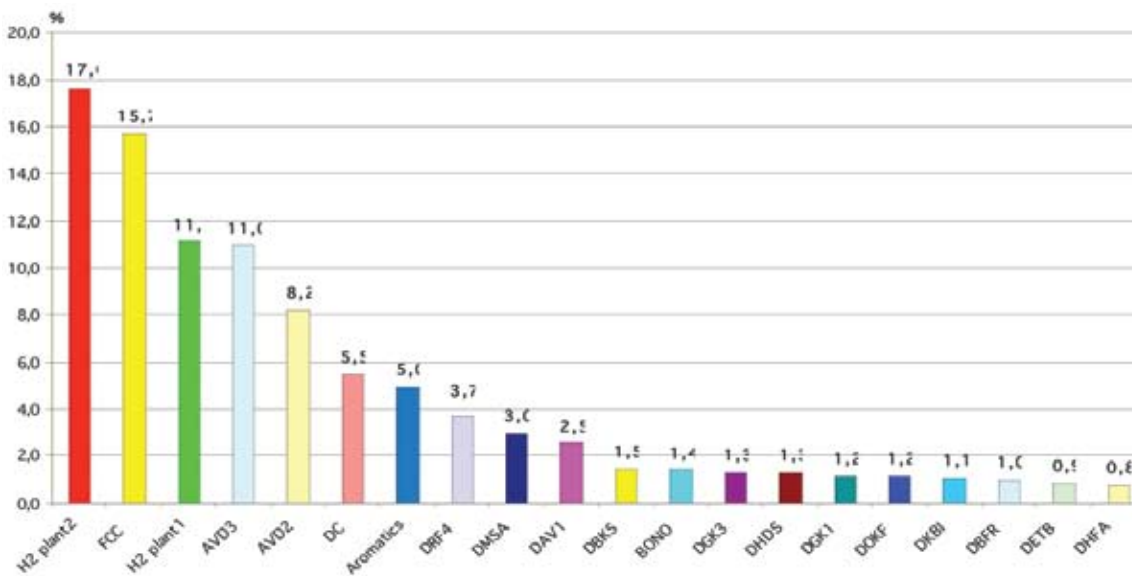


Figure 7. CO₂ emissions of process units (first 20 plants) in 2007, Danube refinery.

The pressure and temperature of the flue gases are not favorable for gathering and capturing the CO₂ content.

The sources of CO₂ identified in MOL Group refining activity are listed in Tables 2 and 3.

Site	No. of point sources	Heating and fuel burning, compressors	Process origin		Capture Proposal
			FCC Coke burn	H ₂ "chemical"	
Refining					
• Danube Refinery	54	927	231	282	Only CO ₂ "chemical"
• Slovnaft Refinery	50	1831	218	201	
• TR+ZR	15	64			
Availability @					
Pressure barg		0,01-0,02	25-28		
Temperature °C		130-400	40		
CO ₂ wt% %			6-14	65	

Table 2. Sources of CO₂ emissions identified in MOL group refineries per year 2007, (kt CO₂/year).

The source of the "chemical" CO₂ is the steam reforming reaction in hydrogen manufacturing and following water shift reaction:

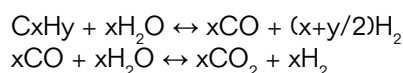


Table 3. Available "chemical CO₂" for capturing will be after the implementation of Hydrogen plant 3 (Y 2010).

	Hydrogen plant 1 DR	Hydrogen plant 2 DR	Hydrogen plant 3 DR*	Hydrogen plant 1 SN	Hydrogen plant 2 SN	Total
CO ₂ Kt/year	77	103	155	50	77	462

Table 3. Available "chemical CO₂" for capturing will be after the implementation of Hydrogen plant 3 (Y 2010).

Depending on the recovery efficiency and the utilization of H₂ plants the quantity of CO₂ captured can be about 13-15 % of the total CO₂ emitted from refineries depending on the start up of new technologies.

Based upon the developed data we conclude that for refineries the single potential source is the capturing of CO₂ from Hydrogen plant. We propose to continue the research in this direction in the next period.

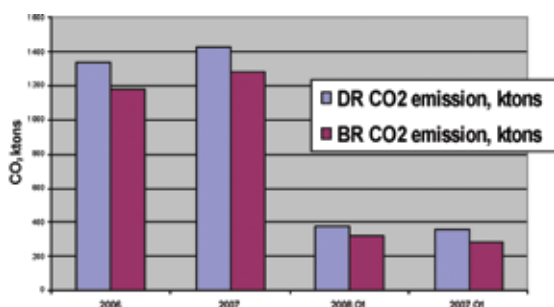


Figure 8. Accounted CO₂ emissions 2007-2008

6. Case study

The Hydrogen plant in Spain, Tarragona is integrated with a CO₂ recovery (capture) system. Until now the Licensor Technip built 3 hydrogen plants coupled with CO₂ recovery.

Wilton, UK	20 KNm ³ /h
Sapio, Italy	20 KNm ³ /h
Repsol, Tarragona, Spain	60 KNm ³ /h

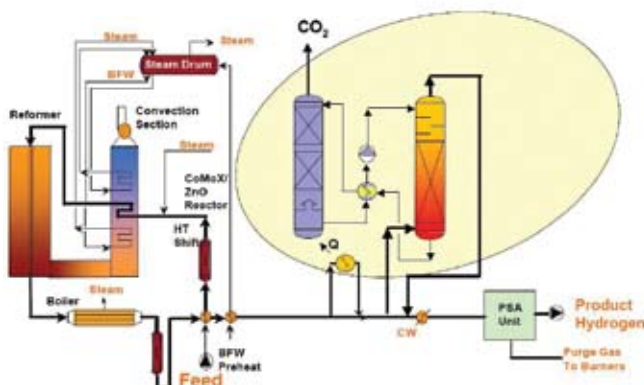


Figure 9. Cogeneration of CO₂

The CO₂ recovery is aiming at the sales of by product CO₂ for food industry (not sequestration). General flowsheet of the Hydrogen plant is shown in Figure 9. The BASF licensed CO₂ recovery part of the plant consists of:

- CO₂ recovery in MDA absorber on high pressure
- Desorption of the CO₂ on low pressure
- Compression of the low pressure gas
- Drying
- Bottling the gas for food industry purposes

7. Legislation – driver for action

For the first three-year period of ETS legislation in 2005-2007 both refineries were under the allowed quota.

This was due to the facts that:

- MOL Group carried out an energy efficiency program prior to the introduction of mandatory quota. The main driver of the program was to improve energy efficiency (rationalization of heat utilization, changing steam tracing with electric cables, modernization of burners and furnace instrumentation) but it resulted lower CO₂ emission too.
- Real and monitored CO₂ emission was lower than the estimated quantity
- Authorities had no practice in setting the quota levels; the allowance was higher than the real requirements in EU and also in Hungary.

MOL Group CO₂ performance in 2nd phase 2008-2012

In the future period appear new problems making the emission balance more difficult:

- The National Allocation Plan II intends to reduce the allowed quota in line with the increased CO₂ reduction in EU.
- MOL Group will face approximately 4 Mt CO₂ quota deficits in the full period in case of the worst

scenario, including the emissions of the planned new developments.

- Awarding quota for new entrants is getting more difficult in the future

3rd phase 2013-20: The allocation scheme is not accepted yet on EU level. There are some preliminary expectations, that there will be no free allocation for energy sector, and decreasing allocation is planned to the player of oil industry till our industry would reach the zero allocation as well.

Later phases: The goal is to reduce CO₂ emission by 50% by 2050 based on the 1990 level. The view is that there will be not free allocations at all, inspiring companies to spend more on developing carbon free or low carbon technologies.

MOL Group commitments in promoting sustainable development and the more stringent legislation are the motives to realize the CO₂ capture in due time. Emission reduction achieved by capturing the CO₂ from hydrogen plant process gas could mean 5% reduction on MOL Group level and above 10% reduction on refining level.

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Revised by: Géza Horváth PhD,
Pannon University