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Literature review of current capture technologies

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SUMMARY:

A coarse literature review of the current CO₂ capture technologies has been made. The literature review covers the main capture technologies within post-combustion capture, oxy-fuel capture and pre-combustion capture. The review serves as a theoretical introduction to the case studies to be done in task 4.2.

KEYWORDS: Post-combustion capture, oxy-fuel combustion, pre-combustion, CLC

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1. INTRODUCTION

An introductory literature review has been made for current CO₂ capture technologies. The review covers post-combustion capture technologies as chemical solvent absorption, chemical adsorption with cyclic regeneration and membrane capture.

2. POST-COMBUSTION CAPTURE

Post-combustion capture of CO₂ refers to the separation of CO₂ from other flue gases produced as a result of combusting fuel with air¹. The separated CO₂ is stored, usually underground or under the sea bed, while the remaining flue gases are released to the atmosphere.

The concept of capturing and storing CO₂ underground was originally developed as a technology to enhance oil recovery in the 1970's and 1980's. The purpose of the EOR technology was to inject the CO₂ gas into the reservoirs in order to increase the potential and productivity of the reservoir by increasing the oil mobility underground^{2,8,13}. Although this concept was not implemented fully commercially, the technology is the same for the current capture of CO₂ before gas release to atmosphere out of environmental considerations.

Post-combustion capture of CO₂ includes a variety of technologies such as:

- Chemical absorption
- Chemical adsorption
- Membrane separation
- Other less developed technologies such as for instance cryogenic capture and novel solutions such as microbial/algae systems

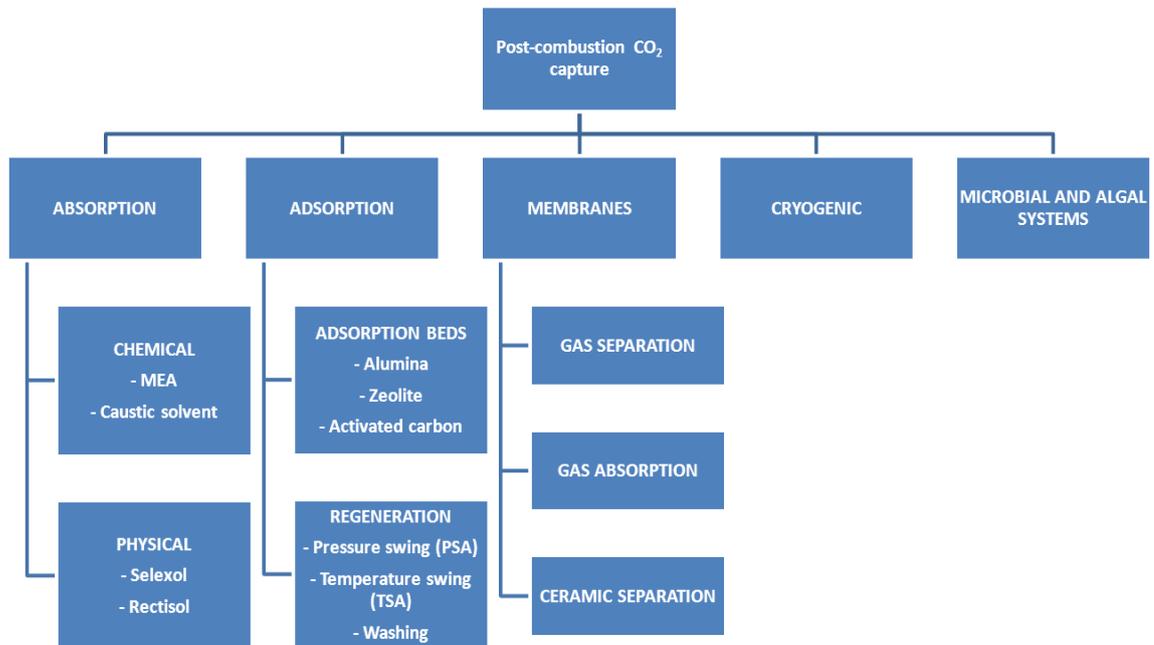


Figure 2.1 Selected options for post-combustion CO₂ capture. Partly reproduced from¹³.

Other flue gas cleaning techniques can be applied simultaneously with CO₂ capture to further decrease the amount of harmful gases or substances emitted to the atmosphere, for instance nitrous oxides, dust and sulfur compounds.

The industrial processes most apt for post-combustion cleaning technology are oil, coal and natural gas fired power stations, supercritical pulverized coal fired plants and natural gas combined cycle plants (NGCC)¹. Post-combustion capture technologies can be applied both to large and small scale processes. The technology can also be applied regardless of the fuel used for combustion, but the range and type of impurities decides the type of capture system that needs to be utilized.

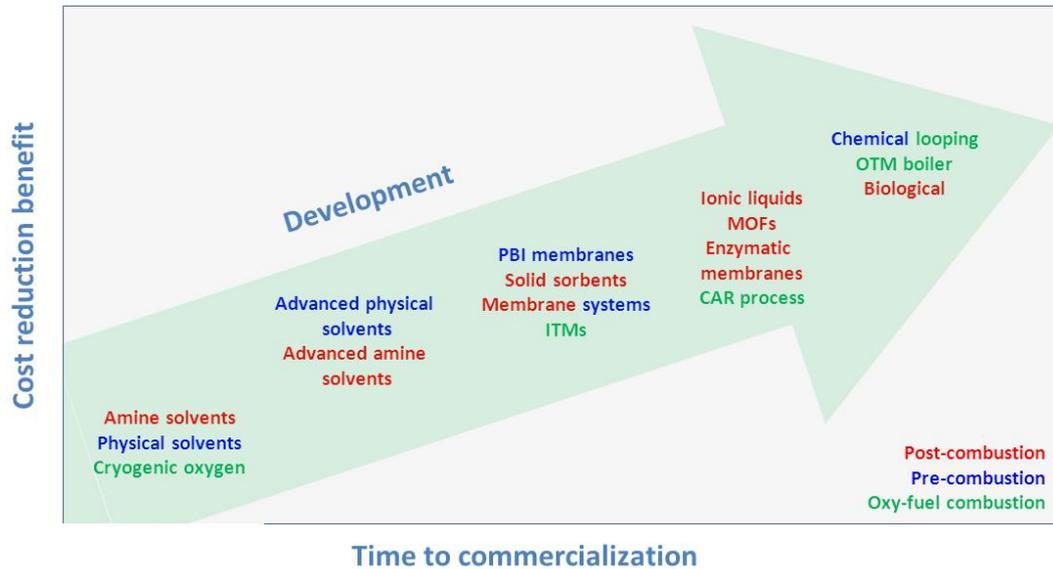


Figure 2.2 Innovative technologies for post-combustion capture of CO₂. Cost reduction benefits vs. time to commercialization. Reproduced from¹⁷.

2.1 Chemical absorption

The most mature capture technology today, and the most frequently deployed commercial technology for overall CO₂ capture, is chemical absorption with amines⁷. Amines are organic derivatives of ammonia where some of the hydrogen atoms have been replaced by a hydrocarbon compound (methyl or ethyl group). Typically amines contain a reactive chemical group based on nitrogen atoms^{2,4}. Alkanolamines are usually favored for reduction of sour gas from gas streams^{7,14}. Typical alkanolamines are monoethanolamine (MEA), diethanolamine (DEA) and diisopropanolamine (DIPA). The typical absorption reaction can be described with the following exothermic reaction⁷:



where R is an alkyl group. The amine capture technology has already been applied in industrial oil and gas installations for tens of years as a way to remove acid gases from natural gas production^{13,14,18}. Thus it is a proven technology for CO₂ capture. However, transferring this technology to post-combustion flue gases from other industry segments is a relatively new development and poses new challenges to the process. Industrial flue gases have a higher content of impurities and the impurities can be of very different nature and properties. Impurities in industrial flue gases are oxygen, sulfur compounds,



nitrogen and particulate matter that will decrease the amine life and complicate the absorption reaction³. In addition, the partial pressure of CO₂ in industrial flue gases is often quite low compared to natural gas.

Amines dissolve in water and are often used at approximately 20-30% concentration². As organic compounds, amines are vulnerable to certain inhibitors, such as nitrogen dioxide, oxygen, dust, sulfur dioxide and certain heavy metals. All of these inhibitors are frequently found in industrial flue gases and will cause the amine to degrade by reacting with the amine to form heat stable salts, thereby reducing the capture capacity of the amine¹³. In addition, amines are often strongly corrosive¹⁵ and require proper material selection and handling accordingly.

In a chemical absorption process based on solvents the combustion flue gas is purified to remove amine inhibiting sulfur components and cooled down to around 40-50°C before it is fed to the bottom of the amine absorber. In the absorber, the flue gas flows upwards through a packed bed and is forced through a solvent spray in a counter current stream. The solvent captures the CO₂ in a chemical mass transfer reaction between the CO₂ and the solvent to produce a new, water soluble compound^{7,17}. The solvent properties permit a specific degree of diffusion of CO₂ into a weakly bonded intermediate compound in the liquid film at the gas-liquid interface, thereby determining the capture capacity^{1,13,14}. As a consequence, factors affecting the gas-liquid equilibrium, such as mass flow rates, pressure, temperature, flue gas composition, amine inhibitors, CO₂ concentration, amine concentration, vessel design, etc.), directly affect the CO₂ capture capacity¹³. The same pre-requisites are valid for the regenerator operation. Amines are suitable for CO₂ capture from gas streams with low partial pressure of CO₂, but as a consequence the absorption capacity is limited by the reaction equilibrium¹⁷.

In selective gas capture the solvent is especially chosen to extract only the target gas – in this case CO₂. The composition of the solvent is favorable for dissolution of CO₂ and the CO₂ is transferred from gas phase to liquid phase². The solvent CO₂ capture capacity is a direct result of the gas-liquid mass transfer process that takes place in the absorber.

The resulting pressure drop in the spray tower is compensated for by a fan prior to the absorber. Typical reaction temperature in the spray tower is 40 - 60°C^{1,14,15}. Some solvents address also other gases simultaneously, such as H₂S. After scrubbing with the solvent in the absorber the flue gas is washed with water to ensure that no solvent droplets are carried away with the cleaned flue gases that is released to the atmosphere^{1,2}.



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The solvents used are mainly those that can reverse the chemical reaction with CO₂ that takes place in the absorber. The CO₂-rich solvent is withdrawn from the spray tower and fed to the desorber where it undergoes a heat- and/or pressure-based regeneration treatment to release the captured CO₂. This reverse reaction when regenerating the absorption liquid in the desorber is endothermic⁷. The heat contained by the rich solvent solution can be utilized by applying a heat exchanger. This regeneration process usually consists of increasing the temperature (100 - 140°C) or decreasing the pressure (approximately atmospheric pressure), or sometimes by other changes in conditions in the desorber vessel^{1,15}. Usually steam is used as a source of heat in the regeneration column, and processes that have steam readily available offer an opportunity for integration with the core process. Once the CO₂ has been released from the solvent, the steam/CO₂ mixture is cooled in order to condense the water leaving almost pure CO₂ for downstream compression and storage/use.

After regeneration the solvent is ready for reuse in the scrubber and the captured CO₂ is taken to decompression and storage. In this way the solvent loop is closed and only natural decay and loss of solvent activity will have to be replaced by fresh solvent. Solvents used for absorption can be either physical or chemical¹.

A major drawback with solvent based post-combustion CO₂ capture is the significant energy penalty related to the process^{1,2,7,13,15,18}. The majority of the energy requirement is due to the heat needed in the reboiler for releasing captured CO₂ from the solvent in the desorber. In addition, depending on the capture capacity of the sorbent/solvent, large flows of solvents are required in order to meet the capture requirement of the CO₂-rich flue gases. The energy penalty translates into a considerable cost penalty and is therefore an area of CCS capture to which significant resources for research are allocated. A general figure is a reduction in efficiency by 10-13 %-points in a coal-fired power plant¹⁸. Nevertheless, the option of wet scrubbing with a chemical sorbent/solvent is the most cost-effective and energy-effective of the post-combustion CCS technologies available today and offers very good capture efficiency and selectivity.

Another drawback with wet scrubbing of flue gases for CO₂ capture is for instance the use of alkaline amines as sorbents and the possibility that these convert into volatile alkanolamine components during the process. These unstable components degrade and convert into harmful nitrous amines in the atmosphere²⁰. The full extent of the impact of such nitrous amines on health and environment has not been established yet^{19,20}. Furthermore, using amines will lead to decomposition and create effluents and corrosion



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products, primarily ammonia and heat-stable salts. This causes an environmental problem as these effluent streams are sometimes categorized as hazardous.

Ammonia based post-combustion

There are in general two processes for liquid ammonia-based CO₂ capture^{5,18}:

- **Chilled ammonia process** – Absorption at 0 - 10(20)°C with precipitation of ammonium carbonate compounds
- **Ambient ammonia process** – Absorption at 25 - 40°C without precipitation

The absorption of CO₂ by aqueous ammonia is done in the similar absorber-desorber column process as for the amine process. Before entering the absorber the flue gas is cooled down, preferably to below 10°C. The chemistry in ammonia capture of CO₂ is somewhat less complicated than for amine solutions. Nevertheless, chemical reactions between ammonia and CO₂ are several. One of the most usual is ammonium carbonate reacting with CO₂ to form ammonium bicarbonate. The ammonium bicarbonate will precipitate as a solid at lower temperatures, for instance in the chilled ammonia process^{2,17,18}. This is a potential energy saver in solvent post-combustion capture of CO₂. Furthermore, the ammonia is thought to have a higher loading capacity than alkanolamines^{12,18}. Also the chemical itself is less expensive than amines. Although several studies conclude with the aqueous ammonia process having high potential compared to conventional amines^{9,12,21,22,23}, there are also studies that indicate its similarity, or even disadvantage compared to amine-based solvents^{24,25}.

The recirculation principle of the absorbing solvent is similar as for the amine-based absorption process where rich solution is sent to a regenerator while the lean solution is re-circulated back to the absorption tower. The regenerator is operated at a higher pressure than in amine-based processes, and can require a pressure up to more than 130 bar. The high pressure and a temperature of 50 - 200°C will evaporate the CO₂ off the water-ammonia solution in a relatively clean gas stream⁵. As a consequence, so no additional compression stage is needed.

During absorption of CO₂ in the absorber gaseous ammonia (NH₃) is released from the solution. The low temperature is needed in order to minimize the volatility of ammonia and thus the release of gaseous ammonia in the absorber (ammonia slip). The low temperature also decreases the gas volume and consequently the equipment size and investment costs^{2,5}. Ammonia is considerably less corrosive to the process



equipment^{2,6,17}. It is also more stable than most amines, will not form harmful degradation products and has no complicated chemistry. However, there are concerns about the release of ammonia vapor, especially during the regeneration stage due to the elevated temperatures¹⁷. Other by-products from the chilled ammonia process can be a value-added product, such as for instance ammonium sulfate for fertilizing purposes. Amine inhibitors as nitrogen oxides, oxygen and SO₂ will both react with ammonia and produce ammonium sulfate and ammonium nitrate^{2,6,14,15}. In addition, ammonia solutions are less corrosive than amine-based solvents². It has also been suggested that the CO₂ capacity of ammonia can be as high as three times the capacity of conventional MEA^{9,10}. The chilled ammonia process also uses less heat for solvent regeneration^{11,12} and can in certain geographical areas take further advantage of the ambient temperature in air, sea or lake for refrigeration.

2.2 Chemical adsorption and cyclic regeneration

Solids or solid oxides can be used as adsorbents in post-combustion capture of CO₂. In chemical adsorption the CO₂ gas sticks to the surface of the adsorbent⁷. Adsorbents used for gas separation are natural and synthetic zeolites, activated carbon, silica gel and activated alumina^{2,13,16,18}. Promising new sorbents are carbonates and carbon based sorbents, potassium oxide and lithium-based sorbents¹. Physical adsorption allows for a single gas component to be separated from a mixture, and has the advantage that it does not require any specific inlet conditions of the gas mixture⁷.

The adsorption capture process is principally the same as for chemical absorption where the flue gases are fed into a reaction vessel to meet the solvent. The reaction between a solid sorbent and CO₂ usually needs higher temperatures than liquid solvents which can reduce the energy penalty known from the liquid solvent scrubbing technology.

Adsorbent regeneration is achieved by cyclic changes in temperature or pressure, either in the same vessel switching between adsorption and regeneration modes or the saturated adsorbent can be taken to a separate vessel for regeneration. A minimum of two beds, each with the possibility to be in both adsorption and desorption mode, are applied in the process. As one bed is in adsorption mode, the other bed works in regeneration mode and when the beds have gained full capacity they switch to the opposite mode by opening a valve. The regeneration can either be done by varying the pressure; pressure swing adsorption (PSA), or the temperature; temperature swing adsorption (TSA). In the PSA process the adsorption takes place under high pressure and the regeneration is performed in a series of pressure reduction cycles. Each cycle lasts



for several minutes. PSA requires a higher partial pressure of CO₂ in the gas stream than TSA. Another way to regenerate the adsorbent and release the captured CO₂ is to use temperature swing adsorption (TSA). In TSA the adsorbent is regenerated and CO₂ desorbed under high temperature cycles. The TSA cycles are significantly slower than the PSA cycles as the heating process is rather slow (hours or days). The PSA cycle process is based on the original Skarstrom cycle that was originally developed for drying of air^{7,18}.

Adsorption of CO₂ from flue gases based on solid adsorbents with TSA/PSA regeneration technology is not yet available at commercial stage. A major drawback is that the process needs large equipment and brings a considerable efficiency penalty¹⁸. Hence, more research is needed for his regeneration technology before it can be regarded as competitive to other post-combustion technologies.

2.3 Membrane capture

Membranes allow selectively for certain compounds to flow through the interface while other compounds are stopped. The compound selectivity depends on the membrane quality and characteristics. Membranes are typically non-porous solids, micro porous or macro porous solids with either gas or liquid in the pore spaces, or a combination of the aforementioned. Membranes used for post-combustion CO₂ capture are usually polymeric (cellulose acetate and polyimide), but emerging technology is underway concerning both ceramic and carbon membranes. The diffusion of a component through the interface is directly connected to its molecular weight and the material moves through the membrane interface either by physical (pressure), chemical (concentration) or electrical force. In all cases it is the pressure gradient that is the driving force for the diffusion, and for this reason membrane separation is better suitable for high-pressure streams such as in for instance natural gas purification. Membrane in large-scale CO₂ capture for other industrial processes is challenging both from an engineering point of view and from an economic point of view, and the technology is currently more costly than the more traditional chemical solvent based post-combustion scrubbing techniques. Large-scale use of membranes for CO₂ separation from other gases is widely used in natural gas purification^{1,2,7,17}. However, application of membranes in industries with low partial pressure of CO₂ in the flue gases is not suitable due to the large amounts of gas that need to be moved through the membrane interface¹⁸.

One major advantage with membrane separation techniques is that there is no interrelation between the flue gases and the solvent as in for instance wet scrubbing with



amines. Problems like fouling, channelling and foaming are eliminated and the flue gas flow rate is adjustable. There is no need for membrane regeneration and there are no complicated physical or chemical operations. As a consequence, operational costs are lower than for solvent based post-combustion capture systems. Also capital costs are lower, but some processes require certain pre-treatment processes, and the extent of these can affect the capital cost significantly⁷.

2.4 Carbonate looping for CO₂ capture from flue gases

Carbonate looping is a temperature-swing adsorption process driven by the difference in equilibrium CO₂ vapour pressure between the adsorption and desorption temperatures. The process is usually assumed to operate with fluidised-bed reactors, with CaO and CaCO₃ particles circulating between the adsorber/carbonator and desorber/calciner. The use of carbonate looping for CO₂ capture from flue gas was first introduced in 1999 by Shimizu²⁶. The calcination process is otherwise a standard process in the cement industry for producing lime (CaO with CO₂ as by-product) from natural limestone (CaCO₃).

A standard carbonate looping capture process is principally shown in Figure 2.. Flue gas enters the carbonator from below and is contacted with a fluidized stream of CaO particles which also enters the reactor in the bottom area. Decarbonised flue gas exits from top the reactor while CaCO₃ particles formed by reaction with CO₂, as well as unreacted CaO particles, are collected and transported to the calciner. For post-combustion CO₂ capture both carbonator and calciner will operate at approximately atmospheric pressure. In the carbonator the exothermal and spontaneous carbonation reaction (Eq. 2) takes place with a standard reaction enthalpy of -178 kJ/mol. In the calciner the reaction is reversed by adding heat, most commonly assumed to be supplied through internal oxy-firing of fuel.



Heat generated in the carbonator as well as the high temperatures of cleaned flue gas and captured CO₂ can be utilised for steam generation. In general, internal heat recuperation in the carbonate looping cycle is very important for the overall efficiency of such a decarbonised power process. This also includes the solid streams crossing between the reactors. The solid stream leaving the carbonator at temperatures typically between

600°C and 650°C should be pre-heated by heat exchange with the hot stream of CaO leaving the carbonator at typically 950°C. Lack of heat integration between these streams will yield a double penalty in form of heat surplus in the carbonator and a corresponding heat deficit in the calciner, resulting in a higher energy requirement. The issue of effective heat transfer between the fluidised streams is, however, still an unresolved issue²⁷. Several principles for how this can be done have been presented by Martínez et al.²⁷

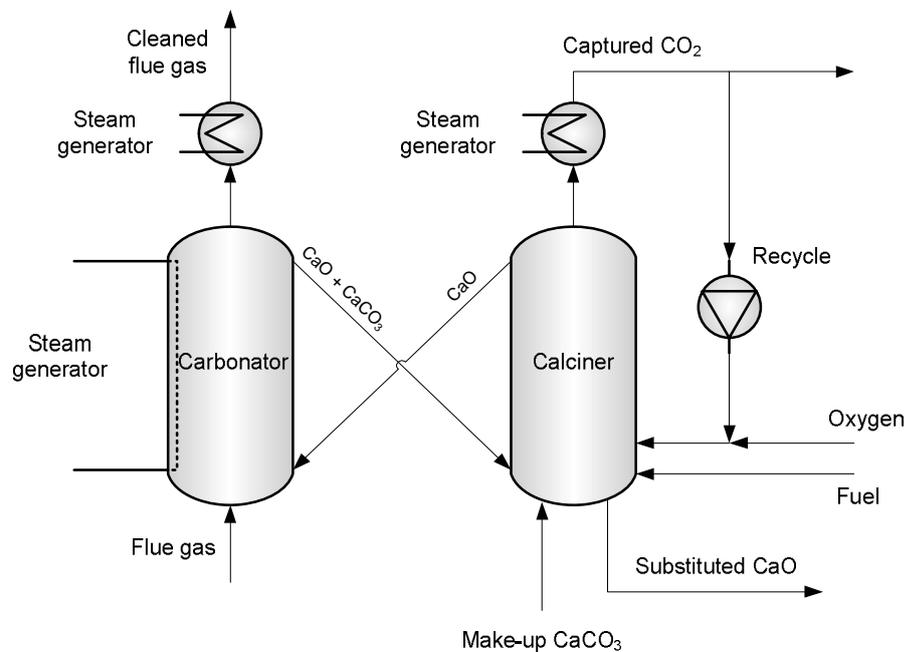


Figure 2.3 Process flow diagram for the carbonate looping capture cycle. Partly reproduced from²⁸.

For the carbonation and calcination reaction described in Eq. 2, the equilibrium partial vapour pressure of CO₂ as function of temperature is shown in Figure 2.4²⁹. According to the vapour pressure equilibrium line the desorption temperature must be above to 900°C to obtain complete calcination, which in theory corresponds to a CO₂ vapour pressure of 1 atmosphere. As full equilibrium may not be obtained in practice, even higher temperature may be required. 950°C is commonly assumed for calciner operation temperature, corresponding to an equilibrium CO₂ vapour pressure of about 1.9 bar.

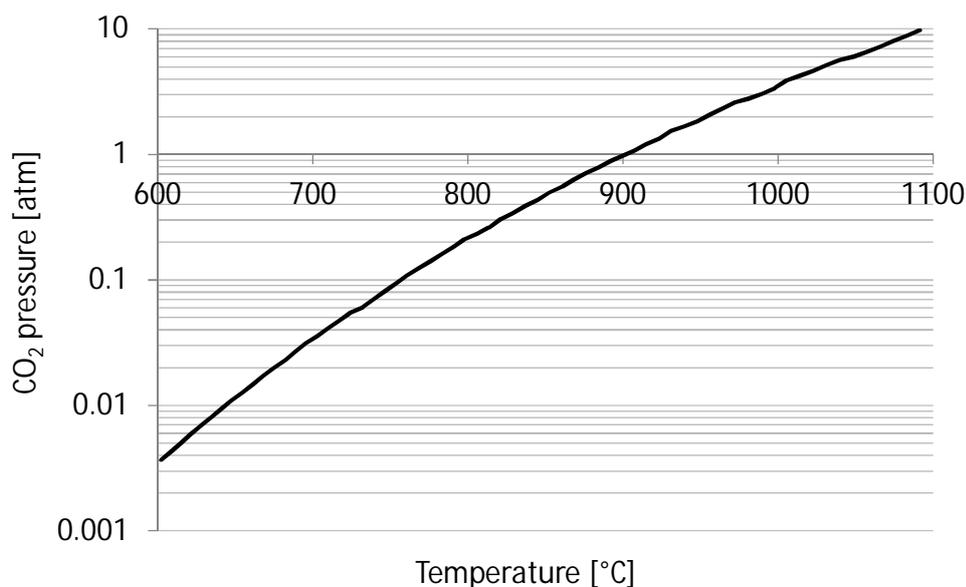


Figure 2.4 CO₂ equilibrium vapour pressure in the carbonation/calcination reaction regime. Diagram reproduced from³⁰.

On the other hand the operating temperature for the carbonation reactor must be sufficiently low to allow sufficient capture rate. Although a lowest possible temperature difference between the carbonator and calciner would be beneficial to the efficiency due to lower thermal losses in the cross-stream heat recuperation, the carbonator temperature is, given a targeted capture rate, limited upwards by the CO₂ equilibrium vapour pressure as well as flue gas CO₂ concentration. This carbonator temperature constraint is illustrated in [Figure 2.](#) Based on equilibrium calculations assuming atmospheric carbonator pressure, the equilibrium lines describing the relation between reactor temperature, flue gas CO₂ concentration and specified CO₂ capture rate, are plotted. It can be observed that in the case of 90% capture from a flue gas with 12% CO₂ concentration, the maximum allowed carbonator temperature is approximately 650°C. For flue gases with lower CO₂ concentration such as natural gas combined cycles (3–4%), the maximum carbonator temperature is about 600°C or lower, given a 90% capture rate.

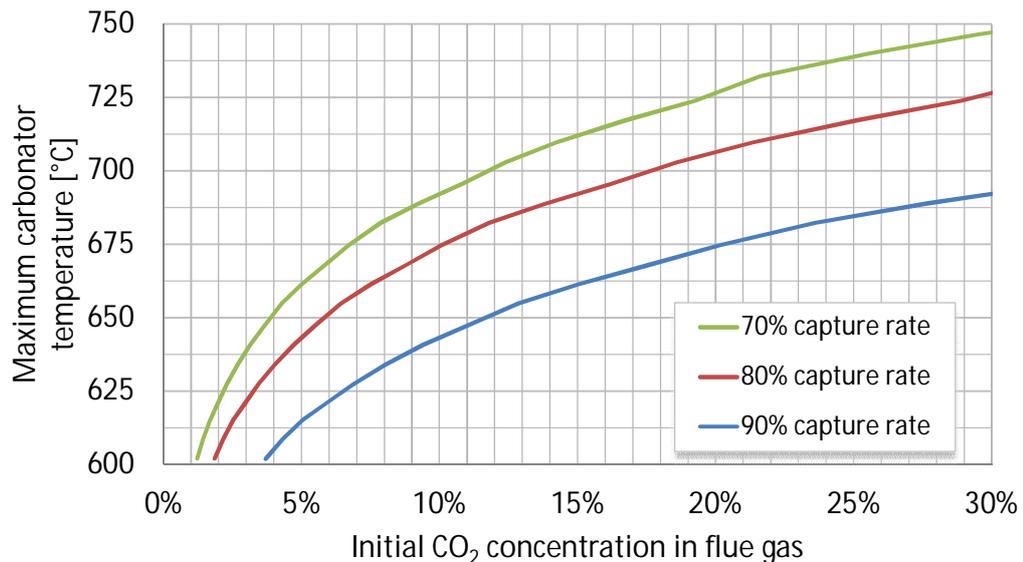


Figure 2.5 Maximum carbonator operating temperature as function of atmospheric flue gas CO₂ concentration and targeted CO₂ capture rate.

With the use of naturally occurring CaCO₃ in the capture cycle, a constant substitution of sorbent material is required in order to maintain sufficient adsorption capacity in the carbonator. This is done by adding fresh make-up sorbent to the calciner while CaO is removed at an equal rate, keeping the overall inventory constant. The average adsorption capacity is determined by the average cyclical age of the adsorbent inventory, and different models for describing this parameter exist. For an average particle in the cycle the average carbonation efficiency, the number of moles CO₂ absorbed per mole of CaO at equilibrium, will decrease with the number of carbonation/calcination cycles undergone. This decay of capacity is described in [Figure 2.](#). As can be observed, the carbonation efficiency decreases rapidly with the first cycles and eventually stabilises at a value commonly denoted as the residual capacity.

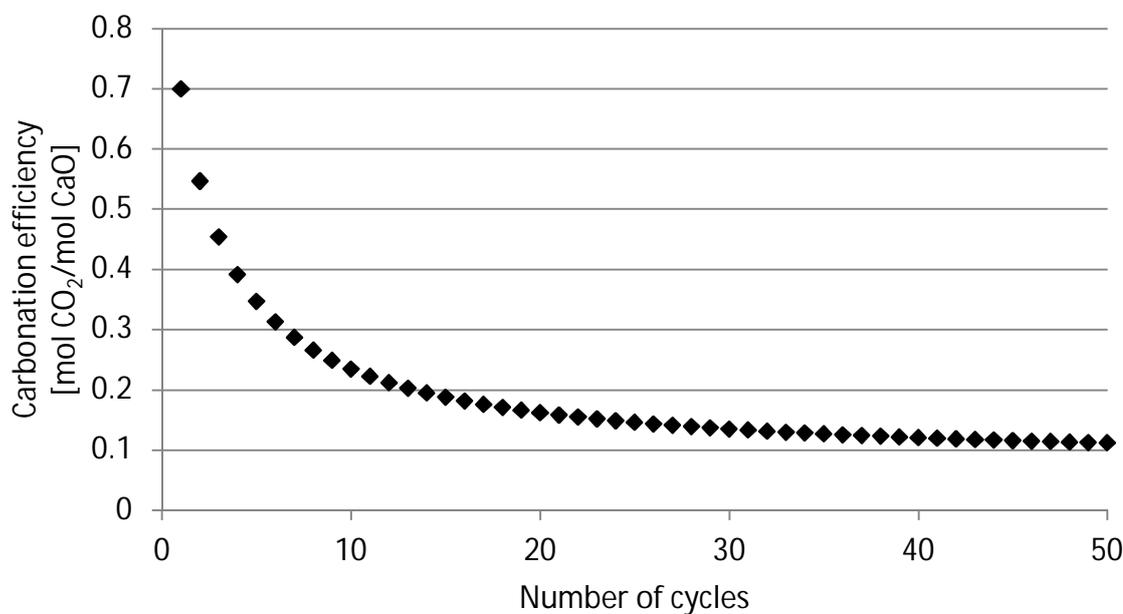


Figure 2.6 Carbonation efficiency for an average CaO particle as a function of number of cycles undergone.

Calculations on finding the energy-optimal average carbonation efficiency, and thus energy-optimal sorbent make-up rate, have been presented by Rodriguez et al.³⁰. Values in the range 5–6% CaCO₃ make-up rate relative to the total molar flow of sorbent in the cycle, has been used in some recent studies. If the cycle were operated without any sorbent make-up, average carbonation efficiency in steady state would equal the residual value, resulting in an excessive mass flow of inactive CaO and thus large thermal losses. As CaCO₃ is a naturally abundant and cheap sorbent material, high make-up rates may be possible for a full scale capture plant, provided that the infrastructure allows for this. An obvious example for adequate infrastructure would be co-location with a cement production site. However, if a solid sorbent CO₂ capture cycle is to be operated without or with a very small make-up rate, synthetic sorbents with significantly higher residual carbonation efficiency would likely be required.

A summary of publications on the carbonate looping cycle for CO₂ capture from is given in [Table 2.1](#).

Table 2.1 Summary of publication results for carbonate looping capture cycles.
Table partly reproduced from²⁸.

Study	Type of process	Reference power cycle efficiency (without capture)	Power cycle efficiency with capture	Efficiency penalty [%-points]	Capture rate ^a
Shimizu et al. ²⁶	Coal-fired power cycle with primary super-critical and secondary sub-critical steam cycle.	n/a	33.4% (HHV)	n/a	90.4%
Abanades et al. ³²	Coal, biomass and petcoke. Five different carbonate looping cycles.	n/a	37.7–40.0% (LHV)	n/a	90%
Romeo et al. ³³	Coal-fired super-critical steam cycle.	44.93% (LHV)	37.04% (LHV)	7.89	85%
Li et al. ³⁴	Coal-fired power cycle with three different CaO-based sorbent materials.	38.3% (HHV)	32.8% (HHV)	5.5	85%
Martínez et al. ³⁵	Super-critical coal-fired power plant.	45% (LHV)	37.5% (LHV)	7.5	86%
Martínez et al. ³⁵	Super-critical coal-fired power plant.	45% (LHV)	34.8% (LHV)	10.1	96%
Kunze et al. ³⁶	IGCC integrated with membrane oxygen separation.	n/a	43.2% (LHV)	n/a	98%
Martínez et al. ³⁷	Three novel capture cycles in a coal-fired power plant.	44.35% (LHV)	n/a	n/a	90%
Berstad et al. ²⁸	Natural gas combined cycle with standard primary and three different options for secondary steam cycle.	58.1% (LHV)	45.6–48.1% (LHV)	10.0–12.5	> 90%

^a Accounting for both fuel fired in power cycle and in calciner



2.5 Low-temperature and cryogenic CO₂ capture technologies

Within the field of CCS technologies where CO₂ is separated from flue gas or synthesis gas by either condensation or solidification, the term “cryogenic” is commonly used as description. This is, however, inaccurate according to the scientific interpretation of the term. The physical definition of 'cryogenics' refers to temperature levels below -153°C (120 K)³⁸ and since most low-temperature CCS processes operate well above this threshold temperature, they should rather be denoted as 'low-temperature' processes.

Compared to other capture technologies such as solvents, sorbents, oxy-fuel and membranes, the volume of published literature on low-temperature technology is very low. However, the latest years have shown a growing interest in the field and several recent publications on the topic are available in the literature.

Low-temperature capture cycles can in principle be applied for all three capture routes within power generation as well as industrial processes. A literature review of various applications is given in the following.

2.5.1 Oxy-fuel applications

Although oxy-fuel processes have the potential of generating flue gas with very high CO₂ concentration after water removal, additional processing is required in order to meet purity specifications for CO₂ transport and storage. A principal layout of an oxy-fuel process is shown in

Figure 2.7 and as can be observed, a CO₂ processing unit (CPU) and a compression section are located downstream of the CO₂ recycle loop.



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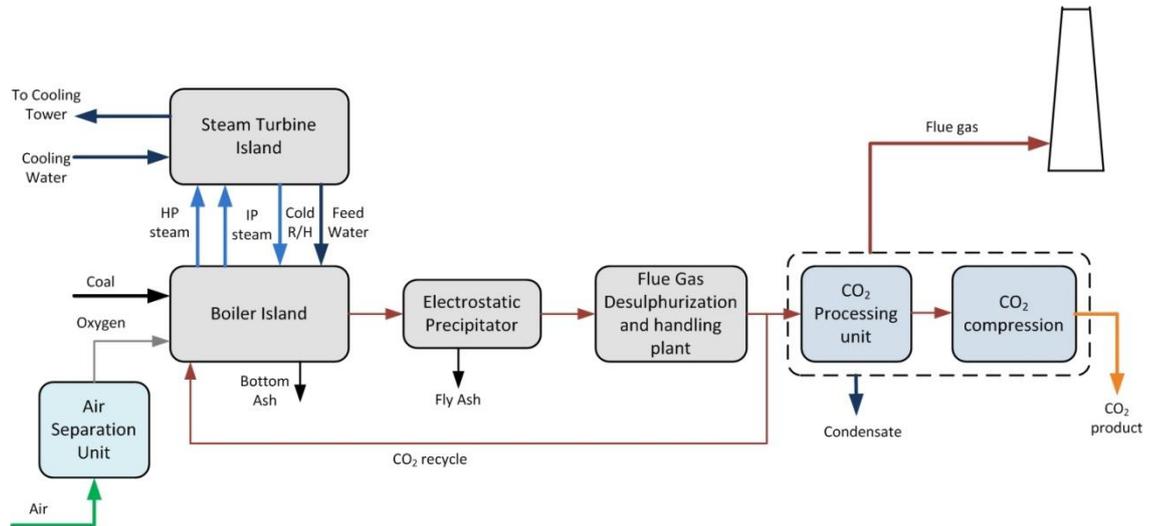


Figure 2.7 Principal process flow diagram for an oxy-fuel cycle with CO₂ capture and conditioning. Facsimile from³⁹.

Since the CO₂ purity of the flue gas is typically 60–90% after water removal, further purification is required by removing non-condensable component such as oxygen, nitrogen and argon. Low-temperature CPUs operating at -50°C or lower is considered state-of-the-art for this processing step. Although several different designs of low-temperature CPUs exist, the processing principles are still the same, as illustrated in Figure 2.. The flue gas is first compressed from near-atmospheric pressure to a pressure level around 30 bar and stripped of pollutants such as SO₂, NO_x, mercury and more. Moreover, the water concentration is reduced to ppm levels to prevent ice build-up and potentially devastating blocking of equipment in cold parts of the process.

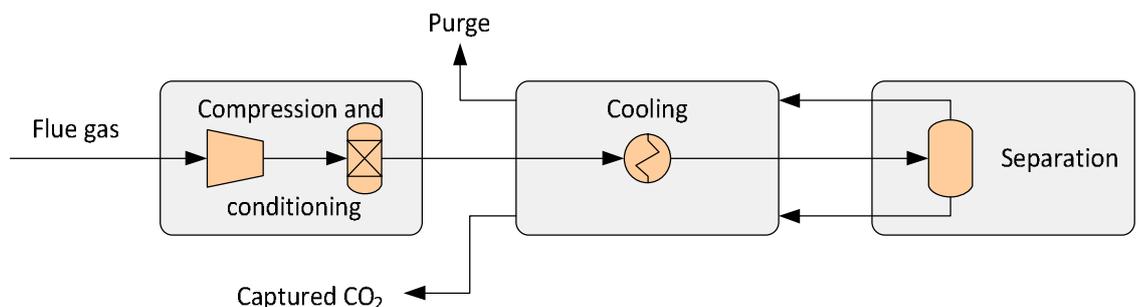


Figure 2.8 Principal scheme of a low-temperature oxy-fuel CO₂ processing unit.



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After pressurisation and conditioning the flue gas is cooled to a separation temperature typically between -50°C and -55°C , possibly -56°C , depending on temperature on the refrigerant side of the heat exchanger as well as required safety margin to the CO_2 freezing point. A large fraction of the total flue gas CO_2 content has then been condensed and the separation between the CO_2 -rich liquid phase and the volatiles-rich gaseous phase is carried out with a single separator or multiple separation stages operating at different temperatures. After separation the cold energy of the gaseous and liquid separation products should be utilised for feed pre-cooling to maximise the energy efficiency. The purified CO_2 stream is then compressed to transport pressure while the volatiles-rich gaseous stream is expanded and vented to the atmosphere.

The design of refrigeration cycles in CPUs varies and can be typically configured as open or semi-closed CO_2 cycles with captured CO_2 as refrigerant (auto-refrigerated process), or closed-loop vapour compression cycles with for instance propane, ethane, CO_2 or mixtures as refrigerants (auxiliary refrigeration).

A summary of recent studies on low-temperature capture processes related to oxy-fuel and similar flue gases is given in Table 2.2.2.

Table 2.2: Recent studies on low-temperature CO₂ processing units.

Study	Process description	Flue gas CO ₂ concentrations investigated	Minimum CO ₂ temperature in process [°C]
Amann et al. ⁴⁰	Three gas–liquid separators with semi-closed CO ₂ refrigeration cycle.	67–86% ^a	-50
Benthum et al. ⁴¹	Dual-pressure process with two gas–liquid separators. Generic auxiliary refrigeration cycles with COP = 2.	35–64%	-55
Berstad et al. ⁴²	Single-pressure process with two gas–liquid separators. Propane and ethane auxiliary refrigeration cycle.	30–77%	-56
Castillo ⁴³	Single gas–liquid separator with auxiliary CO ₂ /NH ₃ cascade refrigeration cycle.	75–80%	-50
Pipitone and Bolland ⁴⁴	Single-pressure processes with: double gas–liquid separators and open CO ₂ refrigeration cycle; or single distillation column with propane and ethane auxiliary refrigeration cycle.	75%, 88%	< -54
Posch and Haider ⁴⁵	Single-pressure processes with: double gas–liquid separators and open CO ₂ refrigeration cycle; or single distillation column with semi-closed CO ₂ refrigeration cycle.	72%, 76%	-55.5
White et al. ⁴⁶	Single-pressure process with two gas–liquid separators and open CO ₂ refrigeration cycle.	75–85% ^a	-55
Wilkinson et al. ^{47,0}	Single-pressure process with two gas–liquid separators and open CO ₂ refrigeration cycle.	77%	-55.8

^a Before final dehydration



2.5.2 Post-combustion applications

CO₂ capture from atmospheric flue gases by compression and partial condensation, as described above, is not practically possible for CO₂ levels in most coal- and natural gas-fired power plants and industrial plants, unless processes are modified to generate more concentrated flue gases. When the CO₂ concentration gets too low for vapour–liquid separation the capture rate and energy demand will not be competitive with baseline technology. This implies that vapour–solid separation must be applied if a high capture rate is to be obtained for flue gases with low CO₂ concentration, for instance in the 1–15% range, by low-temperature capture.

For post-combustion CO₂ capture by vapour–solid separation a rather low volume of publications currently exists. In the following, a brief overview of some important works is given.

Clodic et al.

Clodic et al.⁴⁸ have developed a CO₂ capture scheme applied to flue gas with a CO₂ concentration of 12% by solid freeze-out. In the study a CO₂ capture rate of 90% is assumed from an 800 MW coal-fired power plant.

A process flow diagram for the capture scheme is shown in [Figure 2.](#) The flue gas is first cooled by an integrated cascade refrigeration cycle to -100°C. The cascade cycle is operated with a mixed refrigerant made up by a composition of methane, ethane, propane and butane. The solid CO₂ formed during the cooling is then separated from the volatile components in the flue gas, mainly nitrogen and oxygen, and subsequently defrosted.

Due to the low temperature delivered by the cascade refrigerator the overall energy consumption is highly sensitive to the coefficient of performance (COP) of the cycle. In this study COP is assumed to be 1.97 and 0.75 for -40°C and -120°C, respectively. Overall capture cycle power is calculated to 201 MW, equivalent to a 9.9 %-points electric efficiency penalty for the power plant and 1.18 MJ/kg_{CO2} specific capture and compression work.

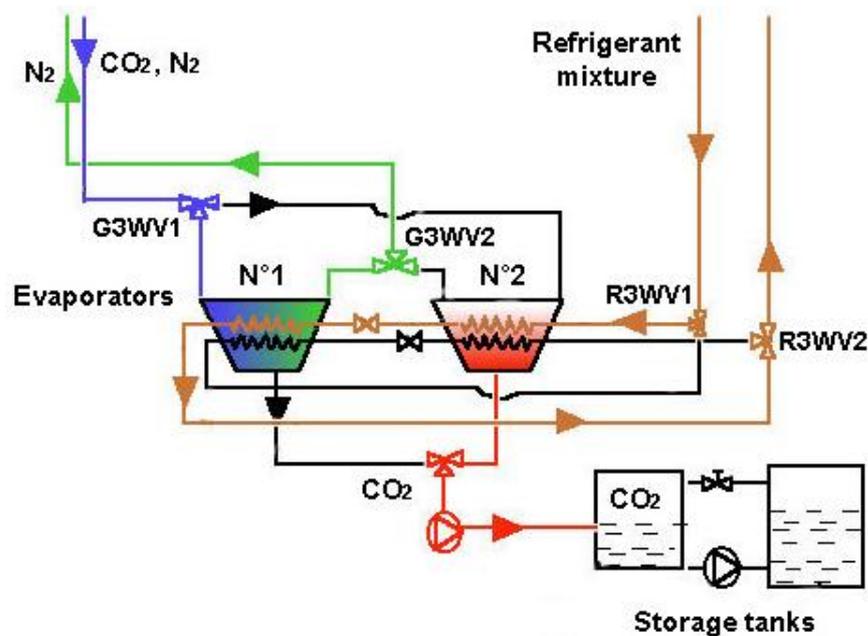


Figure 2.9 Process flow diagram of the low-temperature capture cycle by Clodic et al. Facsimile from⁴⁸.

Tuinier et al.

Tuinier et al.⁴⁹ have documented results for a low-temperature capture method where solid CO₂ is formed on the surface of pre-cooled packed beds contacted with flue gas. A process flow diagram of this process is shown in Figure 2.1 and an illustration of CO₂ solidification on the pre-cooled packed bed is shown in Figure 2.2. The process, consisting of several beds, is operated batch-wise and semi-continuous with each bed undergoing a sequence of cycles⁴⁹:

1. Capture cycle: hot flue gas flows through the pre-cooled packed bed. The initial bed temperature, typically between -150°C and -120°C, ensures that CO₂ is deposited onto the bed while nitrogen stays in the gaseous phase. The capture cycle is run until gaseous CO₂ breaks through at the end of the bed.
2. CO₂ recovery cycle: the bed is flushed with already captured gaseous CO₂ until all deposited CO₂ has been melted and recovered. The exiting stream of pure CO₂ is partly compressed for transport and partly recycled for use in the CO₂ recovery cycle.
3. Cooling cycle: a pre-cooled gas, for instance cleaned flue gas cooled by LNG evaporation or a refrigeration cycle, is flushed through the packed bed until the temperature is reduced to the specified initial bed temperature.

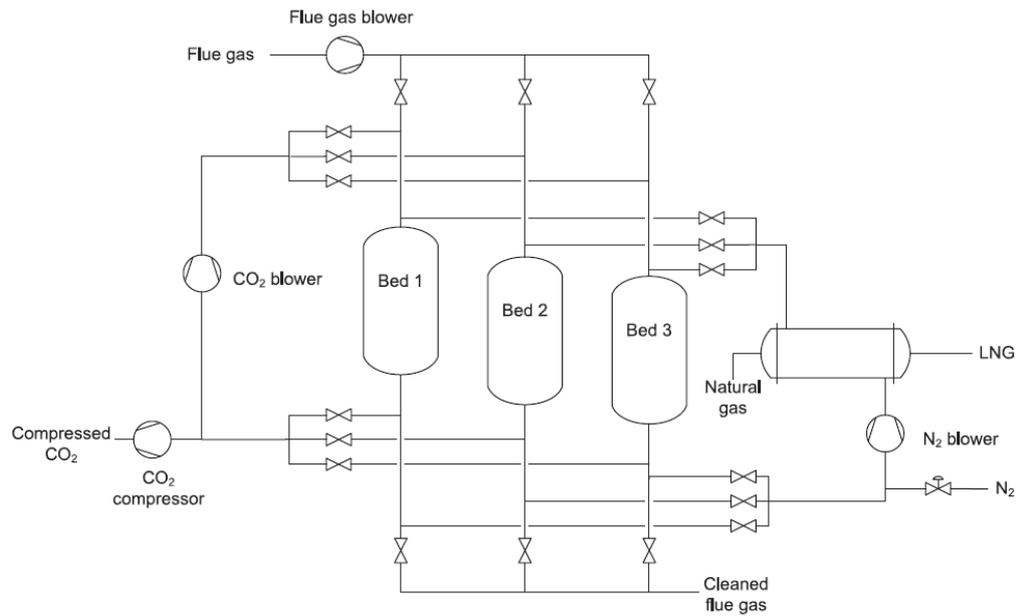


Figure 2.10 Process flow diagram of the low-temperature CO₂ capture process by Tuinier et al. Facsimile from⁵⁰.



Figure 2.21 CO₂ solidification on pre-cooled packed bed. Facsimile from⁵¹.

GE Global Research

GE Global Research will present a low-temperature capture process capturing CO₂ from flue gas by solidification at the 11th International Conference on Greenhouse Gas Technologies (GHGT-11) in November 2012. As can be observed from the process flow diagram in Figure 2.3, flue gas is first compressed from atmospheric pressure, cooled and then expanded to temperature below the CO₂ freezing point. The solid CO₂ formed during the cold expansion is separated from the flue gas by a cyclone, pressurised in solid form and melted to liquid before final pressurisation for transportation by liquid pumping.

At the present time the only available documentation is in the form of an extended abstract to GHGT-11⁵². This abstract claims that preliminary results indicate a 45% reduction of specific energy requirement compared to post-combustion capture by MEA absorption, as well as a 50% reduction in specific capture cost.

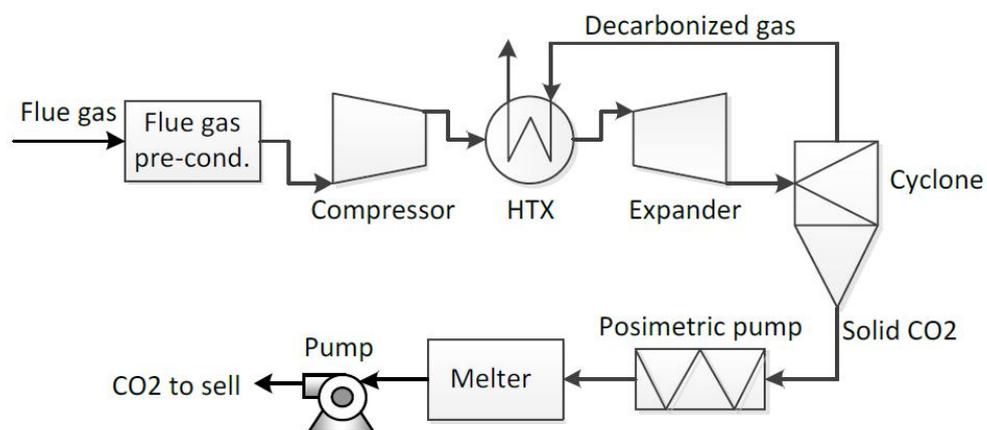


Figure 2.32 Process flow diagram of the low-temperature CO₂ capture process by GE Global Research. Facsimile from⁵².

2.6 Pre-combustion applications

Shifted synthesis gases, principally from coal gasification but also natural gas reforming, are in principle readily available for low-temperature capture by condensation of CO₂ and vapour-liquid separation. The process principles are very similar to those applied in oxy-fuel flue gas purification where pressurised gas is cooled to temperatures slightly above that of CO₂ solidification. However, as the synthesis gas CO₂ concentrations will be lower than for oxy-fuel, typically 30–45% for coal gasification and for instance 15–

25% for natural gas reforming, higher pressure is required for obtaining high capture rates. For binary mixtures of H₂ and CO₂, the relation between initial CO₂ concentration, separation pressure and CO₂ capture rate is shown in Figure 2.4. As real synthesis gas compositions from oxygen-blown processes are made up by mainly H₂ and CO₂ this is a good estimate for what capture rates can be expected.

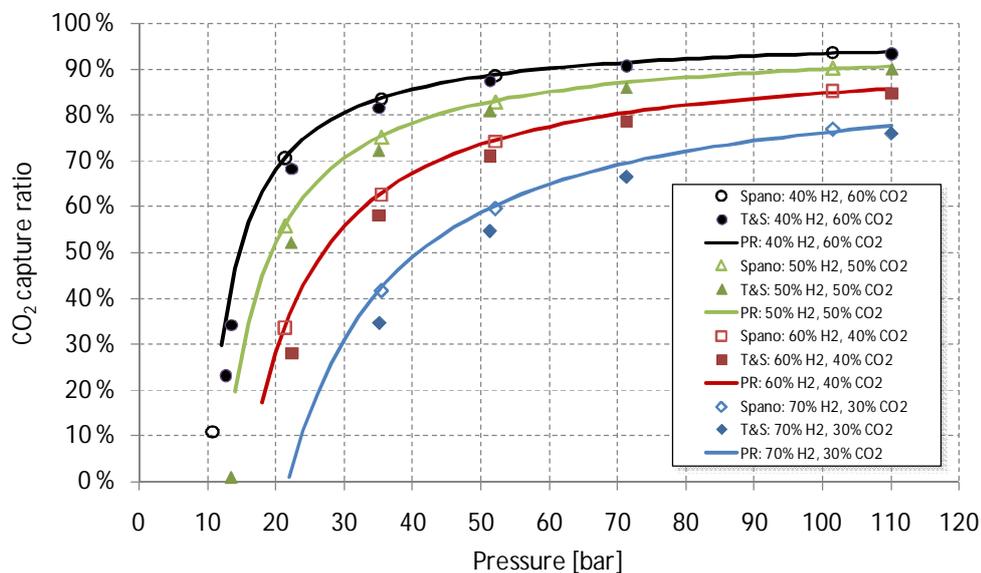


Figure 2.43 Relation between obtainable CO₂ capture rate, separation pressure and chemical composition for a binary mixture of hydrogen and CO₂. Separation temperature is specified to -56°C. Facsimile from⁵³.

A principal process flow diagram for a low-temperature pre-combustion capture process is exemplified in Figure 2.. In this process scheme shifted synthesis gas is first compressed to desired separation pressure depending on targeted capture rate, and subsequently cooled by auxiliary refrigeration cycles as well as by heat exchange with cold separation products. When the gas has been cooled to separation temperature it enters a separation drum where a CO₂-rich liquid product and H₂-rich fuel product are separated. A secondary purification drum is also included in the process for obtaining CO₂ with very high purity and recovering H₂ dissolved in the liquid CO₂ from the first separator. Auxiliary cooling requirements are in the case of Figure 2. provided by propane and ethane refrigeration cycles in a cascade configuration.

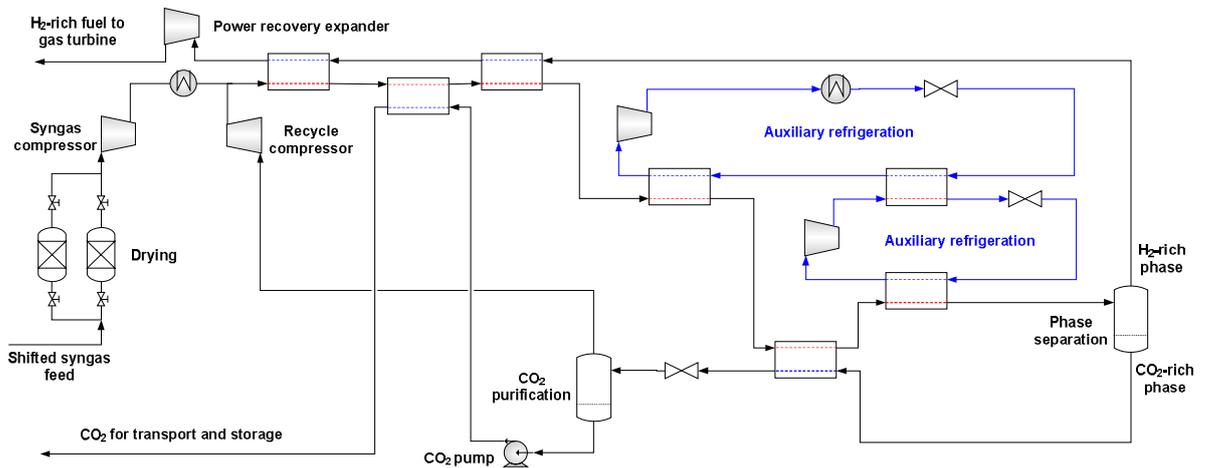


Figure 2.14 Process flow diagram of a low-temperature CO₂ capture process for shifted synthesis gas. Facsimile from⁵⁴.

A summary of publications on CO₂ capture processes based on low-temperature synthesis gas separation is given in Table 2.3.

Table 2.3 Summary of publications on low-temperature synthesis gas separation processes.

Study	Process description	Syngas CO ₂ concentration	Separation pressure [bar]	Separation temperature [°C]	Capture rate
Brouwers and Kemenade ⁵⁵	Condensed rotational separation.	44%	60	-54	80%, 95% ^a
Xu et al. ⁵⁶	Single-pressure process with two gas–liquid separators.	42%	30	-38, -55	90–94% ^b
Berstad et al. ⁵⁷	Distillation column. Propane and ethane auxiliary refrigeration cycles.	38%	51	-56–6 ^c	73%
Berstad et al. ⁵⁴ 0 –	Two gas–liquid separators and propane and ethane cascade auxiliary refrigeration cycle.	38%	110	-56	85%

^a With physical absorption downstream of low-temperature process

^b Combined with pressure-swing adsorption

^c Distillation column with 6°C reboiler temperature and -56°C condenser temperature



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3. OXY-FUEL COMBUSTION

3.1 Introduction

Oxy-fuel combustion is considered as a promising technology and a near-term option for carbon dioxide (CO₂) capture and storage from power plants and carbon intensive industrial processes. The concept of oxy-fuel combustion is removing nitrogen from the combustion medium yielding a flue gas that consists mainly of CO₂ (>90% on a dry basis). Oxy-fuel combustion can be used both for newly built and retrofitted plants. However, in most cases the oxy-fuel operation would require significant changes to the existing plants making it a less attractive option for retrofitting compared to end-of-pipe technologies for CO₂ capture, such as CO₂ absorption.

The development of the oxy-fuel process has mainly focused on employment in the power sector and specifically the combustion of pulverized coal, due to the key role of pulverized coal in base load electricity generation and its major contribution to CO₂ emission. The research work focused on the fundamentals of oxy-fuel combustion of pulverized coal has recently been reviewed by Chen et al.¹ and Toftegaard et al.². Oxy-fuel technology could also be applied to simple cycle and combined cycle power plants using natural gas or distillate oil. Yet, because of the significant modifications to the design of gas turbines required and the higher cost per tonne of CO₂ captured, the interest in gas applications has so far been limited³. The oxy-fuel technology may also be applied to industrial processes, such as refineries, petrochemical industries, cement industry, and iron and steel production. For the refining and petrochemical sector, the oxy-fuel technology is an attractive option and is estimated to be more favorable in terms of CO₂ capture cost compared to other CCS technologies⁴. Integration of the oxy-fuel technology to the clinker burning process in the cement industry has been studied theoretically. The studies performed are summarized by the European Cement Research Academy⁵. Capturing CO₂ from the blast furnace in the iron-making process is possible with the oxy-fuel technology⁶. Different options for application of oxy-fuel to industrial processes and comparison with other capture technologies has been reviewed by the United Nations Industrial Development Organization (UNIDO)⁷ and Kuramochi et al.⁴

This report briefly presents the oxy-fuel process and the application of the technology to power and carbon intensive industrial sectors. Recent achievements in research related to the oxy-fuel combustion of pulverized coal are briefly described. The results gained from the power sector can establish a starting point for the integration of the oxy-fuel



technology to other industries. However, the different conditions in the industrial processes necessitate experiences from demonstration projects for the respective process as well. In the first section of the report, the current status of oxy-fuel combustion development is described and issues regarding commercialization are addressed in brief. In the second section the focus is on the oxy-fuel power plant technology. Fundamentals of oxy-fuel combustion are briefly mentioned and different units of oxy-fuel power plants are described. Different flue gas cleaning approaches are also pointed out. Some alternative oxy-fuel concepts are also briefly mentioned. The second section contains summary of application of oxy-fuel technology to three carbon intensive industrial sectors i.e. iron and steel, cement, and petroleum refineries. The main technical challenges requiring further research are listed in the last section.

3.2 Research activities - the current international status of the technology

The oxy-fuel technology, as one of the three major carbon capture technologies, is currently under development. However, barriers still remain to its commercial deployment. The current significant technical barriers include the cost and energy penalty associated with O₂ production, and CO₂ recovery issues associated with flue gas treatment and cooling⁸. However, at this point in time, issues regarding uncertainties around CO₂ market, lack of regulations regarding quality of CO₂ for transport and storage and public acceptance are more significant than the technical barriers⁸. Currently, the development of large scale projects in Europe has been slowed down mainly due to low carbon prices. It should be noted that these barriers are not specific to oxy-fuel technology and are faced in the development of all CCS technologies⁹. Nevertheless, gaining experience from running demonstration projects is a necessary step toward commercialization. The current and planned demonstration and industrial pilot plant projects applying the oxy-fuel technology are summarized in Figure 3.1. These projects indicate the development of the scale of oxy-fuel technology. All of the projects are power plants and the majority of them use pulverized coal. However, the Lacq project is natural gas fired, the Compostilla project uses a circulating fluidized bed boiler, and the ENEL project applies high pressure oxy-fuel technology.

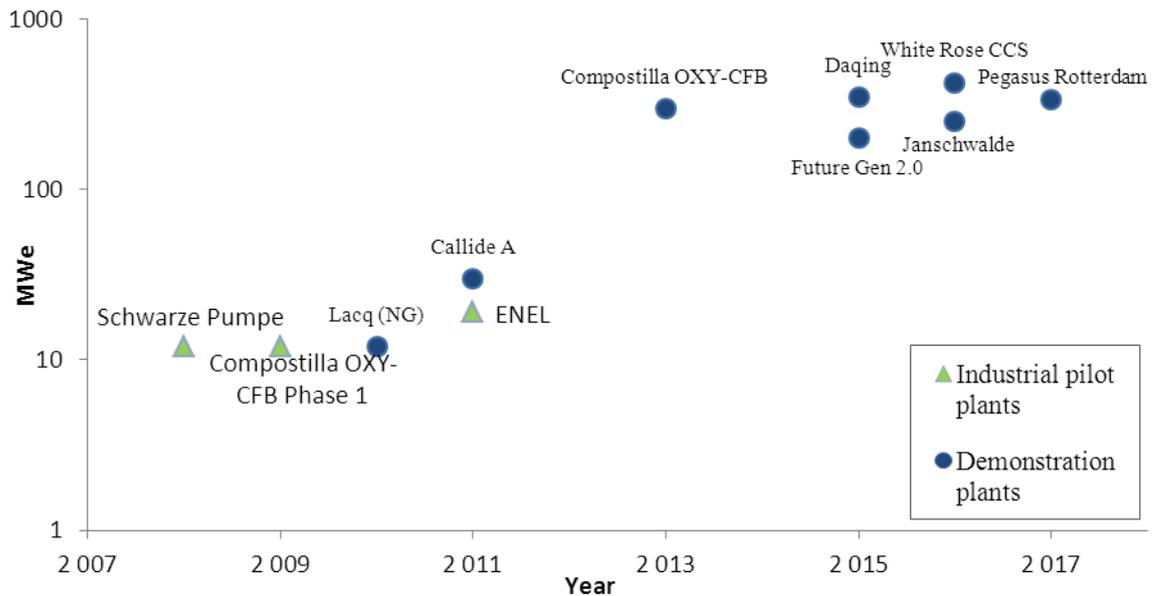


Figure 3.1. Overview of large scale (only industrial pilot plants with power production of more than 10 MWe are included) oxy-fuel projects. Data is received from refs. 10 and 11.

3.3 Oxy-fuel power plant technology for CCS

The oxy-fuel combustion process is schematically shown in Figure 3.2. Pulverized coal is burned in the oxidizer stream i.e. oxygen with purities above 95% and recycled flue gas. The properties of the combustion process e.g. temperature, burner aerodynamics and residence time are controlled by the flow of recycled flue gas. Since the atmospheric nitrogen is eliminated, the flue gas consists mainly of CO₂ and water vapor. Particles are separated from the flue gas downstream of the boiler and upstream of the flue gas condenser (where water is separated from the flue gas). In order to achieve cost-effective transportation and storage, CO₂ has to be condensed and compressed before it is discharged from the power plant.

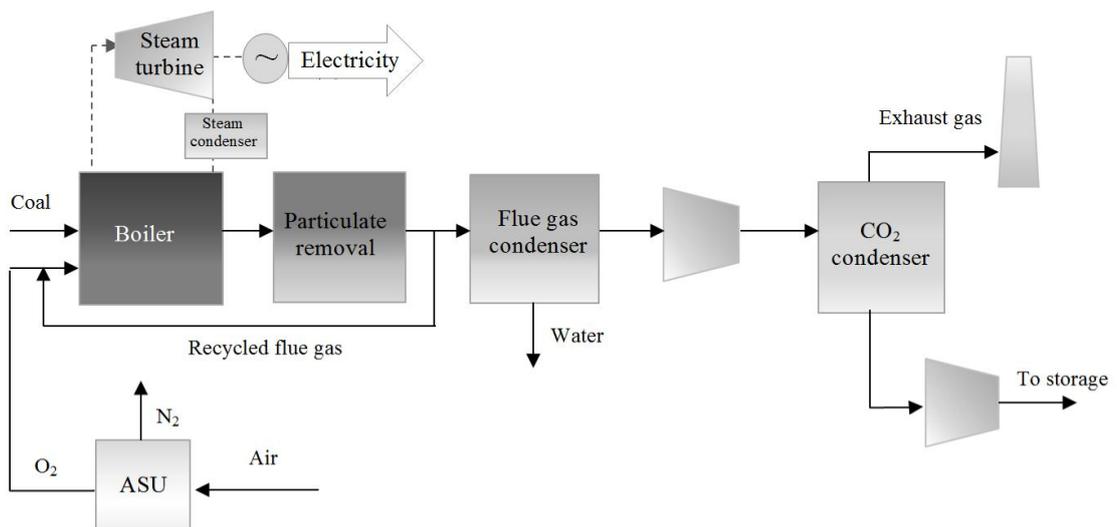


Figure 3.2. Schematic of an oxy-fuel power plant, ASU: Air Separation Unit

The exhaust flue gas consists of around 90-95% CO₂ on a dry basis. The stream also contains oxygen, nitrogen and argon resulting from impurities in the oxygen, the excess oxygen for combustion, and air leakage into the system. The purity of oxygen influences the energy use and investment in the air separation unit. Besides, for safety reasons, coal-fired furnaces usually operate at slightly sub-atmospheric pressures. This results in increased risk of air leakage to the system. The air ingress could be avoided in the furnace by making it gas-tight. However, air leakage is still possible even for a gas-tight or slightly pressurized boiler in the particle separation, in recycle fan and in the coal feeding system. These gases should be removed from the CO₂ stream to avoid increasing the critical pressure of CO₂ and possible development of two-phase flow in the pipeline. This is achieved in the CO₂ liquefaction process with the separated gases vented into the atmosphere.

Nitrogen oxides (NO_x) and sulfur oxides (SO_x), as by-products of the combustion, are also present in small amounts (0.1-0.2 %.). These acid gases have to be removed from the CO₂ stream before it leaves the power plant to meet possible future regulations of the storage sites and prevent corrosion in the pipelines. The removal of these impurities can be carried out in various parts of the process. The resulting CO₂ capture rate is expected to be around 90-95% , in first generation plants². The exact purity requirement of CO₂ stream is not fully clarified and may vary depending on different storage scenarios.



According to the European Union's directive on the geological storage of CO₂, the storage gas should consist "overwhelmingly" of carbon dioxide¹². According to EU 2009¹², the CO₂ stream may contain incidental and added substances if their concentrations are below the levels that would have adverse effects on the storage sites, cause a significant risk to human health or environment or violate the requirements in the legislation of the applicable community. It should also be noted that the higher the purity of the CO₂ stream received at the storage site, the more are the overall efficiency losses and operational costs for purification. On the other hand, higher purity decreases the safety demands of transportation and storage.

The design of oxy-fuel power plants may be divided into two generations¹³ where the first generation oxy-fuel power plants will use, as much as possible, technology proven in air-fired power plants in order to achieve a secure and rapid introduction of the technology (retrofit of existing power plants is also included in this generation). In such first generation power plants the operation of oxy-fuel combustion mimics that of air combustion and conventional flue gas cleaning equipment is employed. In a second generation plant, more innovative techniques could be applied and new operational conditions can be developed. For instance, changing the concentration of oxygen in the oxidizer, which is not a possibility in air combustion, could result in lower gas flows through the boiler (changed dimension of furnace) and higher flame temperatures which in turn can improve the combustion efficiency but influence ash behavior¹³. The second generation technology is expected to emerge due to the need to reduce the efficiency penalties and costs⁸. The design of the second generation oxy-fuel power plants are expected to be accomplished when CCS is established as a part of the energy system and legislation adapted for oxy-fuel conditions exist¹³. Different parts of an oxy-fuel power plant and some of the fundamental differences between oxy-fuel combustion and air combustion are described in the following sections.

3.4 Oxy-fuel combustion

The change of the combustion medium (replacement of N₂ by CO₂ and water) in oxy-fuel influences the characteristics of combustion compared to air firing. The most obvious difference is the gas heat capacity. Replacing N₂ with CO₂ and water vapor results in higher specific heat capacity, resulting in lower flame temperature (if firing with the same oxygen ratio) and thereby possibly yielding issues in stabilizing the flame. In order to achieve the same adiabatic flame temperature as air-fired combustion and obtain a stable flame, higher oxygen concentrations are required. The required oxygen concentration for most types of coal is around 30%². The two major changes due to oxy-



fuel combustion that affect the design of the boiler and downstream flue gas cleaning processes i.e. heat transfer (radiative and convective) and gaseous pollutant formation are further described in this section.

3.4.1 Heat transfer

The radiative heat transfer is a key property for the design of boilers and furnaces. The radiation characteristics depend on gas and particle radiation. The gas radiation strongly depends on the level and distribution of temperature in addition to composition and concentration of combustion gases. The recycle of flue gas in oxy-fuel operation results in higher concentration of CO₂ and water vapor, which in turn alter the radiative heat transfer from the flame. These triatomic gases are not transparent to radiation unlike symmetric diatomic gases like N₂. Thus, the emissivity and absorptivity of the flue gas are expected to increase compared to air firing. The radiative emissivity and absorption of particles such as coal, char, ash, and soot particles also play an important role in radiative heat transfer. The relative importance of particle radiation to gaseous radiation is influenced by the type of fuel and combustion conditions¹⁴. Experimental studies have confirmed the increase in the radiation emitted by the oxy-fuel flame in case of dry recycle due to higher concentration of CO₂ and increased particle radiation¹⁴. The radiation emitted from particles is due to the increase in soot formation in oxy-fuel combustion¹⁴.

On the other hand, the convective heat flux in the boiler depends on the convective heat transfer coefficient and the temperature difference between the bulk gas and the heated object. The convective heat transfer coefficient, in turn, depends on the flow velocity and properties of flue gas e.g. viscosity, thermal conductivity, heat capacity and density. The increased density and heat capacity of the flue gas as a result of increase in the concentrations of CO₂ and water vapor enhances the heat transfer in the convective section of the boiler compared to air firing (if the volumetric flow and the entering temperatures are the same). The ratio between the convective heat transfer coefficient of oxy-fuel and air firing has been studied as a function of the recycle ratio (i.e. the fraction of the total flue gas recirculated to the boiler). These studies show that the ratio increases with increasing the recycle ratio because of the increased gas velocity and changed thermal properties of the flue gas¹.

3.4.2 Gaseous emissions

Two important and harmful emissions from combustion are NO_x and SO_x. The formation of these gaseous pollutants is influenced by the combustion conditions.



During combustion NO_x is formed from molecular nitrogen present in the air and from nitrogen that is chemically bound in the fuel (fuel-N). Normally, around 80% of the NO formed in the combustion of pulverized coal is derived from fuel-N¹⁵. Significant reduction of NO_x formation during oxy-fuel combustion (around 70-75%) compared to air combustion has been reported^{2,16}. The recirculation of NO with the flue gas in oxy-fuel combustion is the major reason for the overall reduction in NO_x emission rate^{2,16}. This considerable reduction of NO_x formations brings a potential to reduce the NO_x emissions from a power plant.

The fuel is the source of SO_x formation in combustion and the amount is highly dependent on the type of fuel. The conversion of coal-S to SO_2 as well as the SO_2 emissions per unit energy supplied is reported to be lower under oxy-fuel conditions than in air-fired conditions¹⁷. However, the concentration of SO_2 in the flue gas is higher in oxy-fuel combustion due to the recycling of SO_2 and reduced volume flow of the flue gas¹⁷. The formation of SO_3 is enhanced under oxy-fuel conditions and the concentration of SO_3 is reported to be four times higher than in air combustion¹⁷. This is due to presence of SO_2 in the recycle stream, decreased volume flow through the furnace and presence of CO_2 in the combustion environment. This could cause operational problems due to the corrosion risks associated with the formation of H_2SO_4 from SO_3 in both high and low temperatures. The high concentration of sulfur oxides in the boiler can also increase the retention of sulfur in the fly ash which could lead to problems with further utilization of the fly ash, such as in concrete production².

3.5 Oxygen production/Air separation unit

In order to produce the oxygen required for combustion, an Air Separation Unit (ASU) is required in the power plant. The purity requirement of the oxygen stream for oxy-coal combustion is in the range of 90-98%^{13,18}. However, purities of more than 95% are more favorable since for purities less than 95% the oxygen contains nitrogen in addition to argon¹⁹. Avoiding nitrogen is beneficial in reducing NO_x emissions². The choice of optimum oxygen purity is based on the tradeoff between the cost of producing higher oxygen purity and cost of separating oxygen from CO_2 in the CO_2 compression section²⁰. Currently, the only commercially available O_2 -production technology that can meet the purity and volume requirements of a commercial-scale coal-fired oxy-fuel power plant is cryogenic distillation^{18,21}. In this process air is first compressed and precooled. Subsequently, it enters the purification system to remove water and CO_2 , as well as NO_x and hydrocarbon traces. The air is then cooled to cryogenic temperatures prior to entering the distillation column(s) where one oxygen-rich stream and one



nitrogen-rich stream are produced. In large ASUs the cold temperatures required for liquefaction of air are achieved using expansion turbines or turbo-expanders. The work generated in this step can be used to drive the compressors²¹. The cryogenic distillation process is energy intensive. The main contributor being the electricity required to power to the air compressors²¹. For an oxy-fuel power plant studies show that the power requirement of a cryogenic ASU can be more than 15% of the gross power output^{1,22}, reducing the overall efficiency of the power plant by 7-9 %^{1,19,23} compared with an air-fired plant.

Major improvements are needed to achieve higher efficiencies in the oxygen production. Therefore, alternative air separation technologies with potentially higher energy efficiency, such as ion transport membrane (ITM) are of interest and under development but they are not yet ready for commercial scale applications. In an ITM, oxygen is separated using nonporous, mixed-conducting, ceramic membranes at high temperatures (800-900°C). Application of this process can potentially reduce the capital costs by 30% and the energy requirements of O₂ production by 30-60%²⁴.

3.6 Flue gas recycle (FGR) system

In oxy-fuel combustion recycled flue gas is needed to moderate the flame temperature and make up for nitrogen. The recycle ratio, i.e. the fraction of the total flue gas recirculated to the boiler, affects the flame temperature and the heat transfer in the boiler by means of controlling the volume flow through the boiler. Generally, two recycle streams are required. The primary recycle is used for transporting the coal to the burners and the secondary stream is mixed with oxygen to maintain the combustion temperature within the acceptable limits. Flue gases can be recycled wet or dry. The primary recycle has to be dried and reheated to around 250°C-300°C before entering the coal mill to be able to absorb the moisture from the coal at the typical exit temperature of the coal mill (60-90°C)^{1,2,25}. Low drying capacity of the primary recycle gas could lead to clogging in the mills by the wet coals. Due to the risk of corrosion in the coal mill and flue gas pipes associated with the accumulation of SO₂ (which is a result of recycling flue gas containing SO₂), it is recommended that the primary recycle should be at least partially desulfurized for medium and high sulfur coal¹. For the secondary stream, wet, reheated and de-ashed (taken after the particulate removal) recycle is considered to be the most promising configuration^{1,2,25}.

The addition of oxygen to the primary recycle is not recommended due to safety reasons to avoid explosion in the coal mills². Avoiding oxygen addition to primary recycle can also be beneficial with respect to NO_x formation since limiting the oxygen concentration



in the primary stream will result in formation of a fuel-rich flame core². If no oxygen is to be added to the primary stream, it should be entirely added to the secondary recycle. However, this might increase the risk of spontaneous ignition of dust in the recycle stream. Another solution is to inject the oxygen directly to the combustion zone or to the over-fire ports².

3.7 Flue gas cleaning and CO₂ processing (compression and purification unit)

The aim of the flue gas cleaning in oxy-fuel power plants is different from other CO₂ capture technologies for coal-fired power plants (post-combustion and pre-combustion) in a manner that the main purpose is to control the non-CO₂ components rather than selective capture of CO₂ from flue gases. The flue gas passes the CO₂ processing unit to remove water, particulate matter and other pollutant gases prior to being compressed for transportation and storage. The composition of the flue gas and the desired CO₂ product specifications has great impact on the design and cost of the CO₂ processing unit. In the first generation of the oxy-fuel power plants conventional methods of pollutant removal e.g. selective catalytic reduction (SCR), electrostatic precipitator (ESP) and flue gas desulfurization (FGD) are applicable. On the other hand, since the oxy-fuel process offers new process conditions, it is possible to apply innovative techniques for emission control as well. Some of these possible techniques are described in the desulfurization and NO_x removal sections.

In order to efficiently transport large amounts of CO₂, it should be transformed into a high density form i.e. liquid, solid or supercritical phase. For pipeline transport, CO₂ must be compressed to high pressures in order to overcome the frictional and static pressure drops. Additionally, the pressure of CO₂ at the storage site should be higher than the critical pressure to avoid two-phase flow in the pipelines. The suggested conditions of the CO₂ stream at the delivery point are pressures of 80-200 bar and temperatures of 0-50°C^{2,26}. However, pressure of 100-120 bar and a temperature above the critical value (31,1°C) are reported to be favorable².

3.7.1 Particulates

The most common particulate removal system in large-scale power plants is the electrostatic precipitator (ESP). The possible effect of the changes in the gas composition during the oxy-fuel combustion (e.g. change in the size distribution of ash particles) on the collection efficiency of ESPs should be investigated. So far, the performance of a full scale ESP at oxy-fuel combustion conditions has been tested at Schwarze Pumpe oxy-fuel pilot plant burning low-sulfur lignite. The results have



indicated the size distribution and total amount of particulate matter emitted for ESP are similar to air firing²⁷.

3.7.2 Water and non-condensable gases

Water imposes operational problems and must be removed to avoid gas hydrates, corrosion and freezing of water. The initial dehydration of water is suggested to be carried out before the initial compression step to reduce the flue gas volume and subsequently costs and equipment sizes². The major part of the water is separated from the flue gas in the flue gas condenser (FGC). However, since the subsequent processing of CO₂ requires that water is removed to ppm levels an adsorption process should also be combined with the condensation^{15,26}. A large part of the remaining particles after the ESP will also be captured in this step. Some CO₂ will dissolve in the water and if not regenerated, it will result in a slight decrease in the capture efficiency²⁶. If the main part of the water is removed from the flue gas at relatively high temperatures and low pressures the CO₂ loss is decreased²⁶. The condensation could also remove gas phase components that are soluble in water as well as other species with higher boiling points than CO₂.

As discussed before, avoiding air ingress in the oxy-fuel combustion system is difficult. For a newly built plant, the amount of air ingress into the boiler and flue gas ducts is estimated to be around 3% of flue gas mass flow². The rate of air leakage for boilers will increase over time and could reach 8-16%². Since the non-combustible gases are to be removed from CO₂, significant air leakage will result in increased costs for CO₂ cleaning. The inerts removal could be performed in a flash or distillation column since CO₂ forms non-azeotropic mixtures with N₂, O₂ and Ar. The distillation systems is reported to be more effective and less energy consuming compared to the flash system²⁶. The thermodynamic properties, i.e. dew and bubble points, heat capacity and enthalpy and entropy, of the CO₂ stream entering the gas purification unit is affected by its content of impurities. This will, in turn, affect the operating condition, energy consumption, and configuration as well as separation performance of the purification system².

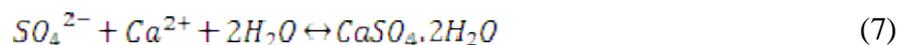
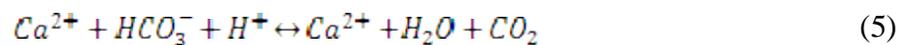
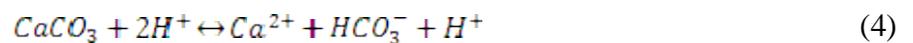
3.7.3 SO_x and NO_x

The requirement on SO_x and NO_x removal in the oxy-fuel process is still unclear. Historically the limitations on SO_x and NO_x have been driven by emission legislation, however, in oxy-fuel power plants corrosion issues might place even more stringent requirements²⁸. Removal of NO_x and SO_x, if required, could be achieved by either



conventional methods or by methods proposed especially for oxy-fuel combustion. The reduced volume flow in oxy-fuel power plants leads to more compact systems compared to conventional power plants. However, the performance of the conventional methods in atmospheres with high CO₂ concentrations is yet to be clarified. Below the most common measures for SO_x and NO_x removal are presented as well as promising technologies proposed for simultaneous removal in the high-pressure section of the flue gas train.

Conventional SO_x removal: The most common process that is considered for the flue gas desulfurization (FGD) in the oxy-fuel power plants is based on the wet scrubbing process using limestone (CaCO₃) as absorbent. This process results in production of gypsum (CaSO₄·2H₂O). The process can be described by the following reactions:



However, this system is originally designed to operate under air-fired conditions and major differences exist between the composition of flue gas (mainly in terms of CO₂, acidic gas components such SO₂ and SO₃ and water vapor) in the oxy-fuel power plant compared to the air-fired power plant. It should also be noted that the degree of desulfurization in oxy-fuel power plants should be based on downstream processes e.g. CO₂ purification, transport, storage and environmental regulations.

The high concentration of CO₂ could limit the wet desulfurization process and high concentration of water vapor in both wet and dry flue gas could result in reduction in the degree of desulfurization². The higher concentrations are due to removal of nitrogen in the oxy-fuel systems. In addition, in order to supply oxygen to the system for the oxidation of the hydrogen sulfite according to Reaction 7, air is added to the FGD unit in conventional power plants. This however, could result in undesirable dilution of CO₂ with nitrogen². Alternatively in oxy-fuel power plants, pure oxygen or a portion of the



secondary recycle stream could be added to the desulfurization unit. Another way is to add an external oxidation tank to avoid this problem.

The quality of the gypsum produced should also be within certain specifications so that further utilization of produced gypsum in for example cardboard industry is possible. Pilot scale tests performed in the 30 MWth oxy-fuel power plant in Schwarze Pumpe have shown no major differences in the gypsum quality compared to air firing conditions²⁹.

The performance of this desulfurization unit under oxy-fuel conditions should thus be further investigated and verified. Studies performed so far in pilot and laboratory scale have shown no considerable change and no fundamental problems in the performance of a conventional wet FGD scrubber^{2,29,30}.

Conventional NO_x removal: Different techniques are available for the control of NO_x both in terms of emissions to the atmosphere and the content in the captured carbon dioxide. These measures can be applied either during combustion (primary measures) or downstream of the combustion process (secondary measures). Primary measures intend to adjust the combustion parameters to decrease the NO_x formation from fuel-bound nitrogen and N₂, or to decrease the nitrogen oxides formed inside the furnace. Conventional primary measures, i.e. fuel staging, air-staging and low-NO_x burner technology, are possible to be applied to oxy-fuel combustion. Besides the conventional measures, recirculation of flue gas that results in re-burning reduction of NO_x brings new opportunities in the oxy-fuel power plants¹³. The aim of secondary measures is to convert or capture NO_x from the flue gas downstream of the combustion process. The disadvantage of the secondary measures is that they require additional equipment and additives. However, these measures usually perform better in terms of NO_x reduction compared to primary measures and they also do not interfere with the combustion process. The most commonly used secondary measures are selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). Some studies have been performed to verify the performance of an SCR plant in oxy-fuel power plants. The SCR systems are thought to be more effective under oxy-fuel conditions due to higher content of NO₂ which causes a mechanistic change in the SCR reaction³¹. On the other hand, the increased levels of SO₂ and SO₃ in flue gas are thought to reduce the performance of the SCR unit².

The conventional methods are expected to be sufficient for a first generation of oxy-fuel power plants to meet the current emission regulations, if based on emission per unit of fuel supplied¹³. On the other hand, new conditions in the flue gas train of the oxy-fuel



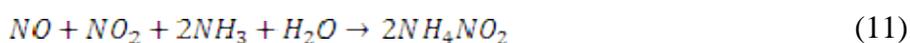
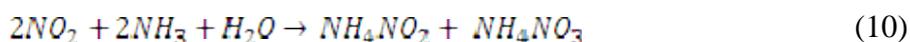
power plant that affect the nitrogen chemistry give rise to new opportunities for controlling NO_x . The development of these methods depends on the future emission and storage regulations for carbon capture schemes.

Pressurized flue gas cleaning: The high pressure and low temperature needed in the CO_2 condenser affect the chemistry of nitrogen which is of great importance for NO_x control. The oxidation of NO by the oxygen present in the flue gas as described by the following reaction is enhanced at low temperatures and high pressures.



In the high pressure part of the flue gas train (downstream of the flue gas compressor) pressure is sufficient enough (around 30 bar) for most of NO to be converted to NO_2 ¹³. Control of NO_2 is possible with other techniques than those available for NO since NO_2 is highly soluble in water. Absorption of NO_x in water at pressures around 30 bar is considered a feasible technology and removal efficiencies of up to 90% can be achieved¹³. A new sour compression process has been proposed by Air Products³² which uses a staged compression process to utilize residence time for the removal of impurities during compression. This process is an alternative way to remove both NO_x and SO_2 from the CO_2 stream. This is achieved by cooling the flue gas to remove water vapor as well as traces of ash, SO_3 and HCl in a condensation stage. The flue gas is then compressed firstly to 15 bar and then to 30 bar. Sufficient contact with water is provided after each compression stage to remove NO_x and SO_2 as HNO_3 and H_2SO_4 ³³.

Another concept proposed by Linde³¹ called LICONOX, is a cold de NO_x process which is also capable of simultaneously removing NO_x and SO_x . In this process, SO_x is first removed in a FGD system up to 95-99%³¹ and then headed to the compression unit. NO is oxidized to NO_2 due to high pressure condition of flue gas, and is then chemically absorbed in ammonia water as shown by the reactions below:





The enriched washing medium is frequently sent to a nitrite reduction reactor resulting in production of N_2 and the regenerated washing medium is headed back to the scrubber. Pilot scale tests performed in the Schwarze Pumpe oxy-fuel plant has shown the satisfactory NO_x removal efficiency of this process³¹.

3.8 Alternative oxy-fuel concepts

Chemical looping combustion and pressurized oxy-fuel combustion are two concepts presently being developed to increase the energy efficiency of the CO_2 capture process and consequently decrease the cost of carbon capture. Development of oxy-fuel natural gas turbine power cycles has also gained some limited attention. These concepts are further from commercialization than the conventional concept in focus in this report. All concepts are briefly summarized in this section. More information can be found in the review by Adanez et al.³⁴ on chemical looping combustion and the review by Chen et al.¹ on pressurized oxy-fuel systems and the study on different combined cycles by Bolland et al.³⁵.

3.8.1 Chemical looping combustion (CLC)

Chemical looping combustion (CLC) is a novel technology related to oxy-fuel combustion which is currently under development. A CLC system consists of two reactors, an air reactor and a fuel reactor. The fuel is introduced to the fuel reactor where it is oxidized. The oxygen is carried to the fuel reactor using a metal oxide (MeO). In the fuel reactor the metal oxide either releases its oxygen as O_2 or reacts directly with the fuel. The exit gas stream from the fuel reactor contains only CO_2 and H_2O . The reduced metal oxide is transferred back to the air reactor where it oxidizes by an air stream. The schematic of this process is shown in Figure 3.3.

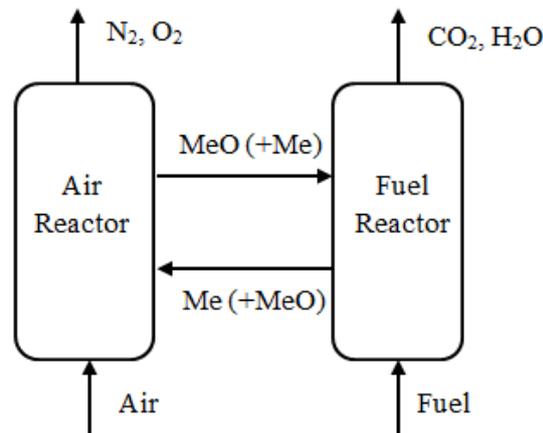


Figure 3.3 Schematic of a chemical looping combustion (CLC) process

The air will, thus, never be in contact with the fuel and the produced CO_2 will not be diluted by N_2 . Chemical looping is still in an early development stage but if successfully developed, it will decrease the costs of carbon capture. However, it still faces some challenges in oxygen carrier selection and materials handling³. It seems as CLC is rather straight forward when using a gaseous fuel whereas using solid fuel such as coal imposes a greater challenge, especially to avoid a slip of un-burnt char into the air reactor, while maintaining an overall low ash loss. An alternative process, chemical looping with oxygen uncoupling (CLOU) has been recently proposed³⁶ which is suitable for combustion of solid fuels. In this process fuel is burnt in gaseous oxygen released from the oxygen carrier particles during the oxidation of fuel³⁶.

3.8.2 Pressurized oxy-fuel systems

In pressurized oxy-fuel systems also the furnace is also pressurized. Pressurized combustion will improve the thermal efficiency of the oxy-fuel power plants by recovering the latent heat of steam present in the flue gas¹. Another advantage is the reduced flue gas volume under elevated pressure resulting in smaller components and reduced capital costs compared to atmospheric oxy-fuel plants with the same power output. In addition, the air ingress into the system will be eliminated. However, this process is still under development and challenges associated with combustion and heat transfer at elevated pressures impose a need for redesigning the fuel feeding, burners, heat exchangers and condensing heat exchangers¹.

3.8.3 Oxy-fuel gas turbine systems

Oxy-fuel combustion can be applied to gas turbine based power generation plants where the recycled flue gas may either be CO₂ or H₂O. A simplified thermal cycle of an oxy-fuel gas turbine based power plant is shown in Figure 3.4.

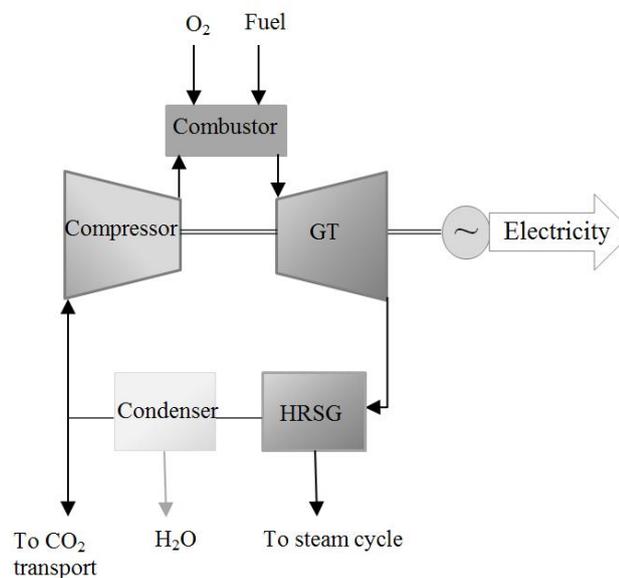


Figure 3.4. Schematic of thermal cycle for an oxy-fuel natural gas fired power plant, HRSG: Heat recovery steam generator.

Oxy-fuel firing in combined cycles results in a CO₂-enriched working fluid in the gas turbine. New composition of the working fluid necessitates significant modifications to the design of the combustors, boilers, process heaters and turbines. On the other hand, use of oxy-fuel combustion provides an opportunity to design new cycles that may offer higher efficiencies than the air based combined cycle systems hence partially compensating for the efficiency losses due to oxygen production³⁵. However, the new cycles require significant development work. One major challenge for oxy-fuel cycles is the combustion. The simultaneous consumption of the oxidant and the fuel requires good mixing and sufficient residence time to achieve complete combustion and avoid CO formation. In addition, development of turbo machinery that is capable of working with CO₂/H₂O mixtures at high temperatures and pressures is challenging.



3.9 Industrial applications of oxy-fuel technology

Although the power sector has been the focus of the CO₂ capture-related research, industries account for almost 40% of CO₂ emissions worldwide⁴. Typically, Industrial CO₂ streams are smaller than CO₂ streams from coal power plants, thus the cost per kg of CO₂ captured may be higher for the industrial processes. However, integrated process designs which are currently under development can possibly decrease this cost⁷. Furthermore, due to the diversity of the technologies required in industry compared to power sector, more diverse demonstration programs are required⁷. Application of the oxy-fuel technology to the carbon intensive industrial processes in the iron and steel, cement and refinery sector is briefly discussed in this section.

3.10 Iron and steel sector

The iron and steel production sector is one of the largest industrial emitters of CO₂. The integrated iron and steel production is divided into three sub-processes: iron-making, steel-making and steel manufacturing. About 60% of world total steel is produced from pig iron which is produced in blast furnaces and the rest is mostly produced from steel scrap⁴. The integrated steel-making process using blast furnace is schematically shown in Figure 3.5. The iron-making process consists of coking, iron ore agglomeration and blast furnace. Coal or lignite is pyrolyzed in a coke oven to produce coke which is used in the iron ore agglomeration process and in the blast furnace. In the blast furnace, the iron ore is reduced by coal and coke to produce pig iron and blast furnace gas. The pig iron is converted to steel in the basic oxygen furnace (BOF) where most of the carbon in the pig iron is removed by pure oxygen. The steel manufacturing processes include steel casting, rolling and finishing. Large fraction of the total carbon input to the iron and steel plant is to the iron-making process. In the blast furnace-based process, which is the dominant process in the industry, around 70% of the carbon flows through the blast furnace⁴ and, obviously, CCS technologies should be focused on the blast furnace.

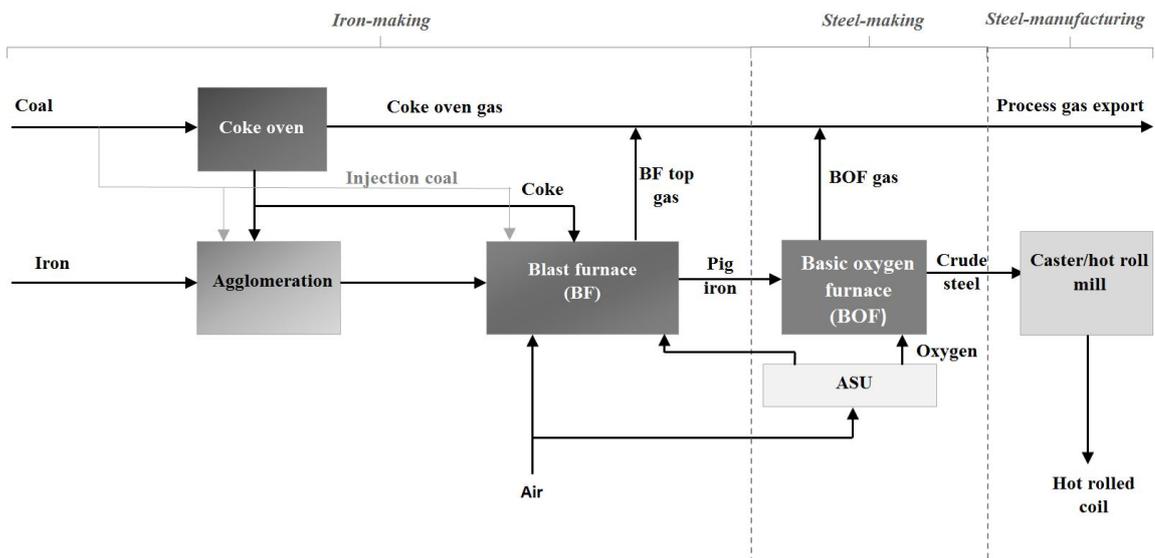


Figure 3.5 Schematic of an integrated iron and steel production process.

Application of the oxy-fuel process to the blast furnace is often referred to as the “Top Gas Recycling Blast Furnace” (TGRBF) in literature. This process is schematically shown in Figure 3.6. The use of pure oxygen instead of air in the blast furnace increases the CO₂ concentration in the top gas, which would then mainly consists of CO (40-50 %) and CO₂ (around 35%)⁴. After CO₂ is removed the top gas can be recycled back to the blast furnace as a reducing agent, which would significantly reduce the coke consumption. It should be noted that in the oxy-fueled blast furnace process, unlike in oxy-fuel power plants, separation of CO₂ from a gas that mainly consists of CO is required. So far monoethanolamine (MEA) and vacuum pressure swing adsorption (VPSA) have been tested in pilot scale^{4,7}. This technology offers a promising near term approach to capture CO₂ in the iron and steel sector since the conventional blast furnaces can be retrofitted to oxy-fueled blast furnaces and consumption of coke and coal is significantly reduced. The European Ultra Low CO₂ Steelmaking (ULCOS)³⁷ program is pursuing the TGRBF process.

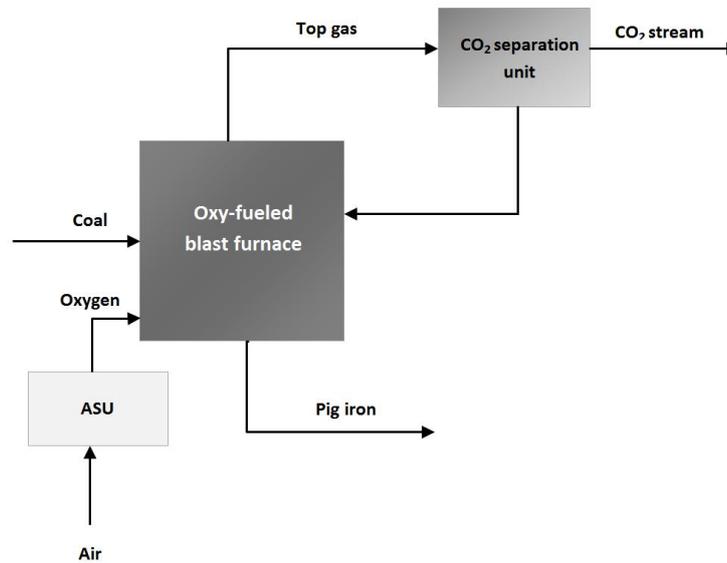


Figure 3.6 Schematic of oxy-fueled blast furnace.

3.10.1 Cement sector

Cement production is an energy intensive process and a major emitter of CO₂. The calcination of limestone (Eq. 12) and combustion (mostly coal) in the kiln accounts for around 60% and 30% of the total CO₂ emission of a modern cement plant respectively³⁸. Production of cement can be classified into four process routes based on the moisture content of the feed entering the kiln. These process routes are: dry process, semi-dry process, wet process, and semi-wet process⁴. Currently, the dry process is considered the best available technique (BAT) for cement production⁴ and is schematically shown in Figure 3.7.

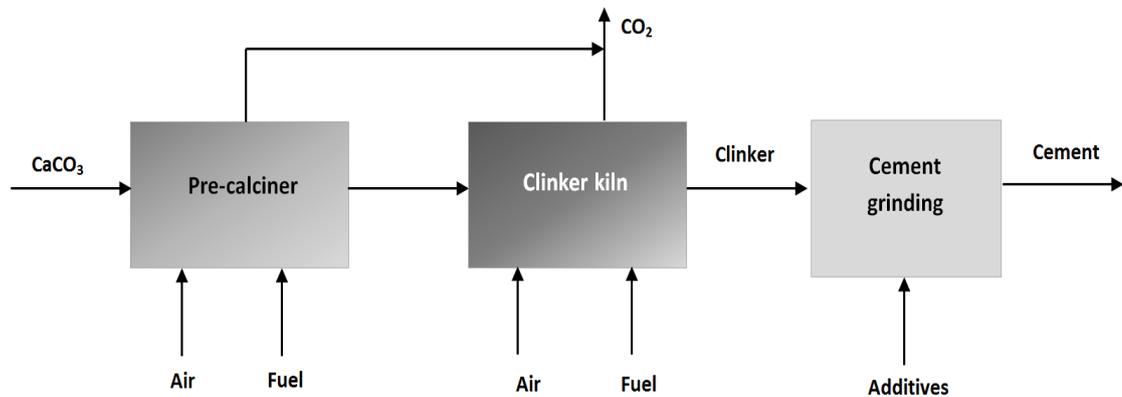


Figure 3.7 Schematic of cement production (dry process).

Calcium carbonate (CaCO_3) which is the main component of limestone in addition to some silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3) comprise the raw material mix. The raw material is heated to over 1400°C in a kiln to produce clinker. The calcination of calcium carbonate is described by the following reaction, which occurs in both the pre-calciner and the cement kiln:



The mix of calcium oxide (CaO) with silica, iron oxide and alumina form the cement clinker. The clinker is cooled and grinded with gypsum and other additives to produce cement. The desired high temperatures in the kiln are achieved by combustion. Today, mainly fossil fuels (e.g. pet-coke, coal, fuel oil, lignite and natural gas) are used in cement plants³⁸.

The calcination process results in a flue gas with high CO_2 concentration, which makes the cement production favorable for application of carbon capture. Two main options for application of oxy-fuel combustion have been proposed: partial capture and total capture. Partial capture refers to oxy-fuel combustion only in the pre-calciner, while total capture is application of oxy-fuel combustion to both the pre-calciner and the kiln⁷. Partial capture is suggested to have the lowest technical risk and a short term option since the difficulties of undertaking oxy-fuel combustion in the kiln and air leakage into the kiln can be avoided⁴. However, in the longer term, total oxy-fuel capture from cement plants is likely to be favorable for new-built plants⁴. Retrofit of existing kilns to



oxy-fuel combustion is possible, but significant modifications are required to the core units in the cement plant⁷.

The implementation of oxy-fuel combustion will also affect the cement production process, which must be considered. The reduced nitrogen content lowers the amount of energy required for heating of inlet gases compared to the conventional process. This energy can be used for the calcination process and increase the capacity of the kiln³⁹. The elimination of nitrogen will also increase the partial pressure of CO₂, which affects the calcination process. If the partial pressure of CO₂ is low, decomposition of CaCO₃ increases until the reaction is completed. But at high CO₂ partial pressures no reaction occurs until a minimum threshold temperature is reached. If the temperature drops below the critical temperature the reaction will be reversed (CaO returns to CaCO₃). So far, only process simulations and laboratory investigations have been performed on the oxy-fuel kiln technology and the operation of the pre-calciner in a CO₂-rich environment is not yet proven⁴.

3.10.2 Petroleum refineries

Refineries are a CO₂ intensive industrial process. Refineries process crude oil to produce gasoline, diesel oil, and other products. Refining processes can be classified to separation (mostly distillation), conversion (mostly thermal, catalytic or hydrocracking) and upgrading processes (such as catalytic cracking). Heat is used in all of the processes and the required electricity for the processes is often generated on-site. Large fraction of CO₂ emissions from the refineries are from onsite heat and power production and the fluid catalytic crackers (FCCs)⁴. Oxy-fuel combustion could be applied to the refinery boilers and heaters. However, retrofitting many small scale furnaces and heaters to oxy-fuel combustion are expected to be more complicated compared to a large boiler⁴.

Catalytic cracking is a process to break down the heavy oil into lighter oil products such as gasoline and liquid petroleum gas (LPG) using a cracking catalyst. CO₂ emissions from FCCs are process related unlike most of the other emissions from refineries that are combustion related. During the process, coke is formed and deposited on the surface of the catalytic leading to its deactivation. Catalyst is regenerated by oxidizing the coal using air resulting in production of CO₂. Application of oxy-fuel to the regeneration process is considered to be feasible without major effects on the catalyst regeneration and activity^{4,6}. In the oxy-fueled process oxygen is used instead of air and some of the flue gas is recycled back to the regenerator to control the temperature. The oxy-fuel regenerative process is, despite the relative high capital costs compared to post-



combustion capture, estimated to have lower operating costs, thus, making it a more attractive option with significantly lower capture costs³⁹. However, the process is still in early stage of development.

3.11 Future focus areas

Oxy-fuel combustion is an attractive option for carbon capture from power plants and industrial processes, but it is yet to be commercialized. Important challenges and potential opportunities that require more research and experience could be summarized as:

1. *Oxygen production:* The oxygen production is the major energy penalty for the oxy-fuel process and, thus, the obvious subject for improving process performance. Membranes and chemical looping combustion are two examples of breakthrough technologies that would dramatically reduce cost for oxygen.
2. *The control of acid gas:* Due to the higher pressures in the flue gas train new opportunities and challenges arise for the control of NO_x and SO_x . Innovative and cost effective techniques for absorption of SO_x and NO_x in water could be applied. However, at the same time this might cause problems with corrosion. Better understanding of the behavior of these gases under pressurized conditions is required in order to design the removal process and avoid possible corrosion issues during compression.
3. *Operational issues:* So far research has been focused on isolated sub systems and little is known about how the different parts of an oxy-fuel power plant work together, especially for industrial processes. Results obtained from demonstrations projects for the energy sector is a helpful starting point, but further demonstration and pilot tests are required together with process simulations of the entire chain.
4. *Material issues:* More research on the materials performance in oxy-fuel combustion environment is required in order to identify possible issues with corrosion and erosion, and needs for new materials or operational changes.
5. *Development of second generation combustion concepts:* In the second generation of oxy-fuel plants the combustion process no longer mimics the air firing. In order to maximize the efficiency, minimize the capture cost, and reduce emissions the oxy-fuel combustion processes should utilize the possibility of using oxygen concentration as an operating parameter.
6. *Oxy-biomass combustion:* Capture of biogenic CO_2 is a great opportunity to reduce the total emission of CO_2 to the atmosphere. Combustion of biomass does, however,



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present new challenges that must be considered in the oxy-fuel environment. Co-firing of biomass and coal is a good way of utilizing biomass that should also be considered for oxy-fuel operation.

7. *Novel CCS concepts:* New CCS concepts should be studied to reduce the associated costs and improve the process performance. Oxy-fuel technology could potentially be combined with other capture technology elements such as chemical looping with oxygen uncoupling (CLOU) to reduce the oxygen production costs.
8. *Industrial CCS and oxy-fuel combustion:* Different industrial process configurations should be studied in which oxy-fuel combustion could be utilized as a CCS option. Pure oxygen is already today used in different industrial combustion processes, but research on the possibility for carbon capture from such processes is scarce.



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4. PRE-COMBUSTION CAPTURE

There are three routes of CO₂ capture in power generation (see Figure 4.1). Pre-combustion capture is one of the technological pathways for carbon capture. Pre-combustion CO₂ capture (CC) as its name implies is the process of capturing carbon dioxide before the fuel is burned. The fuel (natural gas or coal) is converted to synthesis gas which is a mixture of carbon dioxide and hydrogen. The carbon dioxide is separated from the CO₂-H₂ mixture, compressed to a higher pressure for transportation and the hydrogen is used as a fuel. The synthesis gas in pre-combustion CO₂ capture is at an elevated pressure with high CO₂ concentration. For this reason, the partial pressure of carbon dioxide is fairly high, consequently driving force for separation is increased, size of equipment and compression cost is reduced. This brief literature review covers studies in both natural gas and coal fired power plant pre-combustion CO₂ capture.

Few of the focus areas of published works on pre-combustion CC includes technology/process selection, performance evaluation (energy and exergy efficiency), techno-economic analysis, energy and process integration, optimization and experiments with novel solvent or process.

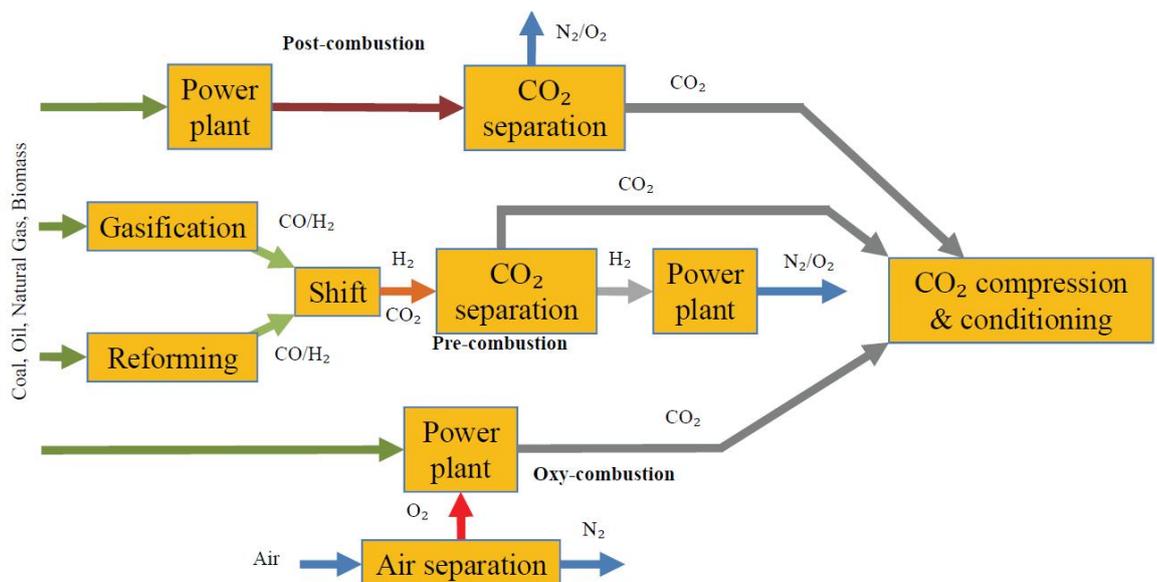


Figure 4.1 Different carbon capture pathways²

Figuroa et al.¹⁵ (Figure 2.2) show the dependence of cost benefit reduction with technological advancement. They show that the cost reduction benefit for pre-combustion process will be higher than other alternatives as the time to commercialization increases.

4.1 Natural gas combined power cycle with pre-combustion CC

There are several pre-combustion CO₂ capture processes. The possible combination of natural gas reforming technologies with CO₂ capture is shown in figure 3. Natural gas combined cycle with pre-combustion CO₂ capture has been studied by several researchers^{1,9,13,14,20,24,25,31}. The focus of previous studies include exergy analysis¹⁴ and techno-economic analysis²⁵ among others.

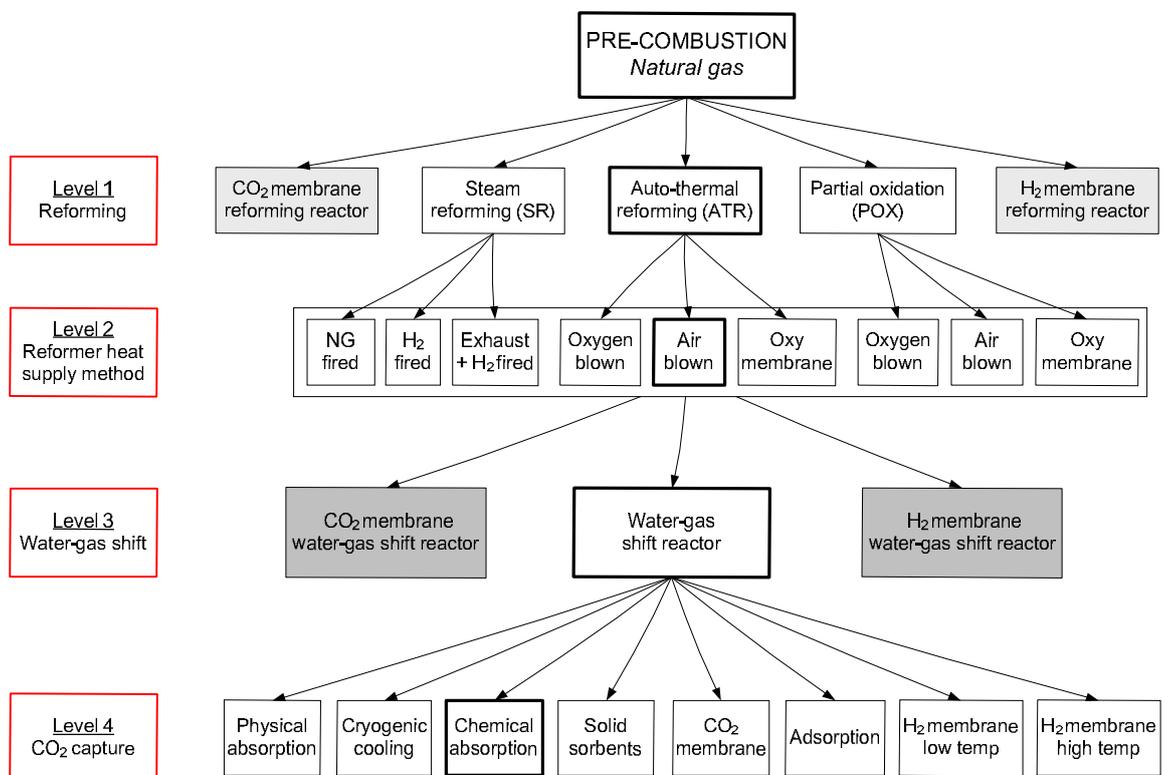


Figure 4.2 Natural gas pre-combustion carbon capture processes²⁷



Nord et al.²⁸ investigated pre-combustion CO₂ capture in natural gas combined cycle (NGCC) power plant at design and off-design conditions. Pre-reformer, air-blown auto-thermal reformer (ATR), water-gas shift reactor, amine-based CO₂ absorption, and CO₂ compressors are components of the pre-combustion CO₂ capture in their study. They found that operation of the plant at part load as low as 60% gas turbine load is possible.

Qualitative reliability and availability of integrated reforming combined cycle plant (IRCC) with CO₂ capture is presented by Nord et al.²⁹. The gas turbine was found to be the most critical equipment in their study. The presence of significant integration and the not-so-matured hydrogen based gas turbine were the reasons mentioned for the gas turbine to be the most critical equipment. Nord et al.³⁰ explored the effect of input uncertainty on output in IRCC with CO₂ capture process modeling. Seventeen uncertain input parameters such as pressure drop, steam to carbon ratio, approach temperature in water gas shift reactor, turbine inlet temperature, efficiency of turbine and compressor, correction factor for steam turbines, efficiency of CO₂ compressor and reboiler duty were considered in their analysis. They found that there exists considerable uncertainty in predicting net power output. On the other hand, net plant efficiency, CO₂ capture rate and CO₂ emitted per kWh of generated electricity were found to be less affected by input uncertainties. Their result showed that the median efficiency penalty is 12.8%-points, but it could be as high as 14%-points. The chance for the actual efficiency penalty to be above the deterministic value was 51%. Uncertainty related to economic parameters of IRCC with CO₂ capture process is also reported in Di Lorenzo et al.¹². Innovative capture processes such as Sorption-Enhanced Water Gas Shift in a natural gas combined power cycle has been published²⁶.

Romano et al.³² studied pre-combustion CO₂ capture from natural gas power plants, with ATR and MDEA. They made thermodynamic and optimization analysis implementing the best available technology by then. Their study revealed that a net efficiency of 50.6%, about 8%-points less than the reference cycle without CO₂ capture, can be achieved. Table 1 is the summary of some representative studies as compiled by Romano et al.³². As it is shown in table 1, the net efficiency and efficiency penalty of natural gas combined cycle with pre-combustion CO₂ capture is in the range of 41-49% and 7.5-14%-points respectively.

Table 4.1 Summary of studies on natural gas -fired ATR-based pre-combustion CO₂ capture³²

Investigator	Pre-reformer	ATR oxidant	ATR temperature (°C)	S/C at ATR	Absorption solvent	Carbon capture rate (%)	Net efficiency (%)	Efficiency penalty (% pts)
Stork Engineering Consultancy ³⁴	Absent	Oxygen	1050	0.9	Selexol	84.8	48.35	7.84
Fluor Daniel ¹⁶	Adiabatic	Air	90	2.4	MDEA	89.6	42.8	-
	HE-reformer	Air	900	2.4	MDEA	89.6	43.1	-
	HE-reformer	Air	N.A.	N.A.	Selexol	N.A.	35.7	
Lozza and Chiesa ²⁴	Absent	Air	980	1	DEA	90.1	48.47	7.64
	Absent	Air	1042	1	Selexol	90.1	48.63	7.48
Ertesvåg et al. ¹⁴	Absent	Air	900	1.6	N.A.	86.2	48.88	10.0
Nord et al. ²⁸	Absent	Air	950	1.5	MDEA	93.4	41.9	14.0

4.2 Integrated gasification combined power cycle with pre-combustion CC

Integrated gasification combined power cycle (IGCC) is a relatively environmental friendly and more efficient technology which converts coal into synthesis gas. The synthesis gas is cleaned from impurities such as H₂S and then is combusted. IGCC is CO₂ capture ready plant. Figure 4.3 depicts IGCC with pre-combustion CO₂ capture process. Cormos et al.⁸ studied pre-combustion CC in IGCC along with post-combustion CC. They found that energy penalty for pre combustion is lower than post combustion. The emitted carbon dioxide in pre-combustion CC is lower than that of post-combustion CC. Techno-economic analysis of pre-combustion, post-combustion and oxy-combustion CO₂ capture in IGCC, PC and NGCC is carried out by Kanniche et al.¹⁷.

They recommended that pre-combustion capture by physical absorption is better than other post or oxy-combustion capture.

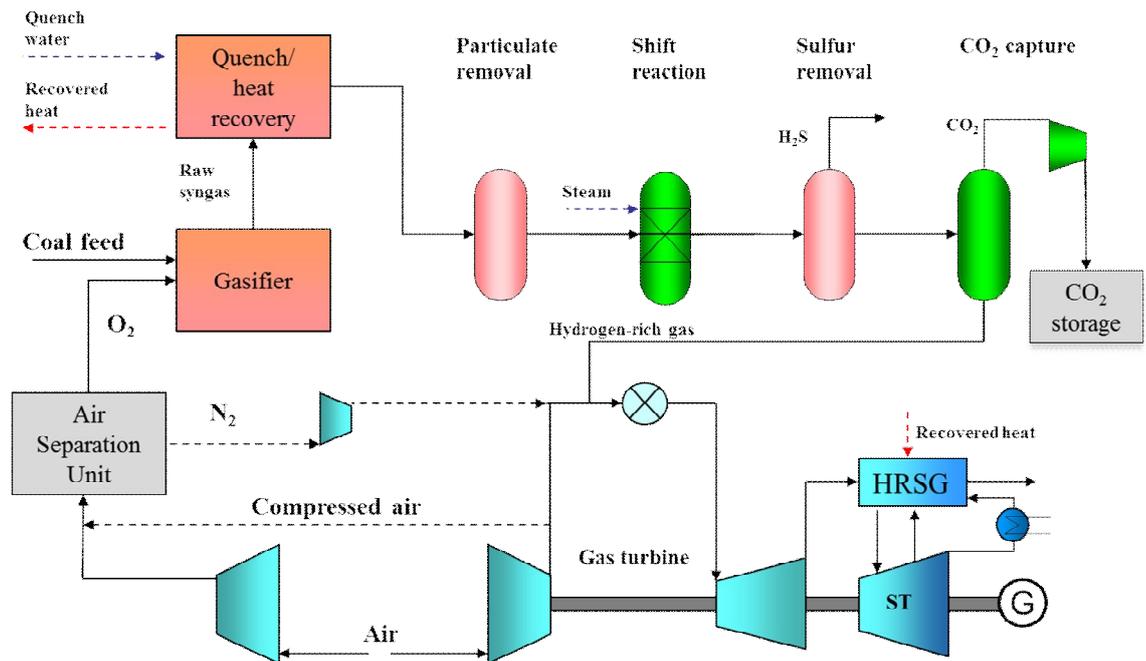


Figure 4.3 IGCC with pre-combustion carbon capture²

Cormos⁶ evaluated IGCC with CCS. He evaluated various gasifiers. Pre-combustion CCS with different solvents was part of his study. He showed that Shell gasifier is the most energy efficient followed by Conoco-Philips E-gas and Siemens gasifier. His result revealed that Selexol® based CCS is better than other solvents. He also found that pre-combustion is more efficient than post-combustion CCS, however chemical looping CCS is the best among the three options according to his analysis. Techno-economic analysis of IGCC with physical solvent (Selexol®) based pre-combustion CCS is also presented by Cormos⁷. Cormos found that introducing CCS to IGCC plant has the following consequences: 7-9.5% energy penalty in terms of net plant efficiency; 10-75% plant construction materials, 22-24% capital costs increase, 10.5- 13.5% operational and maintenance costs increase and 30-35% levelised cost of electricity for 90 % carbon capture. Energy and process integration aspects in IGCC with pre-combustion CC plant for hydrogen and electricity co-production is studied in Cormos⁵. IGCC with pre-



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combustion CCS for hydrogen and electricity co-production is studied by different researchers^{3,4,19}. Scholes et al.³³ reviewed membrane technologies for IGCC with pre-combustion CO₂ capture. Damen et al.¹⁰ discussed pilot plant of IGCC with pre-combustion CO₂ capture plant.

Researchers are looking for different solutions to decrease energy consumption in the capture process. One of the approaches considered to decrease energy consumption in pre-combustion cc is using clathrate or gas hydrate formation^{18,21,22,23}.



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