MEMBER

ADVANCED MEMBRANES AND MEMBRANE ASSISTED PROCESSES FOR PRE- AND POST-COMBUSTION CO2 CAPTURE

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Content

1. EXECUTIVE SUMMARY

1.1. Description of the deliverable content and purpose

The key MEMBER objective is the scale-up and manufacturing of advanced materials and their demonstration in novel membrane based technologies that outperform current technologies for pre- and post-combustion CO_2 capture in power plants as well as industrial H_2 generation processes with integrated CO_2 capture.
In particular, the selected applications are the following:

- Pre-combustion capture in power plants
- Post-combustion capture in power plants
- Hydrogen production with integrated CO_2 capture

The particular aim of this deliverable is:

1. To define the system performance for the mentioned three applications
2. To define the advanced materials (membranes, sorbents, catalyst) scale up requirements

With regards to the point 1, the demo site owners and the engineering companies involved in the construction and validation of the different prototypes have gathered the information available on state-of-the-art systems and identified all the characteristic process parameters such as balance of plant; raw material specifications, process selectivity, current limitations and CO_2 capture cost.

With regard to the point 2, the technical specifications for the advanced materials and the expected performance at every level have been defined and quantified, as well as the optimal manufacturing process. Technical specifications include mainly permeability, perm-selectivity, mechanical & chemical stability, together with CO_2 capture performance.

On this basis, the deliverable has been divided in two sections. Chapter 2 is a general collection of main technologies for CO_2 capture in pre- and post-combustion. After that, the selection of the most appropriate method for each of the three applications has been described quantitatively, in order to derive a benchmark to be utilised for the evaluation of the performance of the three prototypes and to address the techno-economic assessment to be done in the next Task 2.5.
Chapter 3 is relevant to the indication of technical specifications concerning the advanced materials.

The overall deliverable will represent the basis for the definition of the three systems overall performance to be addressed along the project.

2. CO_2 capture systems in the industrial and energy sectors

2.1. General introduction on CO_2 emissions

Carbon dioxide is a by-product of many industrial processes and a final combustion product of carbon containing fuels. As such, it is generated in large quantities and emitted in the gaseous effluents of industrial and energy production sites, and in smaller and distributed amounts in building heating, transportation, etc. In all cases, since process feedstocks and fuels are almost all of fossil origin, the CO_2 emitted contributes to the anthropogenic carbon emission, causing an increase of the CO_2 concentration in the atmosphere and contributing to climatic changes. CO_2 is a primary greenhouse gas and it is estimated that stationery CO_2 emissions contribute for about 60% of the overall global CO_2 emissions [1].

Main industrial sectors contributing to the (concentrated) CO_2 emissions are represented by power plants, and energy intensive industries, according to the breakdown reported in Table 1 (emissions from transportation sector are not included).

Table 1. Globally stationary CO_2 emissions [2].

Process	**Emissions (10^6 metric ton CO_2 per year)**	**% on the Total**
Power production	10,539	78.8
Cement production	932	7.0
Refineries	798	6.0
Iron and steel industry	646	4.8
Petrochemical industry	379	2.8
Oil and gas processing	50	0.4
Other sources	33	0.2

2.2. General introduction on technologies for CO_2 capture

The first objective of CO_2 capture is the decrease of anthropogenic CO_2 emissions contributing to climate change. In parallel there is an effort to develop potential CO_2 applications that could, at least in part, economically support the deployment of CCS technologies. Tables 2 and 3 report a number of existing and emerging uses for CO_2.

Table2. Existing uses and demand for CO_2. Adapted from [3].

Existing uses	**Brief description**	**Current non-captive CO_2 demand (MTPA)**	**Future potential non-captive CO_2 demand (MTPA)**
Enhanced oil recovery (EOR)	CO_2 acts as a solvent that reduces the viscosity of oil fields, enabling it to flow to the production well.	30 < demand < 300	30 < demand < 300
Food	CO_2 is used in different applications in the food industry, including packaging (modified atmosphere packaging or controlled atmosphere packaging), cooling while grinding powders, food spoilage prevention by acting as an inert atmosphere and dry ice as an ideal refrigerant to preserve food storage.	~8.5	~15
Beverages	Carbonation of beverages with high-purity CO_2.	~8	~14
Refrigerants	Used as the working fluid in refrigeration plants, especially for industrial air conditioning and refrigeration systems.	<1	<1
Industrial	Used for steel manufacturing, metal working, welding and other applications.	<1	<1

Table 3. Existing uses and demand for CO_2. Adapted from [3].

Emerging uses	Brief description	Future potential non-captive CO_2 demand (MTPA)
CO_2 concrete curing	Focused on precast concrete production facilities, where the waste CO_2 from onsite flue gas is permanently stored as un-reactive limestone within the concrete, limiting the need for heat and steam in the curing process.	30 < demand < 300
Bauxite residue treatment	Concentrated CO_2 can be injected into bauxite residue slurry to partially neutralize the product and improve the manageability, as well as limiting its potential environmental impacts.	5 < demand < 30
Algae cultivation	Carbonation of beverages with high-purity CO_2.	> 300
Renewable methanol	Combination of the H_2 obtained from the electrolysis of water with captured CO_2, compressed and reacted over a catalyst at moderate temperature and pressure to produce methanol and water.	> 300

Other applications include CO_2 for remineralization of consumption water, pH regulation for sanitation water and usage in greenhouses for plants growth in the agriculture industry. The applications have different requirements when it comes to CO_2 purity, with some applications requiring different level of impurities in their respective processes, as demonstrated in the Table 4.

Table 4. Minimum CO_2 purity requirements per application.

Applications	Minimum Purity (% v/v)	Source
Enhanced oil recovery (EOR)	90	[4]
Food	99.9	[5]
Beverages	99.9	[6]
Refrigerants	99.9	[7]
Industrial	99.5	[8]
Storage	95	[9]

Depending on the application, other parameters also need to be considered. For example, for food applications, it is required to have a maximum moisture content (≤ 20 ppm v/v), as well as a maximum level of other impurities, like carbon monoxide (≤ 20 ppm v/v), total volatile hydrocarbons (≤ 50 ppm v/v) and non-volatile residue (≤ 10 ppm v/v).

For beverages, the requirements are different from food, such as maximum oxygen levels (≤ 30 ppm v/v), moisture (≤ 20 ppm v/v), total sulphur (≤ 0.1 ppm v/v), odour (odourless), appearance in water (no colour or turbidity) and taste (no foreign taste).

However, the implementation of carbon dioxide (CO_2) capture and storage/utilization (CCS/CCU) technologies for most industrial activities – for example boilers, turbines, iron & steel furnaces and cement kilns - requires a mandatory capture step to convert a relatively diluted stream of CO_2 to a higher concentration to allow economic transportation and storage.

CO_2 capture technologies are available in the market but are costly in general, and contribute to around 70–80% of the total cost of a full CCS system including capture, transport and storage [10,11]. Therefore, significant R&D efforts are focused on the reduction of operating costs and energy penalty. There are three main CO_2 capture systems associated with different combustion processes, namely, post-combustion, pre-combustion and oxyfuel combustion. They are shown schematically in Figure 1 and described in the following.

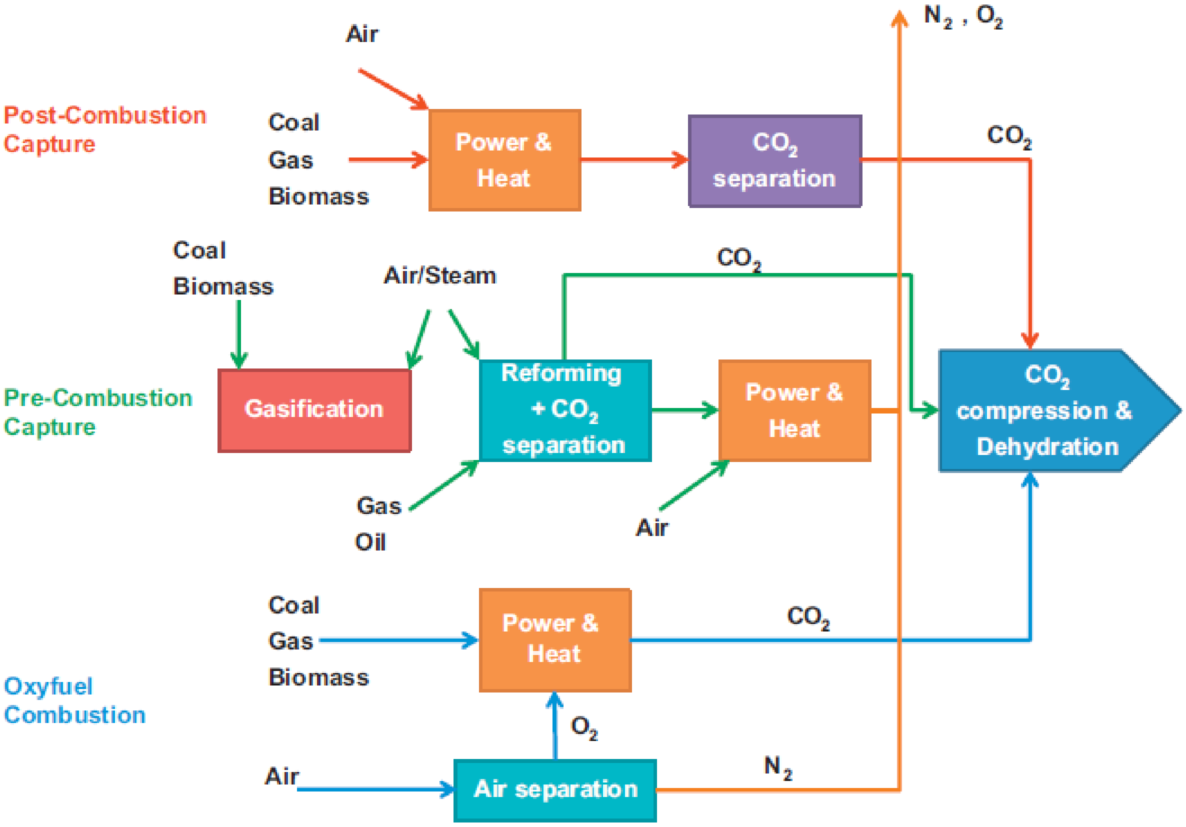

Figure 1. Schematic conceptual representation of CO_2 capture technologies [12].

In ***Post combustion,*** capture processes the removal of CO_2 is performed after combustion has taken place. The flue gases exiting combustion plants are typically treated using chemical or physical sorbents to selectively remove CO_2 from the gas mixture. It is an end-of-pipe solution, where CO_2 is removed from the flue gas before the flue gas is emitted to atmosphere via the stack. The main challenge is that the CO_2 level in combustion flue gas is normally quite low, about 7-14% for coal-fired and as low as 4% for gas-fired [11]

In ***Pre-combustion,*** capture processes the fuel (normally coal or natural gas) is pretreated before combustion. In particular, it is generally gasified or reformed to a syngas stream, which is then subject to water-gas shift reaction and subsequent gas clean up to separate the produced hydrogen from the CO_2. The gas cleans up step is usually achieved using similar methods employed as described for post-combustion processes, although there are advantages to removing the CO_2 from the syngas mainly associated with the pressure of the gas which reduces compression energy requirements. The hydrogen is used as the input fuel to the combustion process, whilst the CO_2 is available in a concentrated form for compression, transport and storage. The high concentration (>20%) in the H_2/CO_2 fuel gas mixture facilitates the CO_2 separation [11].

In ***Oxyfuel*** combustion, oxygen, instead of air, is used for combustion. This reduces the amount of nitrogen present in the exhaust gas that affects the subsequent separation process. The major composition of the flue gases is CO_2, water, particulates and SO_2. After the removal of particulates and SO_2, the remaining gases contain high concentration of CO_2, about 80-98% (depending on the fuel used) [11].
Carbon dioxide can be separated from the flue/fuel gas stream by several separation technologies [11,13], which are based on the following unit operations:

- Absorption by liquid solvents
- Adsorption-absorption by solid materials
- Membrane separation
- Cryogenic distillation

The following sections contain a qualitative description of each technology.

2.2.1. Absorption by liquid solvents

Chemical absorption is the most selective and effective method for CO_2 separation currently available and widely applied in the industrial landscape. A liquid sorbent is used to separate the CO_2 from the gas. It is a mature technology [14] and it has been commercialized for many decades, mainly applied in the field of Acid Gas Removal and syngas purification. It can reach very high percentages of CO_2 removal (absorption efficiency >90% [11], with residual CO_2 depending on the feed gas composition and operating conditions.

It is the most energy intensive method since it entails the creation of a chemical bond between CO_2 and the solvent which needs to be broken during the sorbent regeneration step. A typical absorption system consists of an absorber and a stripper column [15] in which an aqueous solution of the selected chemical solvents is circulated, acting as absorbent in the first stage and being regenerated in the second stage. There are two main categories of chemical absorption processes: a) those based on amines solutions (MEA, DEA, MDEA, a-MDEA, UCARSOL^{TM}); b) those based on hot potassium carbonates (Benfield, Vetrocoke).

The chemical absorption can be applied in principle to both pre-combustion and post-combustion CO_2 capture, although with different performance and specific capture cost. A typical flowsheet for chemical absorption process is reported in Figure 2.

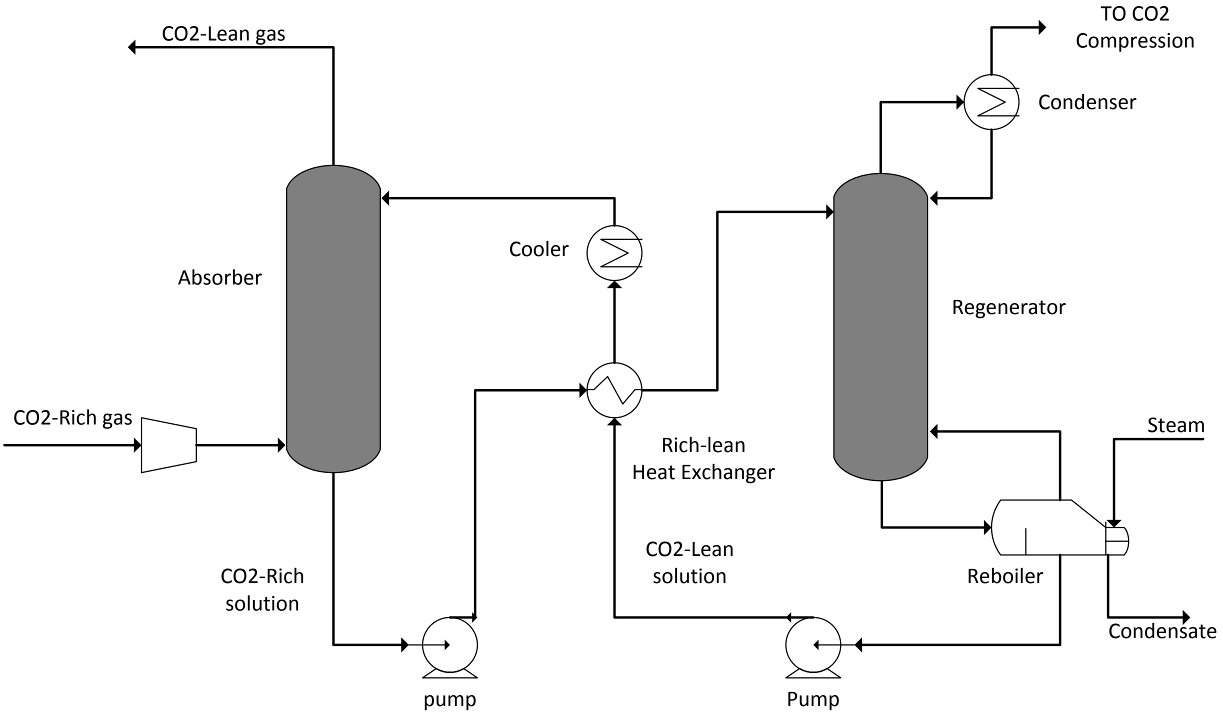

Figure 2. Typical flowsheet of a basic chemical absorption process for CO_2 capture.

One important challenge for the large deployment of this technology for CCS is its potential amine degradation, resulting in solvent loss, equipment corrosion and generation of volatile degradation compounds [16,17].

Physical absorption is less selective and can reach lower percentages of CO_2 recovery, but it has the advantage of a much lower energy consumption. It is applicable when the gaseous stream has a higher CO_2 vol %, which results in higher partial pressure (like in lean natural gas, biogas etc..), since physical absorption is controlled by Henry's law. One of the main advantage of this method is that CO_2 may be recovered mainly by depressurization, thereby avoiding the high heat consumption of amine scrubbing process. This method is widely applied the removal of CO_2 from process syngas, such as in ammonia and methanol plants, since the high syngas pressure allows to obtain acceptable carbon dioxide partial pressures even with molar fractions around 20 %. One of the most diffused technology based on physical absorption utilizes a mixture of dimethyl ethers of polyethylene glycols (Selexol^{TM}); the Rectisol® process is based on methanol and Fluor Solvent^{TM} utilizes propylene carbonate [18].

In general, the economics of CO_2 recovery is strongly influenced by the partial pressure of CO_2 in the feed gas. At low partial pressures, physical solvents are impractical because the compression of the gas for physical absorption is expensive. However, if the gas is available at high pressure, physical solvents might be a better choice than chemical solvents. This makes physical solvents particularly suitable for CO_2 removal from synthesis gas, and therefore applicable for pre-combustion capture, while their application in post-combustion capture is more energy intensive due to the low CO_2 partial pressure [24].

2.2.2. Adsorption-absorption by solid materials

In contrast to absorption processes, which use a liquid absorbent, a solid sorbent is used to bind the CO_2 on its surface. Large specific surface area, high selectivity and high regeneration ability are the main criteria for sorbent selection. Typical sorbents include: molecular sieves, activated carbon, zeolites, hydrotalcites.

In this process, CO_2 is preferentially adsorbed on the surface of a solid adsorbent at high pressure. Then the adsorbed CO_2 can be recovered by swinging the pressure (PSA) or temperature (TSA) of the system containing the CO_2-saturated sorbent. PSA is a commercial available technology for CO_2 recovery from power plants that can have efficiency higher than 85 % [11,19]. In TSA, the adsorbed CO_2 will be released by increasing the system temperature using hot air or steam injection. The regeneration time is normally longer than PSA but CO_2 purity higher than 95% and recovery higher than 80% can be achieved [11,20]. An operating cost of a specific TSA process was estimated to be of the order of 80–150 US $/tonne CO_2 captured [11, 21] Finally, the use of residues from industrial and agricultural operations to develop sorbents for CO_2 capture has attracted significant attention to reduce the total costs of capture.
Other solid sorbents, classified as high temperature sorbents, are also used in CO_2 capture processes based on solid materials. These processes are referred to solid looping cycles and rely on TSA principle. Some examples are the Calcium Looping and Sorption-Enhanced Reforming processes.They can be operated in either fluidized bed reactors with circulation of solids in a continuous mode, or in multi fixed bed reactors in a semi-continuous mode. The sorbents used are usually CaO-based materials, either natural minerals like calcite or dolomite, or synthetic materials produced from chemical precursors. In the latter case, the material is produced by chemical synthesis resulting in a sorbent micro powder which is then granulated/pelletized. The CO_2 is captured by chemical reaction in an exothermic carbonation, and released by the reverse calcination reaction. CaO-based high temperature sorbents are considered as most suited for solid cycle processes, mainly due to the favourable carbonation kinetics and the achievable heat integration. Natural calcites or dolomites are low cost and highly available materials; however, the major disadvantages which limit their use in CO_2 capture processes are a decay in sorption capacity throughout multiple cycles, and relatively low mechanical stability Two relevant research lines for the synthetic CaO sorbents are currently explored to tackle these drawbacks: the development of synthesis methods for integration of nanoscale CaO particles in micro-porous phases, stable at high temperature, like mayenite ($Ca_{12}Al_{14}O_{33}$) [22,23] to increase multi-cycle chemical stability; and the controlled pelletisation/granulation of $CaO/Ca_{12}Al_{14}O_{33}$, to increase mechanical stability.

2.2.3. Membrane separation

The membranes consist of thin barriers that allow selective permeation of certain gases. From the application perspective, different membrane modules can be envisaged: spiral wound flat sheets, supported composites and hollow fiber (HF) membrane modules. Although spiral wound and supported forms were the first commercialized, HFs offer important advantages, being the most important one their high packing density (> 10,000 m^2/m^3), about ten times higher than for flat sheet (plate and frame) membranes. In addition, HF membranes can handle very high transmembrane pressure differences (up to 70 bar) and their fabrication costs are 5 to 20 times lower than that of equivalent membranes for spiral wound modules. The systems are compact and lightweight, with the possibility of horizontally or vertically positioning, making them appropriate for retrofitting applications. In addition, since they have no moving parts on the membranes, they have low maintenance requirements. Lastly, the process does not require a separating agent for regeneration [24]. The driving force for the separation is the pressure differential across the membrane [14].

The membrane process is applicable to high pressure gas streams or gas streams containing a high carbon dioxide concentration, since the driving force is constituted by CO_2 partial pressure. CO_2 recovery is accomplished by pressure-driven mass transfer through a permeable membrane where separation is due to the differences in permeation rate of different compounds.

The commercial membranes for CO_2 separation are prepared from polysulfone, polyimide and cellulose acetate [25], with most of the current membrane research being done in inorganic membranes that can operate at high temperatures and on mixed matrix membranes, as well as facilitated transport membranes. Membrane separation can achieve the recovery of a high purity CO_2 stream (≈ 95% vol.) with one or two stages, depending upon feed gas pressure and percent recovery [26]. In any case CO_2 is recovered at low pressure and needs to be compressed to a suitable pressure for transport and storage. Economic considerations may dictate additional capital and incremental energy requirements to increase feed pressure and/or utilize two-stage separation with recompression of gas from the first stage.

2.2.4. Cryogenic distillation

Cryogenic distillation is a gas separation process using distillation at very low temperature and high pressure, which is similar to other conventional distillation processes except that it is used to separate components of gaseous mixture (due to their different boiling points) instead of liquid.

For CO_2 separation, flue gas containing CO_2 is cooled to its de-sublimation temperature (-100 to -135 °C) and then solidified CO_2 is separated from other light gases and compressed to a high pressure of 100–200 times the atmospheric pressure. The amount of CO_2 recovered can reach 90–95 % of the flue gas [11]. Since the distillation is conducted at extremely low temperature and high pressure, it is an energy intensive process estimated to be 600–660 kWh per tonne of CO_2 recovered in liquid form [27,11]. Cryogenic fractionation has the advantage that the CO_2 can be obtained at relatively high pressure as opposed to the other methods of recovering CO_2. This advantage may, however, be offset by the large refrigeration energy requirement. Special materials are also required for cryogenic service.

This process is typically used for the liquefaction and purification of CO_2 from high purity (>90%) sources [24] In cryogenic separation, there is separation of the CO_2 from the flue gas stream by condensation and vaporization cycles, separating the CO_2 from other gases such as CH_4 and N_2 based on their different vapor pressures and volatilities. This process involves the cooling of the gases to very low temperatures in order to liquefy and separate the CO_2. Due to the costs of the refrigeration, this process is suitable for treating flue gas streams with high CO_2 concentrations [28]. However, this process uses a high amount of energy to provide refrigeration and requires removing components that have freezing points above normal operating temperatures in order to avoid blockage of the equipment of the process. Also, for post-combustion flue gases, the by-products contained in the waste streams, such as NOx and SOx, must be removed before the introduction of the stream in the low temperature section, making it less economical than other post-combust capture processes.

2.3. Specifications and requirements of CO_2 from CCS

The operating conditions and quality of the captured CO_2 stream may vary, depending on the composition of the original gas stream and on the capture technology applied. Specifications and requirements of the CO_2 stream would depend on the intended use and would vary from case to case. Since one of the most promising and wide application of the captured CO_2 is for the Enhanced Oil Recovery (see Table 4), most CCS studies are based on operating conditions and quality selected for an economic and viable process of transport and storage. The here following operating conditions have been adopted in most international studies made by IEAGHG and also referred in the ENCAP report [28]

- Pressure 110 bar
- Temperature < 30°C

In addition to the above operating conditions, Table 5 gives values of composition for CO_2 storage recommended by European Benchmarking Task Force EBTF [4].

Table 5: Limits in the CO_2 stream recommended in EBTF [4].

Component	Value
CO_2	> 90 %
H_2O	< 500 ppm
H_2S	< 200 ppm
NOx	< 100 ppm
SOx	< 100 ppm
HCN	< 5 ppm
COS	< 50 ppm
RSH	< 50 ppm
N_2	< 4 % [a]
Ar	< 4 % [a]
H_2	< 4 % [a]
CH_4	< 2 %
CO	< 0.2 %
O_2	< 100 ppm

(a) :$x+\sum x_i < 4$ % = total content of all non-condensable gases

2.4. Pre-combustion CO_2 capture in power plants

2.4.1. Description of pre-combustion separation system for IGCC

This paragraph presents a summary of the main assumptions and parameters for CCS for pre-combustion separation in power plants.

In gasification reactions, the amount of air or oxygen available inside the gasifier is carefully controlled so that only a portion of the fuel is fully combusted. This “partial oxidation” produces syngas, which is then processed in a (series of) WGS reactor(s), which converts the CO to CO_2 and increases the hydrogen in the syngas stream. At this point, the CO_2 has a high partial pressure, which significantly improves the driving force for separation and capture technologies. After CO_2 removal, the H_2 rich syngas is sent to the gas turbine of a combined cycle plant, where additional electricity is generated by extracting the energy from the combustion turbine flue gas via a heat recovery steam generator (HRSG) and converting it in the steam cycle. In Figure 3 is reported a simplified flow diagram of the IGCC without CO_2 capture.

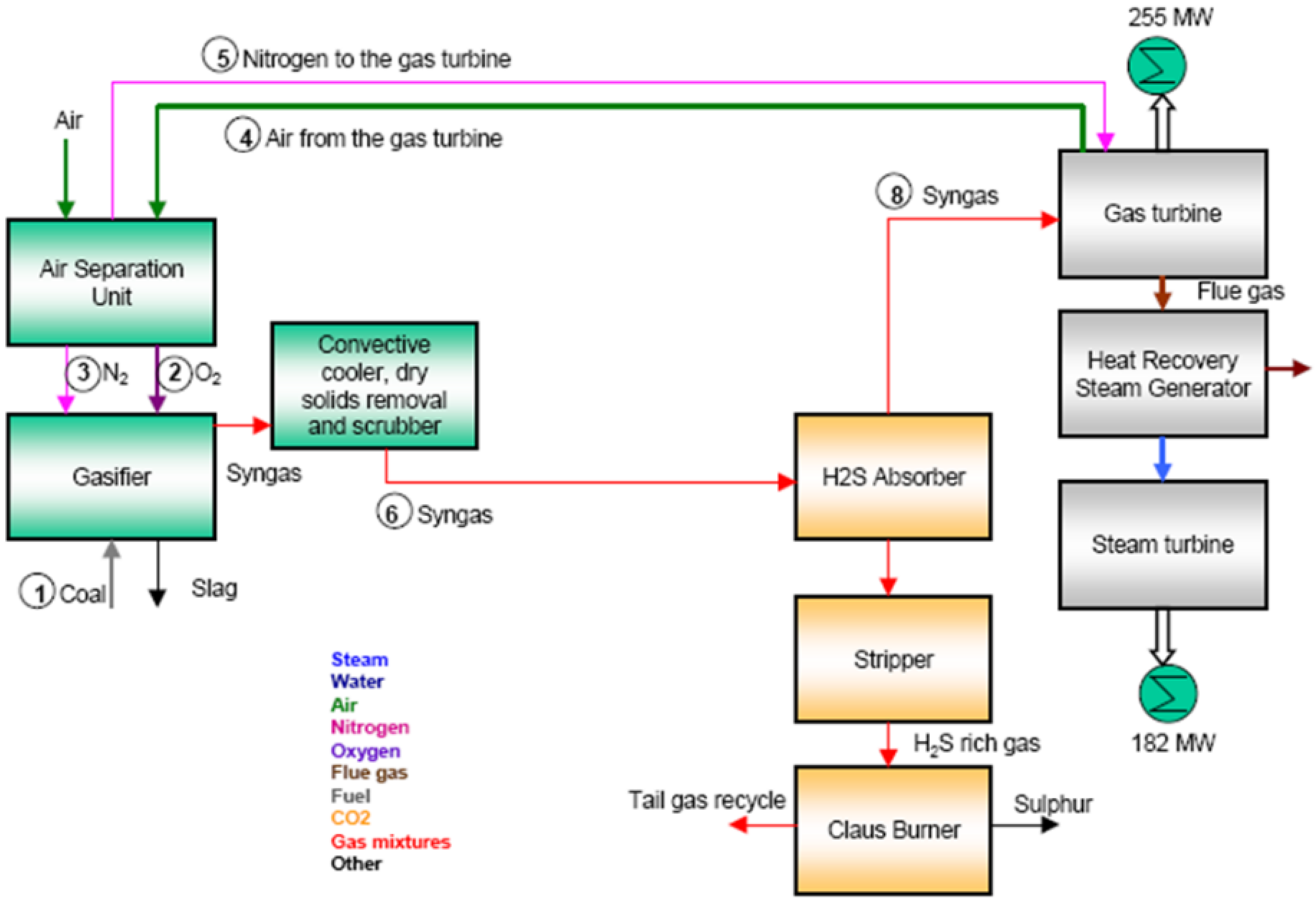

Figure 3. Simplified flow diagram of the IGCC without CO_2 capture (image from EBTF report [4]).

As described in the previous paragraph, conventional processes for removing acid gases typically involve their counter-current absorption from the syngas using a regenerative solvent in an absorber column. A simplified flow diagram of an IGCC with acid gas removal is reported in Figure 4.

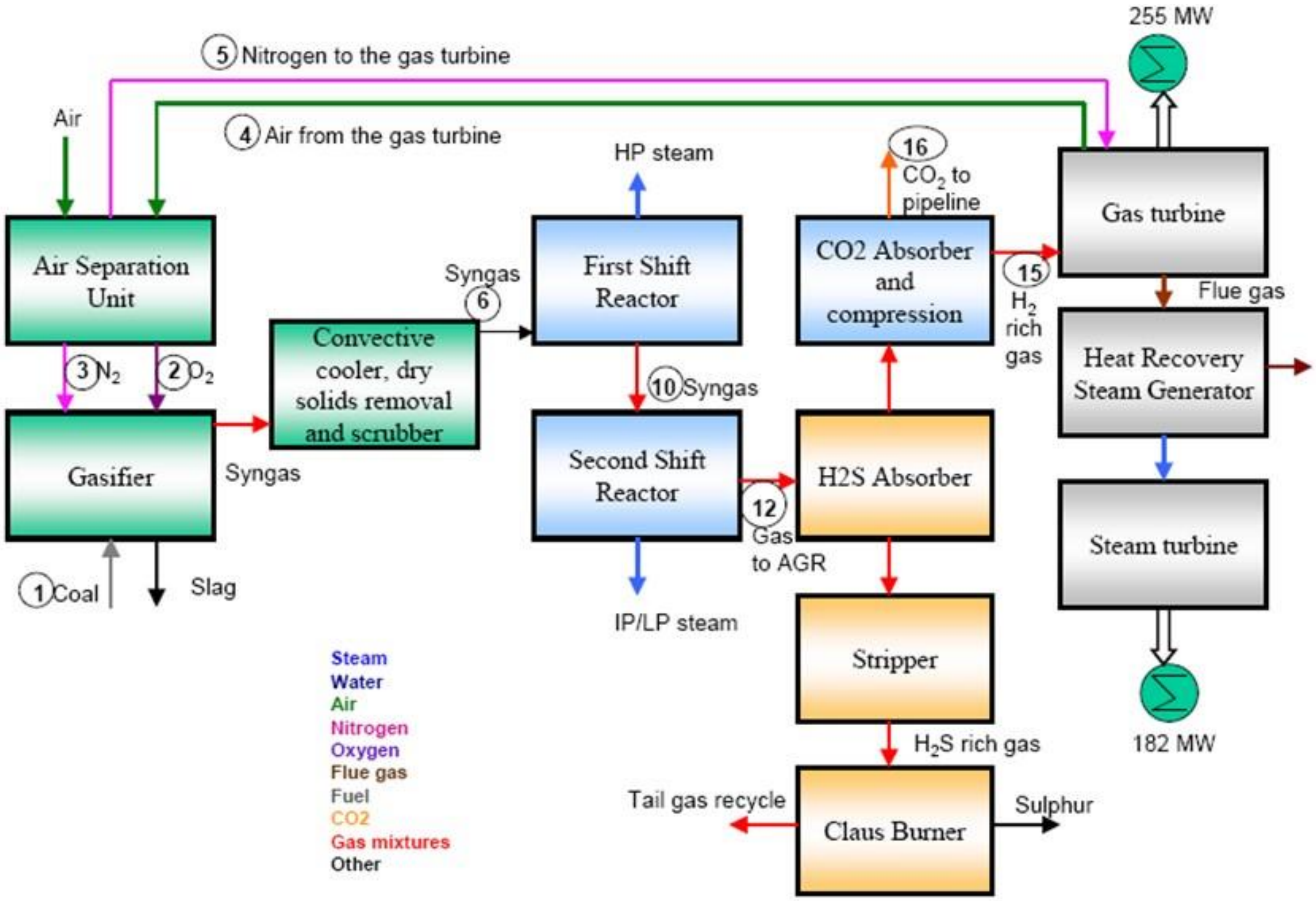

Figure 4. Simplified flow diagram of the IGCC with CO_2 capture (image from EBTF report [4]).

The IGCC with CO_2 capture includes shift reactors for converting CO to CO_2 and the Acid Gas Removal (AGR) unit including a CO_2 capture section. The H_2S is sent to the Claus plant, where the flue gas is recycled. The CO_2 is then captured from the sulfur free syngas. The solvent is regenerated by flashing at staged pressures steps, and then recycled back to the absorption stage. CO_2 is compressed to 110 bar and then sent through a pipeline to storage.

Near-term applications of CO_2 capture from pre-combustion systems will likely involve physical or chemical absorption processes, with the current state-of-the-art being a physical glycol-based solvent called Selexol [29]. Mid-term to long-term opportunities to reduce capture costs through improved performance could come from membranes and sorbents currently under development [30].

Selexol is a physical solvent consisting of a mixture of dimethyl ethers of polyethylene glycols, nontoxic, with a high boiling point, and is an excellent solvent for acid gases. It has the formulation of $CH_3(CH_2CH_2O)_nCH_3$ where n is between 3 and 9. The selectivity for hydrogen sulfide (H_2S) is much higher than that for carbon dioxide (CO_2), so it can be used to selectively remove these different acid gases, minimizing CO_2 content in the H_2S stream sent to the sulfur recovery unit (SRU) with associated benefits on SRU sizing and economics, and enabling regeneration of solvent for CO_2 recovery by economical flashing.

In both physical and chemical absorption processes, the syngas is washed as a first step with lean solvent in the absorber to remove H_2S. Cleaned syngas is sent to downstream systems for further processing and CO_2-removal. The acid gas-rich solvent leaving the bottom of the absorber is sent to the regenerator, where the solvent is stripped with steam under low pressure (reboiling) to remove the absorbed sulfur. The concentrated acid gas stream, rich in H_2S, exits the top of the regenerator and is sent to the sulfur recovery unit (SRU) for sulfur recovery. The SRU consists of a Claus plant, in which the H_2S is converted to sulfur, a saleable by-product. The regenerated lean solvent from the bottom of the regenerator is cooled by a heat exchanger against the rich solvent, followed by water cooling before being recycled back to the top of the absorber to start the absorption process cycle again.

In general, the physical solvents, like Selexol, demand relatively high syngas pressures, high partial pressure of the acid gases, and/or low operating temperature in the absorber (in some cases cryogenic temperatures below -150 °C), for good performance.

Figure 5 depicts more in particular a dual-stage Selexol process. The first column (sulfur absorber) removes most of the H_2S (and a limited amount of CO_2) from the feed syngas, which then flows to the second column (CO_2 absorber) which removes most of the CO_2. The rich solvent leaving the CO_2 absorption column is flashed in drums, from which relatively pure CO_2 is recovered. The solvent in the sulfur absorber column must be stripped in a column with reboiler to remove the high H_2S content gases.

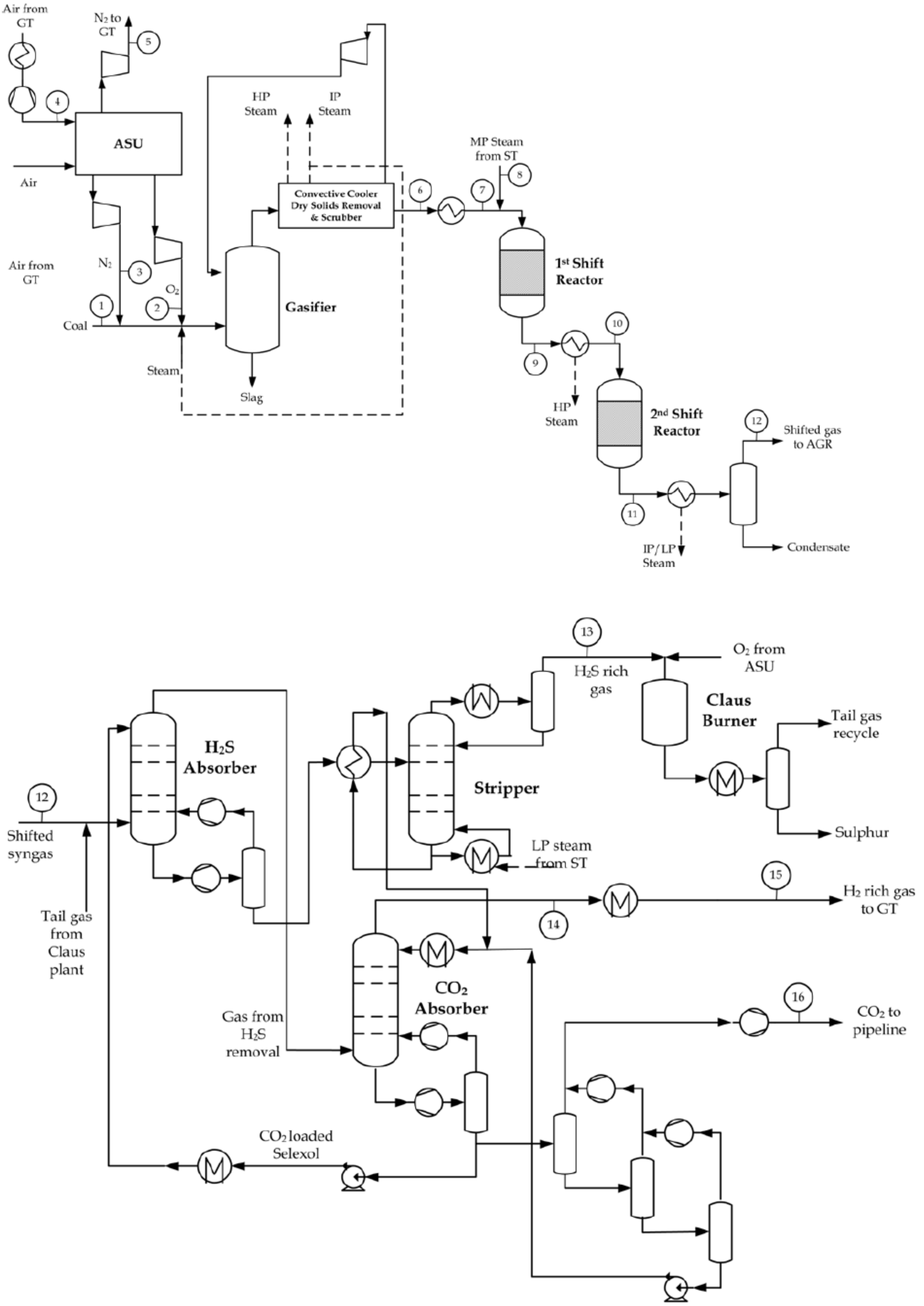

Figure 5. Detailed flow diagram of the IGCC with CO_2 capture (image from EBTF report [4]).

2.4.2. Description of references with CO_2 capture

This paragraph describes more in detail the reference layout and performance parameters for the reference IGCC with and without CO_2 capture. The conditions of the captured CO_2 in this benchmark are based on delivery pressures of 110 bar at a temperature below 30 °C following definitions from ENCAP report [28]. CO_2 quality is defined in Table 5 of § 2.3.

References from state of the art performance of an IGCC are taken from the European Benchmarking Task Force (EBTF) consisting of members of FP7 projects CAESAR, CESAR, and DECARBit [4]. The study case considers a 442 MWe cycle.

The performance and efficiencies of the CO_2 capture technology are evaluated by studying certain parameters. The most relevant are CO_2 avoidance cost, and SPECCA. Energy cost related to CO_2 capture is given by the Specific Primary Energy Consumption for CO_2 avoided (SPECCA), which is defined as follows:

$$SPECCA = \frac{HR - HR_{REF}}{E_{REF} - E} = \frac{3600 \cdot \left(\frac{1}{\eta} - \frac{1}{\eta_{REF}}\right)}{E_{REF} - E}$$

where

- HR is the heat rate of the plants, in kJ_{LHV}/kWh_{el}
- E is the CO_2 emission rate, in kg_{CO2}/kWh_{el}
- η is the net electrical efficiency of the plant
- $_{REF}$ refers to the value found for the same plant without CCS

The IGCC plant without CO_2 capture uses a Shell gasifier with flue gas recycle and Selexol for sulfur removal. The plant with CO_2 capture uses the same gasifier and Selexol for sulfur and CO_2 removal.

Table 6 shows the comparison in terms of operational performance of the IGCC system with and without CO_2 capture. The results from the table show a penalty in net electric efficiency of 10.2 percent points, which translates to 21.7 % in relative change. These values are in agreement with a similar study from IEA [31] indicating 20 % as the relative penalty in net efficiency, taking information from 11 different cases from 7 organizations in EU, US, and China. The CO_2 avoidance cost shown in the table indicates 33.0 €/t_{CO2}, which is also in line with the IEA analysis indicating 32.3 €/tCO_2 [*note 1*]. These values are also in agreement with the data obtained from the benchmark analysis carried out in preceding project M4CO2 where a CO_2 avoidance cost of 34.3 €/t_{CO2} for large scale IGCC with Selexol [32] was calculated.

Similar to an IGCC, CO_2 can be extracted from a biomass- gasification plant. In particular, in the MEMBER project the CO_2 pre-combustion capture will be tested at the premises of a biomass gasifier power plants, aiming to validate the Bio-CCS concept. Accordingly, attention has been given also to CCS from bio-based power generation. This is typically referred to as Bio-CCS or BECCS.

Given the widespread of feedstock qualities and technologies used for bio-based power generation, the technical information about costs of CO_2 avoidance give results with a larger margin of fluctuation when compared to coal based IGCC. Relevant information is available in the 5th Assessment Report (AR5) of the Intergovernmental Panel on Climate Change (IPCC) [33]. The AR5 generally acknowledges the potential of negative emissions technologies (NET) to compensate for residual emissions from sectors where abatement is more expensive. However, there is a lack of consistent and comprehensive assessments of current and expected cost for Bio-CCS [34] and to a limited extent also for CCS. AR5 relies on citing other cost reviews, establishing a ballpark range of 60–250 USD/t_{CO2} [35,36]. Estimations of Bio-CCS costs in Sweden give 75–95 €/t_{CO2} in 2020, with potential for a significant decrease by 2030 [37].

Table 6. Comparison of Operational performance of IGCC with and without CO_2 capture [4].

Parameter	**Units**	**Without capture**	**With capture**
Coal flow rate	t/h	118	137
Coal LHV	MJ/kg	25.2	25.2
Thermal energy of fuel	MW_{th}	828	954
Thermal energy for coal drying	MW_{th}	7.0	8.1
Gas turbine output	MW_e	254	293
Steam turbine output	MW_e	182	168
Air expander	MW_e	5.0	5.8
Gross electric power output	**MW_e**	**442**	**457**
ASU power consumption	MW_e	10	12
Syngas compression	MW_e	0.9	
O_2 compression	MW_e	10	12
N_2 to gasifier compression	MW_e	4.7	5.1
N_2 to GT compression	MW_e	13	28
AGR	MW_e	0.3	
CO_2 capture	MW_e	–	15
CO_2 compression	MW_e	–	21
Coal handling	MW_e	1.2	1.4
Power island auxiliaries	MW_e	9.0	8.6
Other	MW_e	0.6	0.8
Total ancillary power consumption	**MW_e**	**50**	**104**
Net electric power output	**MW_e**	**391**	**353**
Net electric efficiency	**%**	**46.9**	**36.7**
CO_2 capture rate	**%**	**–**	**90.9**
Specific emissions	**kg/MWh**	**734**	**85**
SPECCA	**MJ_{LHV}/kg_{CO2}**	**–**	**3.30**
CO_2 avoidance cost	**€/t_{CO2}**	**–**	**33.0**

Note 1. Cost in this report are in USD currency. 43 USD to EUR with 0.75 EUR/USD considering exchange rate at year of publication

2.5. Post-combustion CO_2 capture in power plants

2.5.1. Description of post-combustion separation system for power plants

For post-combustion capture, there must be separation of CO_2 at low partial pressure from flue gas after the fuel has been completely burned for energy conversion. There are many separation technologies that can be employed with post-combustion capture, including adsorption processes, absorption processes, membrane separation and cryogenic separation, described in §§ 2.2.1 through 2.2.4.

In order to have indication about the CO_2 content in a typical flue gas, as reference, indicated below is a coal power plant with an advanced supercritical boiler and turbine delivering 819 MW_e (gross) without carbon capture, with a final net power plant output of 754.3 MW_e, excluding the auxiliary power and with a net cycle efficiency of 45.5%. The feedstock coal is South African Douglas Premium 2 with a flow rate of 65.8 kg/s, with the composition of the power plant shown in the Table 7.

Table 7. Characteristics of flue gas in a post-combustion coal power plant [38] (reprinted with permission from (X. Zhang, X. He, T. Gundersen, Energy Fuels 27, 8, 4137-4149). Copyright (2013) American Chemical Society).

Parameters	Value	Unit
Flue gas flow rate	781.8	kg/s
Temperature	50	ºC
Pressure	1.016	Bar
Composition		
O_2	3.65	vol % wet
CO_2	13.73	vol % wet
SO_2	85	mg/Nm^3
NO_x	120	mg/Nm^3
H_2O	9.73	vol % wet
Ar	0.005	vol % wet
N_2	72.86	vol % wet
Particulate	8	mg/Nm^3

2.5.2. Description of references with CO_2 capture

In the following several examples of CO_2 capture in post-combustion are given.

Petra Nova CCS Project

The world largest CO_2 capture plant is located in Texas, USA. It is a project promoted by NRG Energy Inc. and JX Nippon Oil & Gas Exploration Corporation and began operations in January 2017. This carbon capture system was added to Unit 8 of the existing W.A., with an installed capacity of 240 MW and designed to capture about 90% of the flue gas emitted by the flue gas slipstream – corresponding to approximately 33% of the total emissions from Unit 8. It uses a KM CDR Process®, a CO_2 capture process that uses amine-absorption liquid with KS-1™ solvent [39]. The process structure is reported in Figure 6.

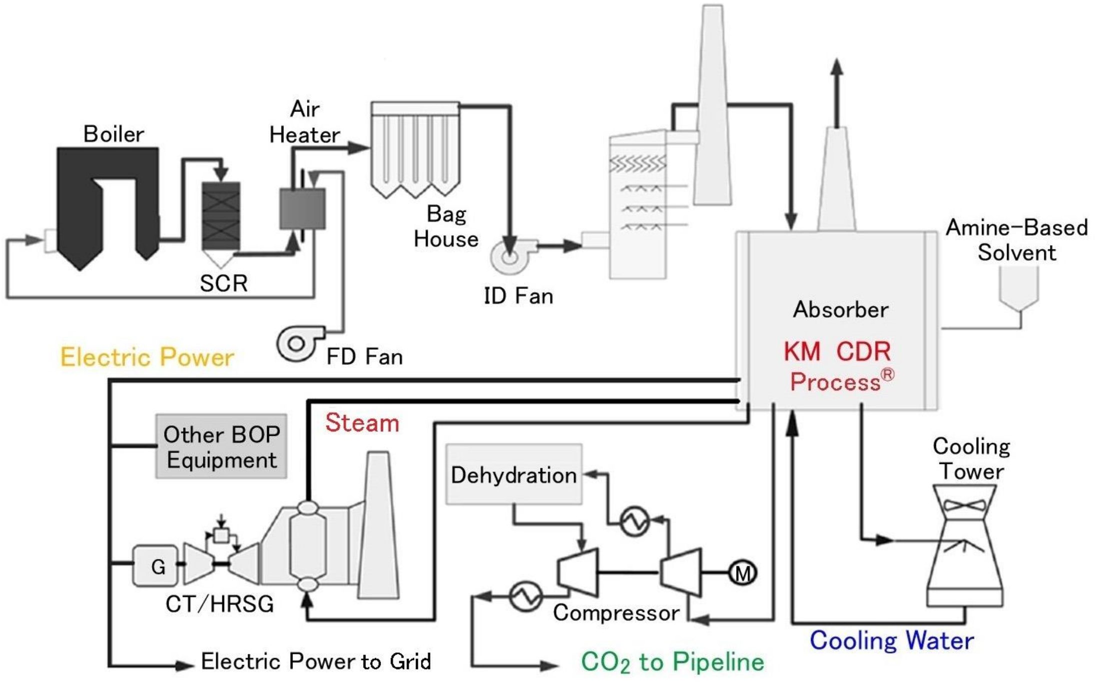

Figure 6. Process structure of CO_2 capture plant for the project Petra Nova [39].

This system is able to capture 4,776 tonnes of CO_2 per day and will inject the captured CO_2 into an oil field approximately 130 km away from the power generation plant. Due to the CO_2 EOR effect, the oil field was producing an average of 300 barrels of oil daily before carbon capture. After the first year of CO_2 enhanced oil recovery, the oil production increased to 4000 barrels per day [40]. In Figure 7 the comparison of plant performance in terms of CO_2 avoided with and without CO_2 capture is shown.

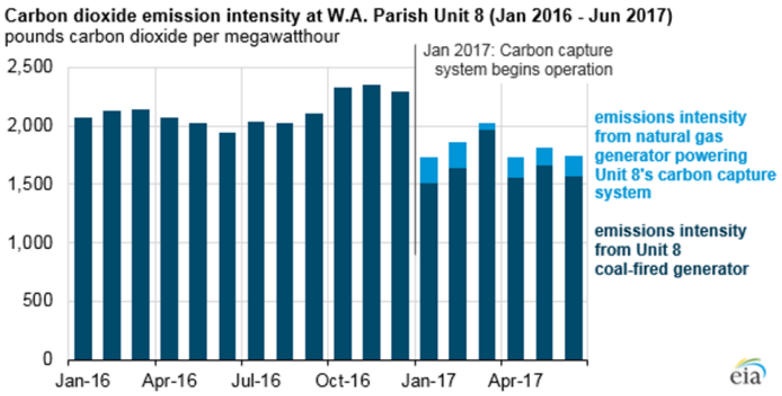

Figure 7. CO_2 emission intensity at W.A. Parish Unit 8 (Jan 2016 - Jun 2017) [40] (Source:U.S. Energy Information Administration (Oct. 2017) gratefully acknowledged).

Delta Electricity pilot plant at Munmorah, Australia

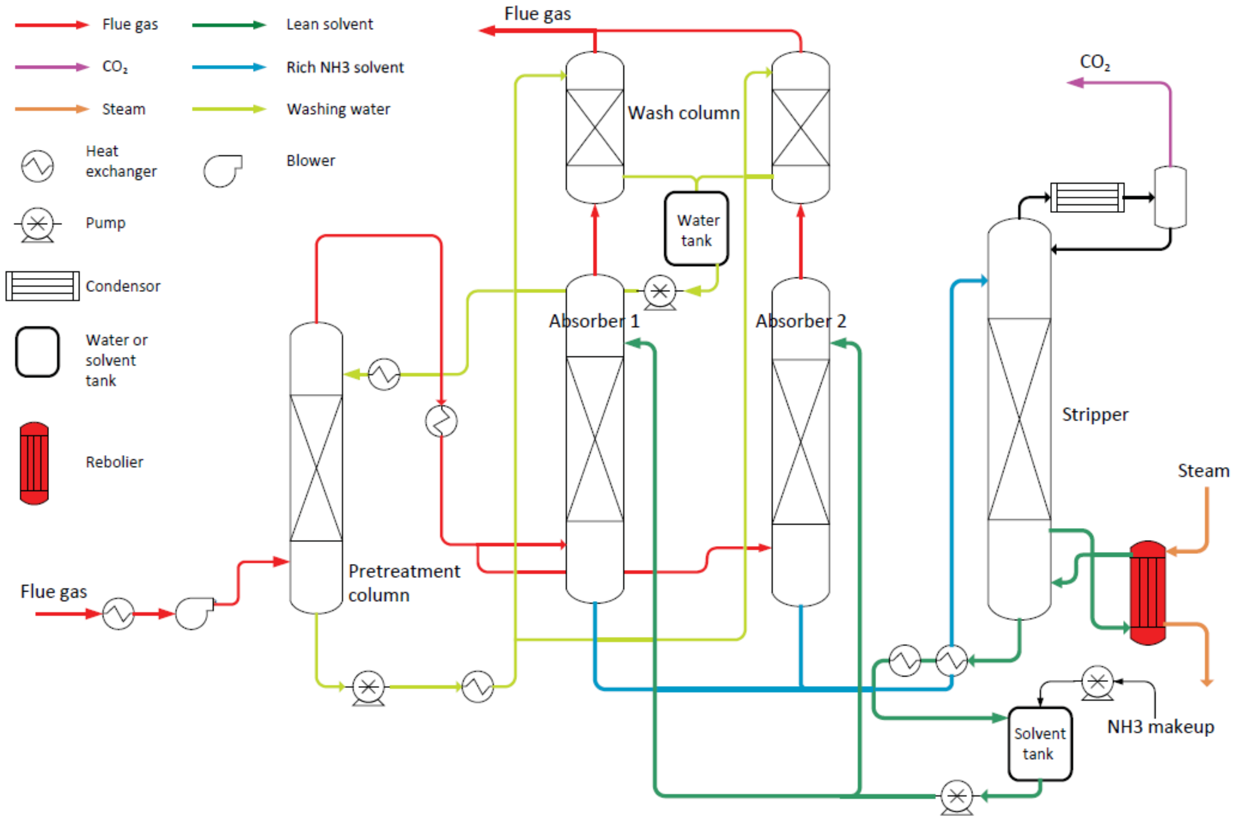

Figure 8. Schematic of the Delta Electricity pilot plant [41] (© Copyright CSIRO Australia, CSIRO Advanced Coal Technology, "Assessing Post-Combustion Capture for Coal-fired Power Stations in Asia-Pacific Partnership Countries" gratefully acknowledged, http://www.canadiancleanpowercoalition.com/files/9713/5303/7000/AS31-204_AssessingPost-CombustionCaptureReport.pdf).

This pilot plant was used to test an aqueous ammonia-based capture process under real flue gas conditions and the power station is a black coal fired power station without FGD or deNOx. The design of the pilot plant was based on a standard absorption/desorption process flow sheet, consisting of one pre-treatment column, two absorber columns with a separate washing column at the top, and one stripper, as represented in the Figure 8.

In Table 8 a typical inlet flue gas composition at Munmorah power station is given [42].

Table 8. Typical inlet flue gas composition at Munmorah power station [42] (© Copyright CSIRO Australia, CSIRO Advanced Coal Technology, "Assessing Post-Combustion Capture for Coal-fired Power Stations in Asia-Pacific Partnership Countries" gratefully acknowledged, http://www.canadiancleanpowercoalition.com/files/9713/5303/7000/AS31-204_AssessingPost-CombustionCaptureReport.pdf)

CO_2	H_2O	O_2	NO	NO_2	SO_2	N_2
8.5-12 vol%	3-6 vol%	6.5-10 vol%	200-330 ppm	<10 ppm	190-280 ppm	76-78 vol%

Indicated in Table 9 below is the performance and economic data regarding the Munmorah Power Plant

Table 9. Techno-economic data for the Munmorah Power Plant [43] (permission requested to University UNSW, Sydney)

Power Plant	**Munmorah**
Performance data	
Registered maximum capacity 2010 (MW)	600
CO_2 emission intensity before capture (t/MWh)	1.16
Thermal efficiency HHV (%)	31
Fuel type	Black coal
Fuel cost ($/GJ)	1.75
Plant load factor in 2010 (%)	12
Capture rate (%)	90
CO_2 captured (Mt/yr)	1.0
CO_2 avoided (Mt/yr)	0.6
Economic data	
Power plant capital cost ($/kW)	-
Fixed OPEX ($/kW)	72
Variable OPEX ($/MWh)	5
Short Run Marginal Cost ($/MWh)	52
Long Run Marginal Cost ($/MWh)	125
Capture Capex ($ million)	149
Capture Opex ($ million)	11
Cost of CO_2 avoided ($/t avoided)	100

The design of the power plant allows the absorber to function at lower temperatures, which is necessary to reduce ammonia losses. It also allows for the test of regeneration process at elevated pressures. In order to avoid the risk of precipitation of ammonium bicarbonate under typical absorber conditions, the ammonia concentration is below 6%.

A CO_2 removal efficiency of more than 85% was obtained, with high purity (between 99-100%) in the stripper under high pressure. Lastly, a regeneration energy requirement of approximately 4-4.2 MJ/kg CO_2 was obtained with diluted ammonia solution (approximately 5%), and more than 50% of regeneration energy being used to heat up the solvent.

Tarong PCC Pilot Plant Project

Tarong Power station is a black coal fired power station based in Australia. This pilot plant was used to evaluate the effectiveness of CO_2 capture from the power station's flue gases with an amine-based solvent. It was designed to capture CO_2 at a rate of ~100 kg/hour and consists of three main columns, as represented in the following Figure 9.

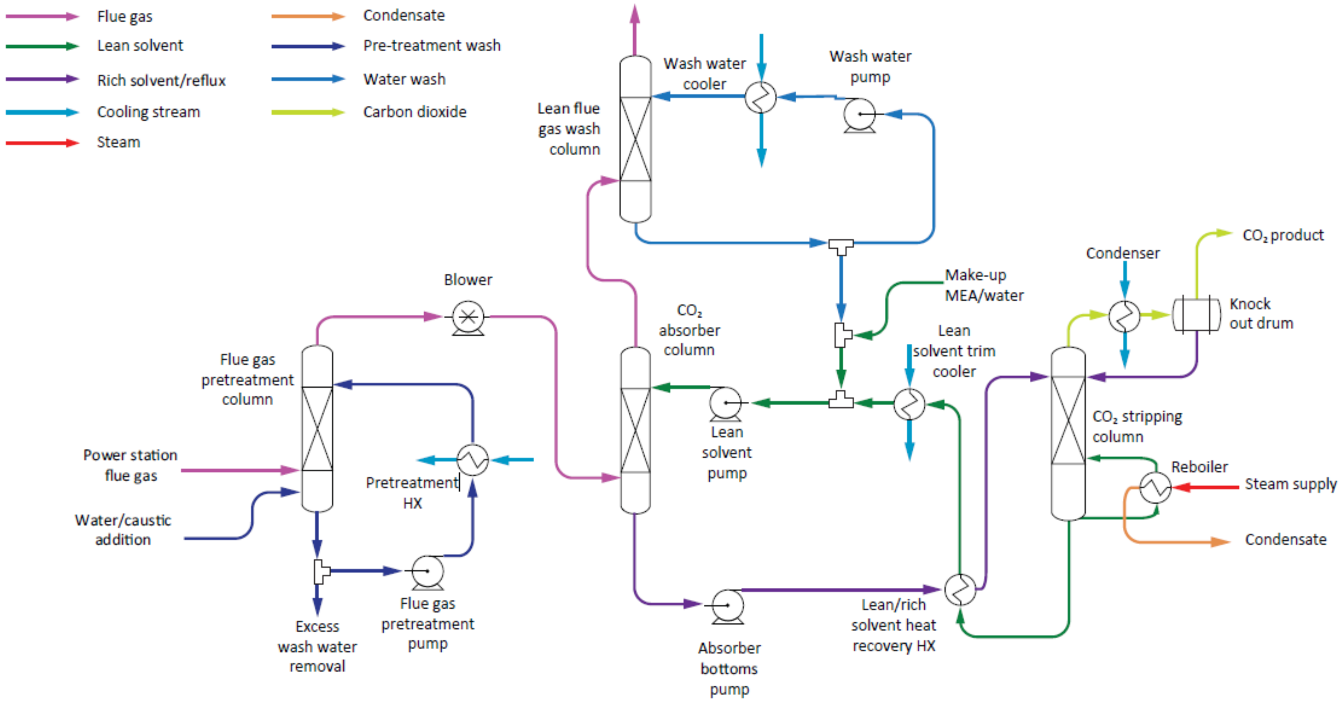

Figure 9. Schematic of the Tarong PCC pilot plant [42] (© Copyright CSIRO Australia, CSIRO Advanced Coal Technology, "Assessing Post-Combustion Capture for Coal-fired Power Stations in Asia-Pacific Partnership Countries" gratefully acknowledged, http://www.canadiancleanpowercoalition.com/files/9713/5303/7000/AS31-204_AssessingPost-CombustionCaptureReport.pdf).

The flue gases are contacted with an amine solvent –30 wt% MEA – in the absorber, to capture the CO_2. A typical flue gas composition entering the pilot plant is described in the Table 10.

Table 10. Typical flue gas composition entering the Tarong PCC pilot plant [44].

CO_2	H_2O	O_2	NO	SO_2	N_2
10 vol%	8 vol%	6 vol%	150 ppm	200 ppm	76 vol%

During the experimental campaigns, CO_2 removal efficiencies of 45-94% were achieved –with the design value being 85% capture efficiency, using an MEA solution with concentration varying from 23-33% and CO_2 concentrations at the Tarong pilot plant varying from 9-12% [42]. The CO_2 product has a high purity, with more than 98 vol% purity, with the main contaminant being water. Lastly, the CO_2 capture process has an energy consumption between 3.8 and 6.2 MJ/kg CO_2, depending on the operating conditions [44].

FP7 Project OCTAVIUS

One of the tasks of the OCTAVIUS project included a benchmark of MEA 30 wt.% CO_2 capture process on a reference bituminous coal power plant [45].

This power plant is a single advanced supercritical unit with an electric gross power output of 804.8 $\mathrm{MW_e}$ and net cycle efficiency at full load operation of 45.4% related to LHV, while the specific CO_2 emission is 761.5 $\mathrm{g/kWh_{net}}$ without post-combustion CO_2 capture. Represented in Figure10 is a flow diagram of the reference plant.

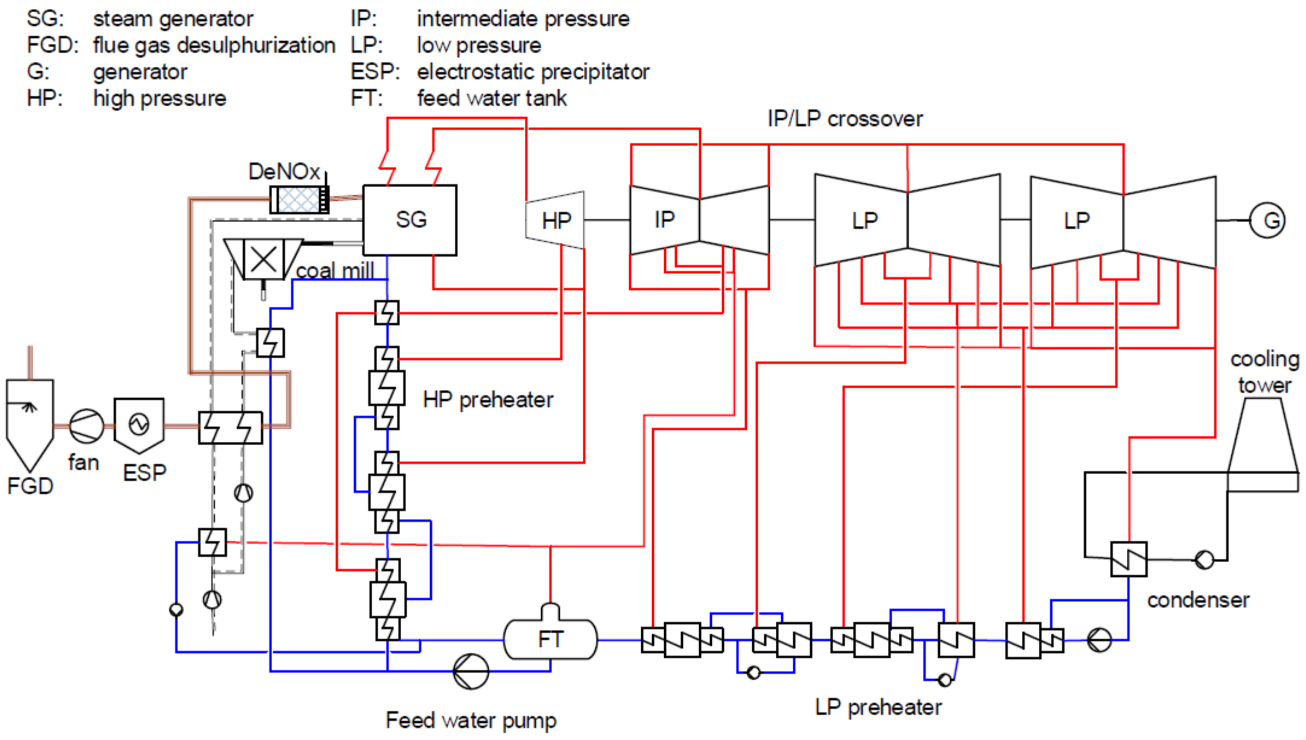

Figure 10. Flow diagram of the reference plant Octavius Project [45] (https://doi.org/10.1016/j.egypro.2017.03.1414, http://creativecommons.org/licenses/by-nc-nd/4.0/)

It is used as fuel the Bituminous Douglas Premium Coal, with a LHV of 25.2 MJ/kg. The conditions of the flue gas for the reference plant are in the Table 11.

Table 11 - Flue gas conditions for the reference plant Octavius Project [45] (https://doi.org/10.1016/j.egypro.2017.03.1414, http://creativecommons.org/licenses/by-nc-nd/4.0/)

Parameters	**Value**	**Unit**
Mass flow rate	786.5	kg/s
Temperature	50.3	ºC
Pressure	101.6	kPa
Composition		
O_2	3.65	vol % wet
CO_2	13.25	vol % wet
H_2O	12.11	vol % wet
Inert (Ar + N_2)	70.99	vol % wet
(SO_X and NO_X are omitted here)		

Two cases (Figures 11 and 12) have been considered for the benchmark of the MEA 30 wt.% process: without and with Lean Vapour Compression (LVC) from 1.1 to 1.9 bara.

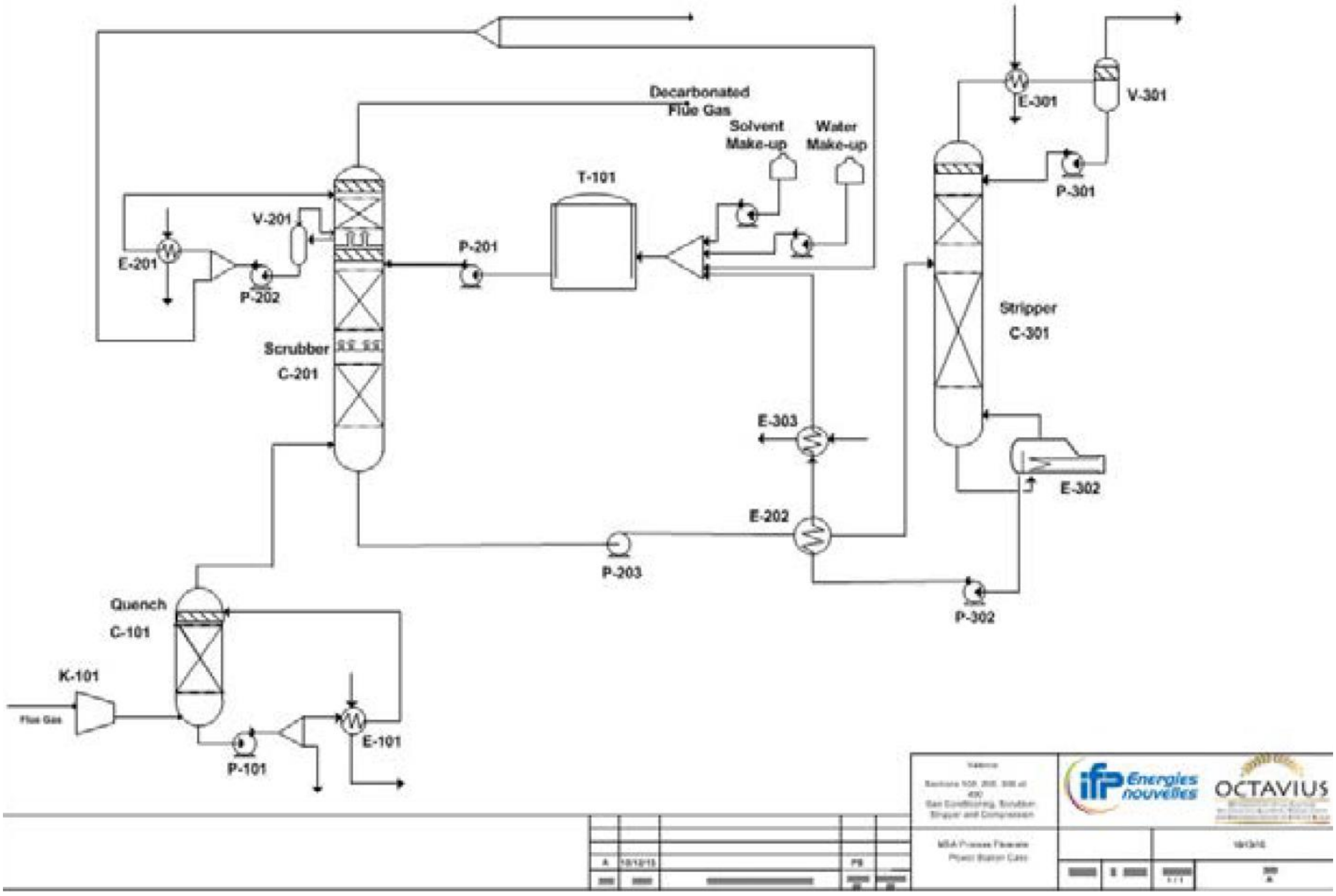

Figure 11. Flow diagram of the CO_2 capture plant for the MEA process without LVC [45] (https://doi.org/10.1016/j.egypro.2017.03.1414, http://creativecommons.org/licenses/by-nc-nd/4.0/)

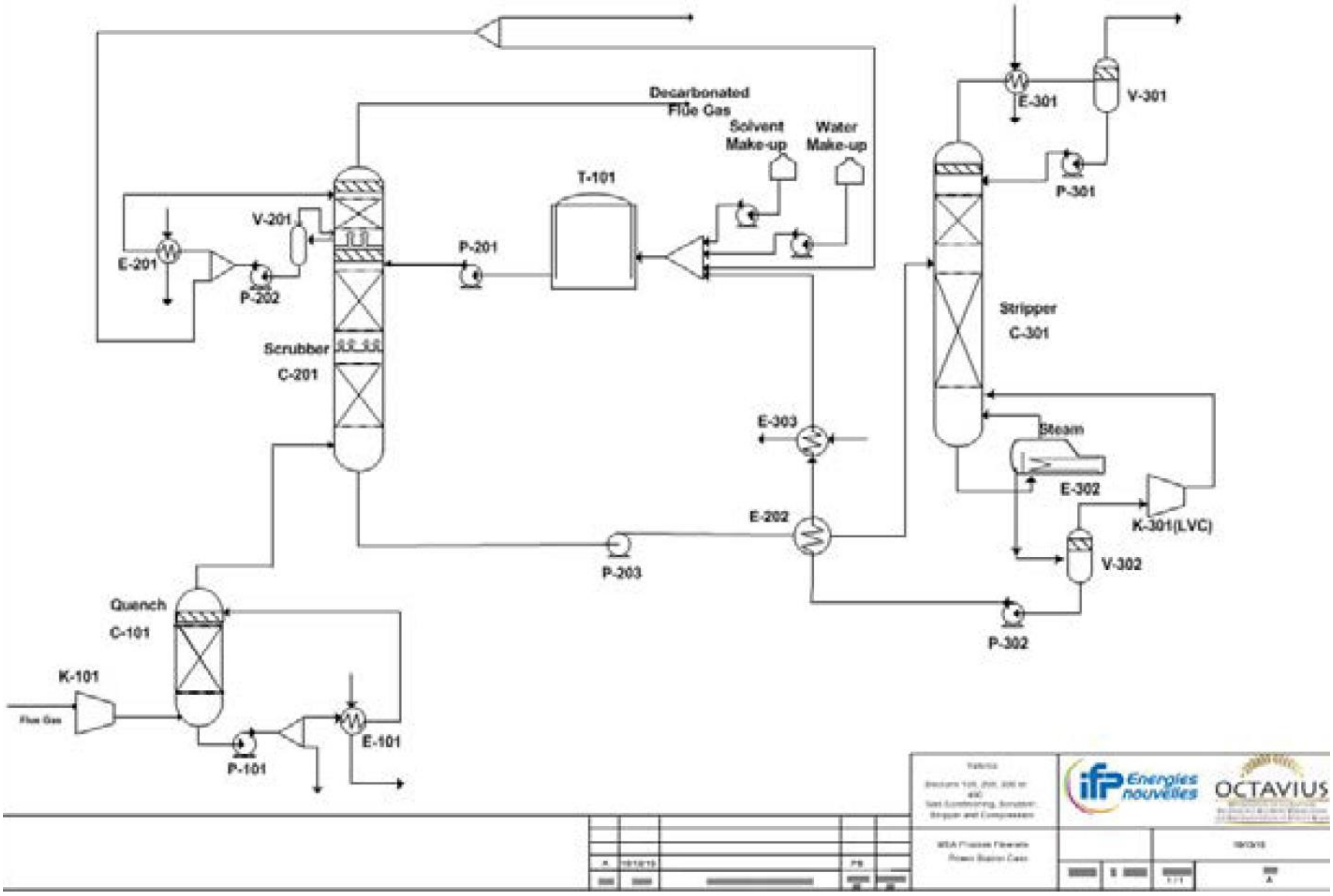

Figure 12. Flow diagram of the CO_2 capture plant for the MEA process with LVC process [45] (https://doi.org/10.1016/j.egypro.2017.03.1414, http://creativecommons.org/licenses/by-nc-nd/4.0/)

Indicated in Table 12 is economic data regarding this power plant.

Table 12. Economic data for pilot unit under OCTAVIUS project [45].

Economic data	**Power Plant (without capture)**	**Power Plant + MEA (No LVC)**	**Power Plant + MEA (With LVC)**
P.E.C (Purchased Equipment Cost) (M€)	607.6	746.9	752.3
CAPEX (M€)	1745.4	2150.9	2166.4
CAPEX Increase (%)		**+23.2**	**+24.1**
CO_2 emissions (ton/MWh)	0.76	0.08	0.09
COE (Cost of Electricity) (€/MWh)	61.18	99.05	97.09
COE Increase (%)	-	+61.9	+58.7
CO_2 avoided cost (€/CO_2 ton)	-	**56.45**	**54.30**

2.6. Hydrogen production with integrated CO_2 capture

2.6.1. Description of CO_2 generation/removal in Hydrogen-rich gas production processes

Industrial hydrogen production from hydrocarbon feedstocks is realised through energy intensive processes which are extensively applied in many sectors of the industrial landscape, with different configurations depending on the required hydrogen purity and final process destination. More generally, one should speak of various process classes suitable for production of a hydrogen-rich gas, optimized with alternative routes depending on the request of a pure hydrogen stream or of a syngas having composition suitable for the downstream petrochemical processes (ammonia, methanol, GTL, oxo-synthesis).

The hydrogen-rich syngas can be produced form a range of fossil feedstocks like coal, oil fractions and natural gas, or from renewable feedstock like biomass and biogas. The main process classes and relevant feedstocks most used in industry are:

- Gasification (coal, pet-coke, biomass)
- Partial oxidation (heavy oil fraction)
- Auto-thermal reforming (natural gas)
- Steam reforming (light oil fractions, natural gas, refinery off-gas)

Among these process classes the steam reforming is the most widespread and economic for pure hydrogen production [46,47], while for syngas production the others can take advantage by using heavier and cheaper feedstocks and combine reaction steps to obtain the required syngas composition (as ex.: H_2/CO, N_2/H_2, etc.). One main issue which is common to all above process classes, is the production of a large amount of CO_2, originated both from internal process reactions (mainly oxidation and water gas shift) and from the external combustion, which supports the endothermic reaction step, if present. The CO_2 amount generated by the internal process reactions becomes part of the syngas, while the CO_2 produced by external combustion ends up in the flue gas which is sent to the atmosphere.

Since CO_2 is derived from the carbon atoms fed to the process, the C/H ratio in the feedstock has a considerable impact on the specific amount originated from internal process reactions, while the overall thermal efficiency has an impact on the thermal input required and therefore on CO_2 produced by external combustion. The CO_2 amount present in the syngas can be captured upstream the syngas utilization with the advantage that it is at a higher pressure, while the flue gas is at atmospheric pressures and would need to be compressed with an additional energy request. Depending on the final destination of the syngas, the CO_2 present is either removed or used in the process downstream, like in the case of methanol production.

For both ammonia and pure hydrogen production CO_2 is necessarily removed from the syngas; in the case of an ammonia production process, it is removed by means of a dedicated absorption/stripping unit upstream the ammonia synthesis loop, while in pure hydrogen production CO_2 is removed from the syngas together with all other undesired compounds via a PSA unit.

In the following §2.6.1.1 we will focus on CO_2 capture in the ammonia production and in § 2.6.1.2 we will examine the case of a steam reforming process for pure hydrogen production.

2.6.1.1. CO_2 capture from Hydrogen-rich syngas in Ammonia production

The process for ammonia synthesis is based on the main exothermic reaction occurring between hydrogen and nitrogen, provided in stoichiometric ratio over promoted iron based catalyst. Hydrogen and nitrogen are usually brought into contact along the upstream process through combined steam reforming and auto-thermal reforming steps, aimed to produce a synthesis gas of the desired composition (H_2/N_2 = 3 mol/mol).

The process syngas is in most cases produced from a natural gas feedstock, through the following main process steps:

- Natural Gas desulfurization
- Primary Reforming with steam
- Secondary reformer with air
- High Temperature (HT) Water Gas Shift reaction
- Low Temperature (LT) Water Gas Shift reaction
- Syngas cooling (water separation)
- CO_2 removal
- Methanation

The process syngas produced at exit of the LT WGS reactor, after cooling and water removal, has the typical composition range reported in Table 13 here following and it is available at pressure of 25-30 bar. Similar composition can be found in [48].

Table 13. Typical dry syngas composition upstream CO_2 removal in Ammonia process.

Component	**mol %**
H_2	60 ÷ 61.5
N_2	20 ÷ 20.5
CO	0.1÷0.3
CO_2	17.4÷19.2
CH_4	≈0.2
Ar	≈0.3

The CO_2 mol % value in the process syngas and the high process pressure makes the removal feasible both by chemical and physical absorption processes, and in fact both methods can be found in operation in modern ammonia plants.

The removal specification is normally quite severe in this process, since CO_2 presence in the ammonia synthesis reactor would contribute to the deactivation of the catalyst caused by carbon oxides and would act as an inert in the synthesis loop, with a negative impact on the performance of the process. CO_2 removal by absorption is specified for less than 500 ppm and can reach targets of 100 ppm; CO_2 residual values are further decreased to < 5 ppm after the methanation step. This fact makes the ammonia process a very good candidate for carbon capture, since the process itself needs to integrate CO_2 removal and this has been done for decades, allowing the achievement of technological maturity. An additional CO_2 amount is also produced by combustion in the primary steam reformer and this amount is currently emitted in the flue gas to stack.
As it results from the overall material balance, the amount of CO_2 separated by absorption in a modern ammonia plants by, for example, KBR technology is in the order of 0.81 Ton CO_2 / Ton NH_3, while the amount emitted to stack with flue gas is 0.24 Ton CO_2 / Ton NH_3 [49]. From material balance around 78% of the CO_2 produced available for pre-combustion capture in an Ammonia plant. A simplified scheme of the ammonia production process is reported in Figure 13.

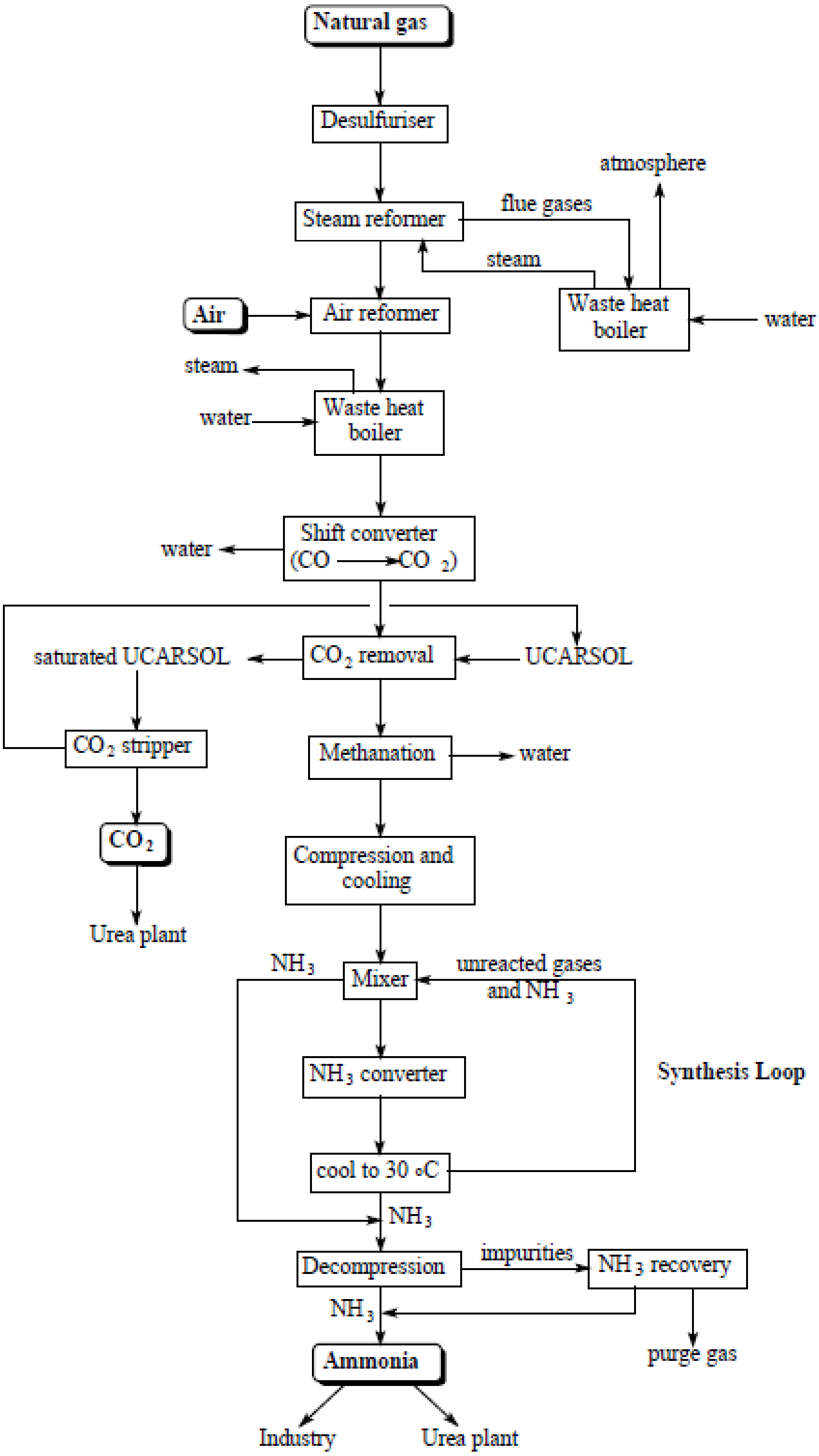

Figure 13. Schematic block diagram of the ammonia synthesis process [48] (New Zealand Institute of Chemistry, Chemical Processes in New Zealand, is gratefully acknowledged).

A favourable aspect related to CO_2 removal in the ammonia process is the possibility to use it directly in the generation site for a combined urea production.At present around 36% of the overall CO_2 produced in the ammonia synthesis is used for the associated production of fertilizers [50]. However, it should be noted that the CO_2 captured in this way is only temporarily stored, since it is soon after released to the atmosphere during the fertilizing process through the hydrolysis of urea.

CO_2 removal method is in most cases a chemical absorption process, which is realised by means of a continuous scrubbing system using an absorber column where syngas is scrubbed in counter-current with the lean solution and the rich solution is regenerated in a stripper column. CO_2 is released in a concentrated stream on top of the stripper. Figure 14 shows a typical process flow diagram of a CO_2 absorption system applied in an ammonia plant.

CO_2 removal from process syngas is a significant step in the ammonia production with respect to investment and energy consumption, therefore it has been continuously improved. Alkanolamines are widely used as the preferred absorbents for CO_2 capture in ammonia plants. Early amine based processes used MEA in low concentrations of about 20 wt% mixed with water, but had some significant drawbacks including a high amount of energy to be regenerated, low CO_2 loading, degradation and corrosion. Improvements resulted in energy savings, by raising the concentration of MEA to about 30%, and adding proprietary corrosion inhibitors to the amine solvent, permitting the use of carbon steel equipment in low temperature sections of the process. Newer formulations of amine based CO_2 removal solvent use MDEA as the main chemical component, with additions of other amines to improve the solvent retention and efficiency in a CO_2 removal.

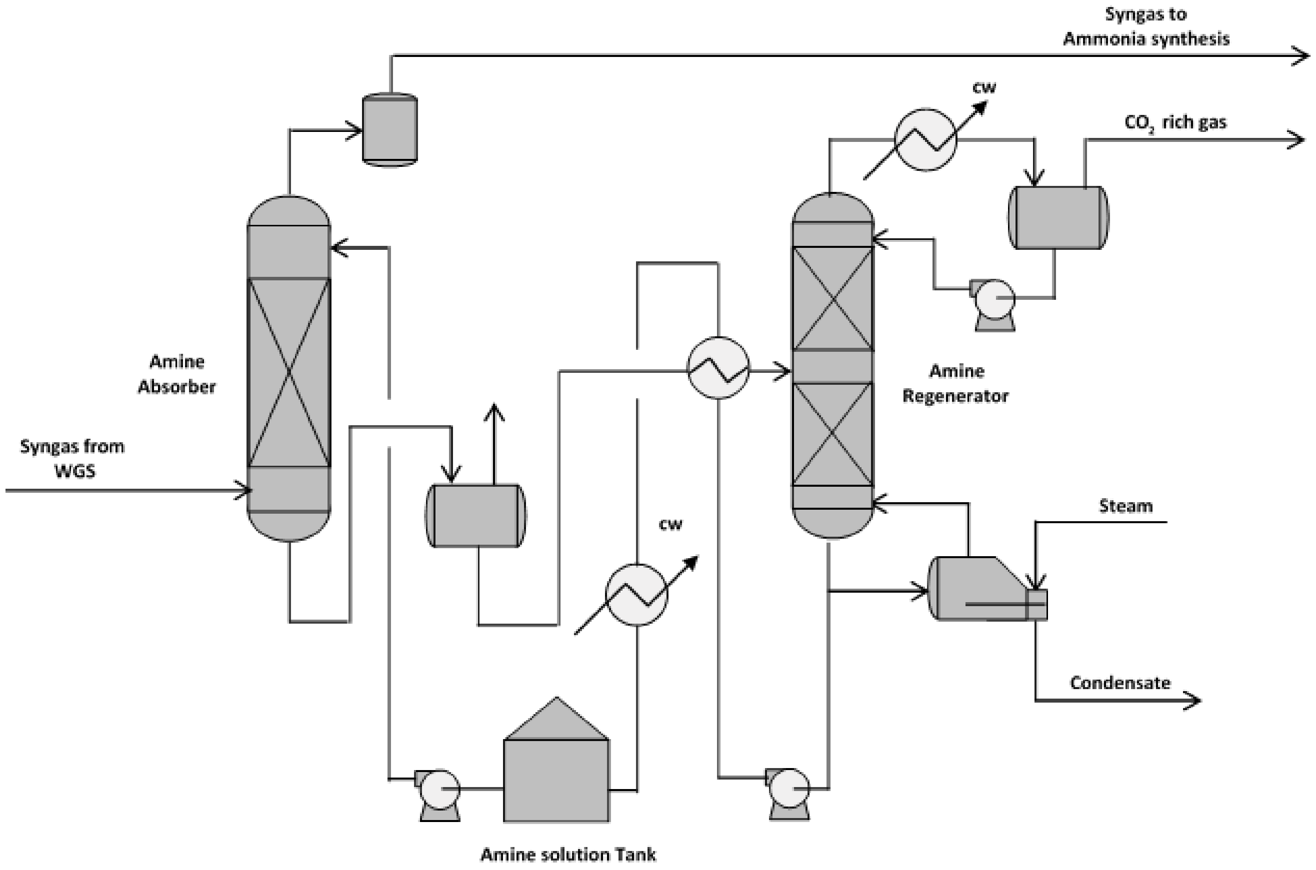

Figure 14. Process Flow diagram of an absorption-regeneration cycle using an amine solution for CO_2 removal from syngas [51].

Physical absorption processes are suitable and widely applied for CO_2 removal in ammonia plants. Physical absorption solvents typically used include glycol dimethylethers (Selexol) and propylene carbonate (Fluor). Regeneration of the solution is performed by vacuum flashing and air stripping and consumes significantly less energy than in chemical absorption.

Both chemical and physical absorption processes are considered applicable for CO_2 capture and their performance can indicate a benchmark and a reference cost based on their wide industrial application.
Table 14 reports main removal technologies and relevant performance operated in modern ammonia plants.

Table 14. Main CO_2 removal technologies/performance in modern ammonia plants [readapted from 52].

CO_2removal Technology	**Solvent**	**Energy Use GJ/t CO_2**	**CO_2 purity**
Chemical Absorption	MEA	3.4	99%
Chemical Absorption	a-MDEA	0.9	99.95%
Physical Absorption	DEPG (UOP Selexol)	0.6	98.5%

Since CO_2 removal is a process step already part of the ammonia plant, the integration of CCS consists mainly in the addition of a compression step and its transfer via pipeline to the storage facility. Ammonia production is therefore one of the most suitable industrial production for integration of CCS at limited cost. In the report by Global CCS Institute [53] it is reported a cost of CO_2 avoidance of 33.1 US$/ton (base Europe-Germany), corresponding to about 26.5 €/ton (at an exchange rate of 0.8 €/$)

2.6.1.2. CO_2 removal from Hydrogen-rich syngas in pure Hydrogen production

The steam reforming process is the most efficient and widespread process for pure hydrogen production, and it is applied to about 80% of overall hydrogen production and therefore we will refer to a benchmark case based on SMR technology. Largest use of hydrogen after ammonia production is in refinery operations, covering about 37%[54].

Typical feedstocks used in refinery range from natural gas to light naphtha and refinery off-gas.

Hydrogen for refinery use is normally produced at pressure of 20-25 Bar g, temperature of 40°C, and purity $\geq$ 99.99 %.

The basic process configuration of a modern hydrogen plant is based on four main process steps:

- Feed purification
- Steam Reforming reaction
- Water Gas Shift reaction
- Purification by Pressure Swing Absorption (PSA)

A simplified process block diagram of a Steam Reforming process is shown in Figure 15.

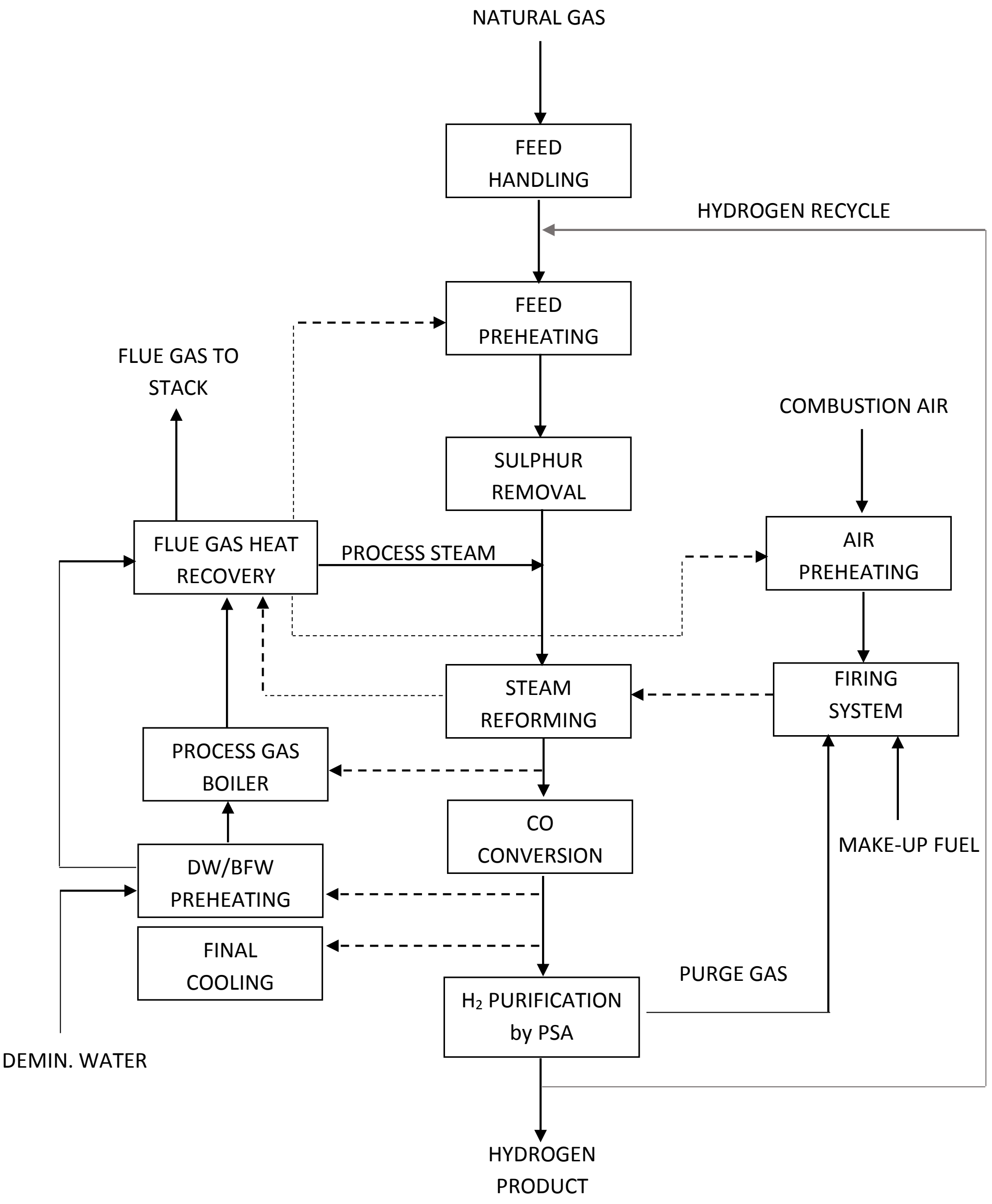

Figure 15. Block diagram of a pure hydrogen production process.

After feed purification, the main reaction step is the endothermic steam reforming reaction between hydrocarbon and steam, which is conducted at high temperature (typically between 850 and 920 °C) and excess of steam in the steam reforming furnace. This step is eventually preceded by an adiabatic pre-reforming which is capable to convert higher HCs without coke formation.

Also in this case, like in other syngas production processes, a part of CO_2 (typically ~60 % of the total amount) is generated inside the process syngas in the steam reforming (SMR) and water gas shift (WGS) reactor stages, and another part (40 %) is additionally generated in the SMR combustion to provide the necessary thermal input to the endothermic reaction [55].

If an auto-thermal reactor was used, the internal combustion would result in a higher CO_2 content in the process syngas, and this larger amount (around 90% from NTNU study [56]) would be available for carbon capture.

In the process for pure hydrogen production, the syngas effluent from the WGS reactor is cooled down and purified via a PSA unit; in this configuration the CO_2 present in the process syngas goes in the purge gas stream together with the other components separated from hydrogen. The resulting purge gas contains also unconverted methane, CO and some hydrogen escaped during the desorption step and it is burnt together with additional fuel, contributing to sustain the endothermic reforming reaction. As a result, the overall amount of CO_2 generated ends up in the flue gas stream and is sent to the atmosphere through the stack.

The two different CO_2 contributions present also an interesting aspect when considering their possible removal; in fact, while the CO_2 generated inside the process is found in the syngas at high pressure, the CO_2 generated by external combustion is in the flue gas at atmospheric pressure. This fact makes its recovery less energy intensive in the first case (pre-combustion), with the additional benefit of reducing the load of the hydrogen purification step by PSA, but in this last case it would be limited to the CO_2 amount generated inside the process.

On the contrary, an eventual CO_2 recovery downstream in the flue gas could include both CO_2 from process and combustion.

The composition of syngas upstream PSA (see Table 15), is similar to the ammonia plant, although in this case nitrogen is present only in lower percentage by volume eventually coming from natural gas composition.

Also, the operating conditions are similar to the ammonia process, and in fact in old hydrogen plants up to the ‘80s the hydrogen purification step was realized with the same method still adopted today in ammonia plants. The diffusion of more economic PSA units has totally replaced the old-style purification section in hydrogen plants, and this makes the integration of CCS much heavier in a modern hydrogen unit than in an ammonia unit.

Table 15. Typical syngas composition upstream PSA in SMR process for hydrogen production [56].

Component	**mol %**
H_2	77.5
N_2	0.1
CO	0.3
CO_2	20.5
CH_4	1.4
H_2O	0.2

2.6.2. Description of references with CO_2 capture

The specific cost of CCS based on MDEA absorption technology upstream PSA (pre-combustion capture) has been estimated within a thesis work in 2016 by the Norvegian University of Science and Technology [56]. The value is reported for different hydrogen production technologies, and in particular it is estimated in 53 €/tonCO_2 for SMR technology and 48€/tonCO_2 for the ATR technology.

A wide techno-economic evaluation is also reported in the paper presented at the 13th International Conference on Greenhouse Gas Control Technologies of Lausanne in November 2016 [57]. The paper presents five different alternatives of carbon capture schemes applied to a Hydrogen plant having a capacity 100,000 Nm^3/hr of via SMR (NG feed and fuel):

- Case 1A: SMR with CO_2 capture from Syngas (downstream WGS) using MDEA
- Case 1B: SMR with increased Syngas production and CO_2 capture (downstream WGS) using MDEA
- Case 2A: SMR with CO_2 capture from PSA tail gas using MDEA
- Case 2B: SMR with CO_2 capture from PSA tail gas using low temperature and membrane separation
- Case 3: SMR with CO_2 capture from fuel gas using MDEA

above cases realize different percentages of CO_2 recovery, and in particular the scheme of Case 3 which is in post-combustion can realize the target value of 90% (as per MEMBER) while all other cases in pre-combustion present more limited CO_2 recoveries between 53% and 67%.

The table 16 here below reports the financial results of the analysis, in terms of LCOH (Levelised Cost of hydrogen) and CO_2 Emission Avoidance Cost, together with CO_2 recovery for each case.

The Levelised Cost of hydrogen is based on a discounted cash flow analysis, taking into account all sales of hydrogen and electricity (by-product) over the plant life (25 years) and the overall production cost by operating and maintaining the plant.

The cost of CO_2 avoidance (CAC) is then calculated according to the following:

$$CAC = \frac{LCOH_{ccs} - LCOH_{basecase}}{CO2emission_{basecase} - CO2emission_{ccs}}$$

Table 16. Typical syngas compositon upstream PSA in SMR process for hydrogen production [readapted from 57].

Case	LCOH € cent/Nm^3	CO_2 Emission Avoidance Cost €/ton	CO_2 Recovery %
Base Case	11.4	-	-
Case 1A	**13.5**	**47.1**	**56**
Case 1B	14.6	62.0	67
Case 2A	14.2	66.3	54
Case 2B	14.0	59.5	53
Case 3	**16.5**	**69.8**	**90**

Case 1A represents the most conventional pre-combustion scheme based on MDEA absorption and will be used as benchmark case for the hydrogen production with CCS in pre-combustion.

Case 3 represents also an interesting benchmark in post-combustion capture, since it can reach the same CO_2 recovery as fixed in MEMBER.

From a survay of the existing applications of industrial Hydrogen production with CO_2 capture, in particular there are two Hydrogen production units, both based on SMR technology, operating with an integrated CCS system.

The first one is operated by Air Products at Port Arthur in Texas since 2013, and the CO_2 captured with vacuum separation technology is utilized for EOR at West Hastings Unit oilfield facilty in Texas [58].

The second one is operating since 2015 at Shell's Scotford Upgrader located near Fort Saktchewan, Alberta, Canada. The CO_2 is captured via an amine absorption unit and it is delivered to a saline aquifer (Cambrian Basal Sands) for storage and possible EOR [59].

2.7. Overall comparison and CO_2 capture targets

In the following Table 18, all main outcomes from state of the art about CO_2 capture in pre- and post-combustion are summarized for the three selected applications. Member project targets are also included. It should be pointed out that the cost targets in this table are strongly affected by the costs of utilities used in the calculations, thus should be compared with care.

Table 18. Overall comparison and CO_2 capture targets.

	Reference Technology	Reference CO_2 Capture [%]	Reference Cost of CO_2 avoided [€/ton]	MEMBER Targets for CO_2 Capture [%]	MEMBER Targets for Cost of CO_2 avoided [€/ton]
Pre-comb. Power (IGCC) [4]	Absorption by SELEXOL	90.9	33	90	< 30
Post-comb. Power (Coal) [45]	MEA absorption	88.1	54.30	90	< 40
Hydrogen via SMR (NG) +CO_2 pre-comb. capture [57]	MDEA absorption	56	47.1	90	<30
Hydrogen via SMR (NG) +CO_2 post-comb.capture [57]	MDEA absorption	90	69.8	90	<30

3. Advanced CO_2 capture methods and materials

New technologies and materials for CO_2-capture are under development. An emerging technology is the use of membranes for gas separation. Generally, membranes consist of porous support with an active layer providing selectivity and permeability. Two types of membranes exist, polymer based and ceramic or metal based membranes. The active layer on a polymer membrane consists of a polymer mixed with active ingredients like Metal-Oxide-Frameworks (MOFs). Type and amount of MOF influences selectivity and permeability. The active layer on a ceramic or metal support is generally a Pd-layer which is highly selective for hydrogen.

For the physical and chemical adsorption processes new sorbents are being investigated.

3.1. Membranes

3.1.1. Polymer, MOF, MMM

Among the different filler particles proposed for application in mixed matrix membranes, the use of Metal Organic Frameworks (MOFs) have been identified as a breakthrough in the research field. Hollow fiber mixed matrix matrix membranes are being developed in the project. PBI polymer based hollow fibers for pre-combustion CO_2 capture (H_2/CO_2 separation). Dual layer hollow fibers are being prepared by spinning with co-extrusion (MOF will be in the outside layer). For post-combustion CO_2 capture (CO_2/N_2 separation) thin film Pebax polymer based composite hollow fibers are being prepared by dip coating of porous hollow fiber supports (MOF will be in the outside coating selective layer).

The key performance indicators for both pre- and post- combustion MMMs is permeance and selectivity - the MEMBER project has stringent goals on these. For pre- and post- combustion application, membranes need to achieve permeance of P_{H2} >100 GPU and P_{CO2} >300 GPU and selectivities of H_2/CO_2 > 18 and CO_2/N_2 > 70 respectively.
Production of the MOF actives for these membranes will need to be demonstrated at the kg scale. For incorporation into the HFs, the MOFs should also possess the correct nano-morphology.

For use in the prototype unit, the membranes modules should contain hollow fibres with a total area of 10 m^2, since this value is representative to bring the technology to MRL 6. Further, the membranes need to be stable up to 200 ^oC at 10 bar, for pre-combustion, and withstand feed pressures of 7 bar, for post combustion applications.

Finally, the cost of these membranes will need to be < 150 €/m^2 and < 100 €/m^2 for pre- and post-combustion respectively. The recyclability of these membranes should also be considered and factored into this final cost a target recyclability of 80 % is specified for membranes produced in the MEMBER project. All these factors are summarized in Table 19 and 20.

Table 19. Target specification for pre-combustion MMMs.

Pre- combustion Specification	Value	Unit
H_2/CO_2 separation	100	GPU
H_2/CO_2 selectivity	18	
Design temperature	200	^oC
Design pressure	10	bar
Cost	<150	€/m^2

Table 20. Target specification for post-combustion MMMs.

Post- combustion Specification	Value	Unit
N_2/CO_2 separation	300	GPU
N_2/CO_2 selectivity	70	
Design pressure	7	bar
Cost	<100	€/m^2

3.1.2. Pd based membranes

Among the membranes for hydrogen separation, Pd based membranes have the highest permeance and selectivity. In order to reduce cost and increase the permeation, thin Pd supported membranes supported on porous ceramic or metallic supports are being developed. Ceramic supported membranes show high H2 permeation, they are cheaper that the metallic ones but they cannot be easily incorporated into metallic reactors.

A perm-selectivty of > 10000 and H_2 permeance values of >8x10^{-7} mol m^{-2}s^{-1}Pa^{-1} at 1 bar and 400°C will be used as the key performance targets for Pd based membranes. These membranes will also need to withstand temperatures greater that 500 ºC for over 4000 hours.

In the frame of MEMBER project, a production of up to eight tubular membranes will be conducted per batch, since this value is representative to bring the technology to MRL 6. The recyclability of the Pd and supports will be studied and considered in the final cost of the membranes. This will ensure sustainability and lower the cost of the final product. These targets are summarized in Table 21.

Table 21. Target specification for Pd based membranes.

Pd based membranes Specification	Value	Unit
Thickness	<5	µm
H_2 perm-selectivity	>10000$^{(*)}$	-
H_2 permeance	>8x10$^{-7(*)}$	mol m^{-2}s^{-1}Pa^{-1}
Life time	>4000	h
Temperature	>500	ºC

(*) At 400°C and 1 bar of pressure difference

3.2. Sorbents

3.2.1. Current manufacturing procedure

Current manufacturing methods for this class of sorbent materials consist of the hydrothermal treatment of calcium and aluminum hydroxides. This reaction results in a microporous mayenite material ($Ca_{12}Al_{14}O_{13}$) with high chemical and thermal stability. The use of high shear granulation has been demonstrated on kg batches which allows for the production of higher density sorbent granules. These granules have a capacity of 0.25 g-CO_2/g-sorbent and are stable up to 200 cycles.

3.2.2. Main performance indicators & targets

A key performance indicator for sorbent is the capacity, measured in g-CO_2/g-sorbent. Importantly the sorbent must remain porous during the lifetime of the material. While no porosity targets are listed, MEMBER aims to produce material that has a capacity greater than 0.3 g-CO_2/g-sorbent.

Additionally, the material will be stable between a temperature range of 20-1000 ^{o}C and pressures between 1-2 bar. This will ensure the material can handle operation condition of the demonstrator units of at least 1000 cycles.

To screen materials for mechanical stability an air jet attrition index (AJI) test will be employed. This will act as a reasonable approximation to mechanical stresses applied to sorbents within operational conditions. Sorbents will need to achieve a AJI no greater than 10 % to satisfy this stability criteria.

Stringent production targets of 50-100 kg/day at 5-10 €/kg have been set, this will ensure the sorbent materials are commercially relevant and at the required technology readiness level of 6 (MRL6).

These key performance indicators have been summarized in Table22.

Table 22. Target specification for sorbent materials.

Specification	**Value**	**Unit**
Design temperature	20-1000	^{o}C
Design pressure	1-2	bar
CaO content	min. 30	wt%
Sorption capacity	min 0.3	g-CO_2/g-sorbent
Cycling stability	min. 1000	cycles
Attrition jet index	max. 10	%

3.3. Catalysts

3.3.1. Current manufacturing procedure

Production of the Ni based reforming catalysts is typically conducted by the impregnation of Ni salts onto various supports prior to calcination. Supports typical consist of various mixed or single metal oxides, which can be tailored to the specific working environment. Ni contents between 15-18 wt% are typical. For any commercial application, the final catalyst will have to be formed into a desired shape with the required mechanical stability.

3.3.2. Main performance indicators & target

Like many commercial catalyst, stability under temperature and pressure need to be considered. The reforming catalysts should maintain activity to a minimum of 1000 cycles at temperatures between 20-1000 ^{o}C, with a demonstrated activity between 600-700 ^{o}C.

Additionally, the catalyst will need to demonstrate that activity is maintained despite being subjected to a slightly oxidative atmosphere in the regenerator unit although it is possible engineering control may reduce the oxidation these materials are subjected too.

Mechanical stability is also to be considered. Formulation of the material into pellets or rings is required for the specified application and so the material will need to be stable to crushing and sieving. The final granulated catalyst should have a AJI of less than 10 % to ensure it can survive cycling within the prototype unit. These key performance targets are summarized in Table 23.

Table 23. Target specification for reforming catalysts.

Specification	**Value**	**Unit**
Design temperature	20-1000	ºC
Design pressure	1-2	bar
Ni content	min. 15	wt%
Cycling stability	min. 1000	cycles
Attrition jet index	max. 10	%

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