Including CO2 removal in Power Plants

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1. Abstract

The appeal and the possible technical solutions for the removal of CO2 in power plants are examined. This lecture wishes to provide a review of the status of advancement of technology in this field, and to underscore the economical and technical problems that remain to be solved.

2. How much CO2 are Power Plants producing?

Figure 1 (DOE, 1999) shows the needs for reduction of CO2 emissions in the near future. The outcome of the figure is that in the near term (2025) there will be a need to spare about 1,5 GtC/year, that is, 5,5 GtCO2/year (1 CtC = 3,66 GtCO2, as the molecular weights of Carbon and Carbib Dioxide are respectively about 12 and 44 kg/kmol). Projected at the mid-term (year 2050), this figure becomes about 11 GtCO2/year.

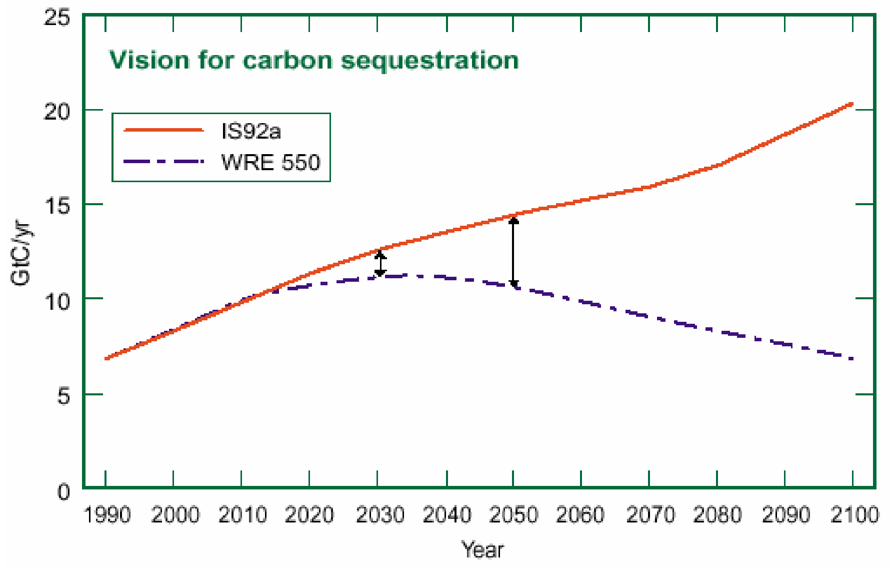

Figure 1 – Evolution of Global Carbon worldwide emissions under two extreme scenarios: Business-as-Usual (IS92A) and WRE550 (limit CO2 cocentration in the atmosphere to 550ppm – nearly twice as present day’s value) (DOE, 1999)

It is interesting to notice that this very large amount corresponds to a very small part of the overall CO2 balance of the atmosphere (Figure 2). Respiration and phtosynthesis alone are responsible of fluxes of the order of 60 GtC/year; however, the whole carbon emissions from combustion total 6 GtC/year; this means that within about 20 years from now, we should be able to reduce of 25% our combustion emissions of CO2.

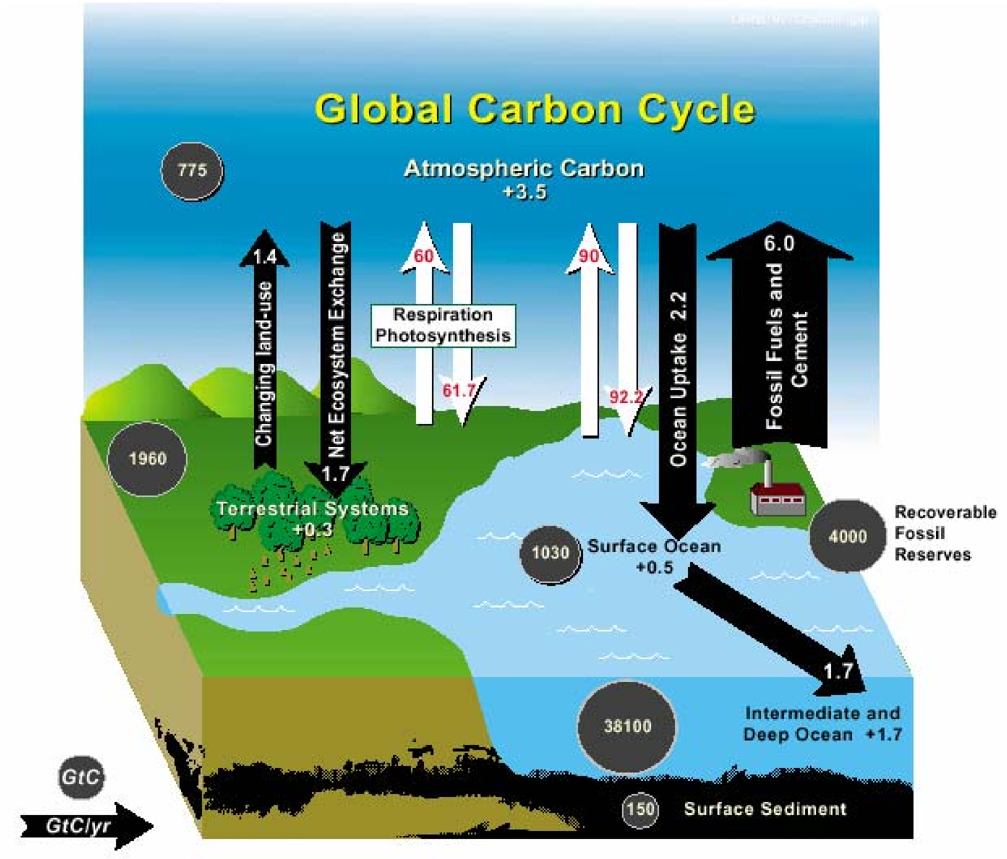

Figure 2 – Global Carbon Cycle (DOE, 1999)

Power plants CO2 emissions figures range from 1200 kg_{CO2}/MWh (coal-fired power stations, including modern circulating fluidised bed plants) to 400 kg_{CO2}/MWh (gas-fired gas/steam combined cycles). As a reference case, a power plant of a reference size of 320 MWe is here considered. Assuming the plant is operating with 42% efficiency for 8000 h/year, on a fuel containing 75% Carbon (that is, approximately pure Methane; the case for a plant operating on coal would generate about 25% more CO2), it is easy to calculate the overall CO2 emissions at about 1,5 MtCO2/year. It is interesting to notice that the size of the largest pilot CO2 separation/sequestration experiments, that is, Weyburn and SleipnerT (Figure 3), is about 1 MtonCO2/year, that is, two thirds the emissions of one large size power plant (by comparison, consider that the overall combustion Power Plants capacity in Italy, for example, is about 50,000 MWe).

Figure 3 – Sleipner-T Platform (DOE, 1999)

3. Can one make money separating CO2 from Power Plants emissions?

As a relevant source of CO2, power plants – as well as other industrial plants, e.g. in the metallurgical field – have some attractiveness for economic investments. In principle, it should be easir to collect CO2 from large point sources, rather than from area sources such as most anthropogenic and natural applications.

For comparison, we will make reference to a well-established practice providing substantial economic opportunities, that is, the Combined Production of Heat and Power (CHP). To this end, our reference 320 MWe power plant, provided with some common heat recovery equpment, could easily achieve an IEN = W_e/W_u = 0,8, that is, it could produce about 400MWs of thermal power. Over the year, its energy balance would score 2560 GWh of electricity and 3200GWh of thermal energy; considering a retail price 12,39€/MWh, the side business of selling heat as well as electricity can be evaluated as a gross yearly income of about 39,500,000 M€/year. This does not include cogeneration system costs, mortgages, service; these costs will not be considered also for the CO2 removal system, which has the same types of cost, even if they are affected by a much larger degree of uncertainty as this type of equipment is completely at prototype level.

At the present stage of development of CO2 capture technology, it is fair to affirm that there is a large uncertainty about what would be the cost of removal and sequestration, applied on a large scale. Even if figures in the range of 40-60 €/tonCO2 have been quoted in several sources, actual costs could probably be larger, depending on the technology and on the scale of the application; for an example of a lower limit - probably optimistic – the 6th European Framework Project of research is referring to cost in the bracket of 20 to 30 €/tCO2, for a removal efficiency of at least 80%. What is probably true, is that capturing CO2 with high efficiency will cost much more that doing the same with a low efficiency; and that there is no way of making money investing in CO2 capture/sequestration, unless there is some financial support from the side of government. This translates into the Carbon tax mechanism, which however can have – depending n the criteria applied – important drawbacks on the development of new technologies.

In order to demonstrate this, the simulation of the reference 320MWe power plant has been extended adding a CO2 capture and sequestration equipment, assuming cost levels as described in Table 1 or Figure 4

Cost of removal €/tonCO2	25	25	25	30	30	30	35	35	35	35	35	40	40	40
Removal efficiency	0,25	0,3	0,35	0,4	0,45	0,5	0,55	0,6	0,65	0,7	0,75	0,8	0,85	0,9

Table 1 – Assumed cost of CO2 sequestration as a function of removal efficiency

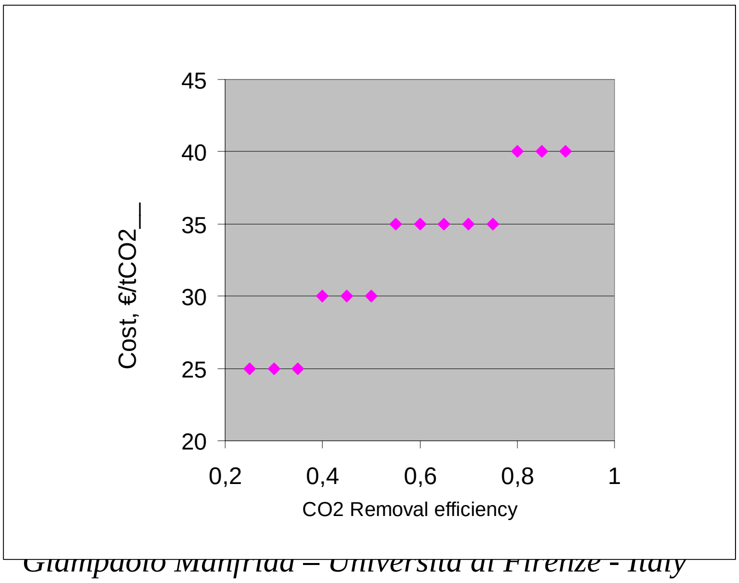

Figure 4 -

Assumed cost of CO2 sequestration as a function of removal efficiency

As for what could be the expectable level of an European Carbon tax, there is currently much debate; for governments and NGOs (GRIAN, September 2003), introducing carbon taxes directly at the source (as an additional tax on the fuel price) is the most effective way to collect money, even if it should be guaranteed that this money is re-invested into fuel decarbonization programs[1]; A progressive level, starting from 7,50 €/tCO2 in 2005, and raising at 20 €/tCO2 in 2005, has been quoted[2], but figures as high as 50 €/tCO2 have been reported in political meetings at international level.

These figures have been retained in the present study. When considering the lowest level of financial support (7,50 €/tCO2, Figure 5), including CO2 removal in the reference power plant would cause the plant owner an economic damage ranging from 8 to 45 M€/year.

Only if the carbon tax is raised at about 30€/tCO2, some economic advantage becomes possible. The largest benefits are obtained at low CO2 removal efficiencies, because the cost of removal is smaller. If the Carbon Tax were raised to the largest value (50€/tCO2), then removal would be convenient also at high efficiency levels; however, the benefit (10 to 16 M€/yr; to be compared to the about 40M€/yr achievable by the CHP application) does not depend much on the level of the removal efficiency.

This study is very crude, yet it provides some explanation of why there is so much reluctancy, on the part of suppliers of power plants, to start even prototype demonstration units: there is a large political pressure, stating high targets (high removal efficiency at low cost), and presently still very little financial support from governments. It is not surprising that most companies prefer business-as-usual scenarios, even if few will admit this in public.

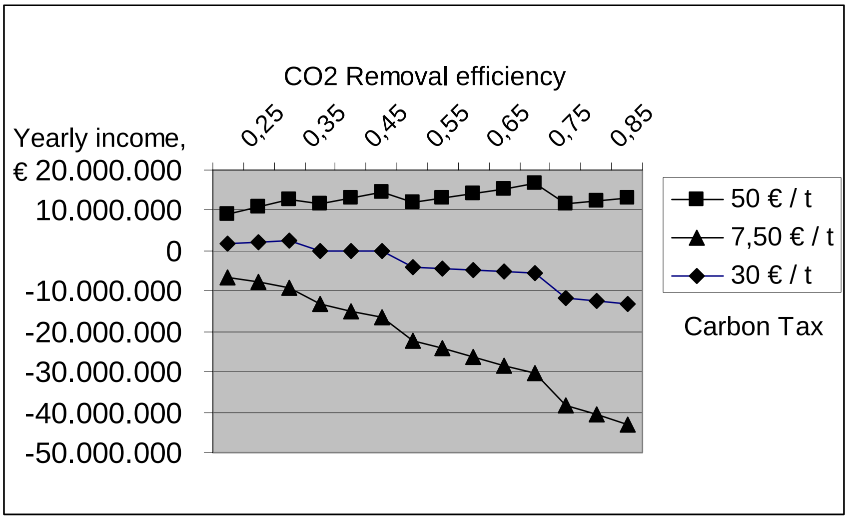

Figure 5 -

Simplified economic balance of CO2 removal as a function of removal efficiency and Carbon tax level

This simple study also shows that there is a neglected area of development, that is, that of low-efficiency but low-cost capture technologies, which could be easier to introduce on the market and could lead – with the introduction of even low Carbon Taxes – to some economic benefits. It is true that these benefits are much smaller than more traditional opportunities for investors, such as CHP

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[1] *RECOMMENDATION 11: The tax should be collected upstream, parallel to existing fuel duty collection arrangements. New arrangements will have to be made for fuels not currently covered by existing excise obligations. The tax, however, should be accounted for, and returned, separately from existing excise duties , albeit on the same forms and at the same time as existing arrangements. The object is the creation of a firm-based decarbonisation fund to be used for subsequent rebate and/or allowance-based claims in favour of decarbonisation (GRIAN, Sept. 2003)*

[2] *RECOMMENDATION 9: The tax should be introduced on Jan 1 st 2005 at € 7.50 / tonne CO2, escalating on an annual basis through the bands proposed (TSG 02/23 10) so that it reaches € 20 / tonne for the opening of the FCP/ first phase of the ETS on Jan 1 st 2008. (GRIAN, Sept. 2003)*

applications: however, the CHP market has been saturated in many European countries, so that it should be possible in the near future to raise the interest of private investors and local communities with simple, niche applications of Carbon removal.

4. CO2 separation technologies

For a complete documentation of CO2 separation technologies a good source are the DOE documents of 1999 and 2002. In the following, only some of the most promising technologies, with a special eye to power plant applications, are examined.

4.1 Chemical Absorption

Even if significant research efforts are on the way on alternative techniques for CO2 separation, at present the mature technology consists in scrubbing the exhaust gas stream with a suitable alkaline solution, which is able to effectively capture the CO2. Chemical absorption is usually recommendable for separation of emissions ranging less than 12-14% [Cussler, 1997]; under stoichiometric conditions (upper limit), the typical concentration of CO2 in the exhaust of a power plant does not exceed 15% in mass, with much lower values (even less than 5%) possible by gas turbines, where combustion is adiabatic and large dilution in air is necessary in order to limit the turbine inlet temperature.

The solvent should have a good affinity with CO2; it should be cheap and non-toxic (at normal concentrations), and last but not least almost fully regenerable by simple means (e.g., by thermal desorption stripping). Here again, several options are possible (for example, regenerative application of Ammonia scrubbing is currently investigated), but the consolidated technology (derived from refineries) is that of scrubbing by aqueous solutions of Amines. A typical arrangement is shown in Figure 6, and is made of an absorber and a desorber (stripper) column; absorption of CO2 takes place at low temperature (60-80°C), while CO2 is released – concentrated – at the stripper at high temperature (110-150°C). Cooling (for the absorber) and heating (for the desorber/stripper) are required, and in order to reduce these loads it is convenient to include regeneration through a thermal recuperator on the liquid solution. Figure 6 includes separation of CO2 from waer vapour, and compression of the CO2 stream (for transport through pipelines or liquefaction).

The desorber heat load is often taken from within the power plant plant (for example, by means of a steam extraction: low temperature heat is sufficient): in order to limit the penalty in plant efficiency, it is crucial to minimize the energy required for the regeneration of the solution. To this end, the original aqueous solutions of MEA (Mono-Ethanol-Amine), requiring as much as 6 $\mathrm{MJ/kg_{CO2}}$ (captured) can be substituted by more advanced mixtures containing secondary (DEA for Di-Ethanol-Amine) and tertiary (MDEA) amines; the increase of the amine content, up to 50% (the carrier being water) is possible with the addition of special non-foaming additives, and by a careful optimisation the heat demand for regeneration can be lowered down to less than 4 $\mathrm{MJ/kg_{CO2}}$.

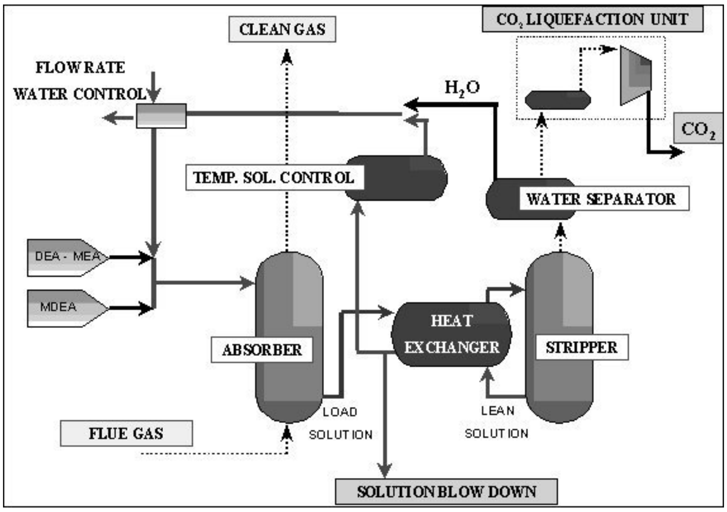


Figure 6 – Schematic of chemical CO2 scrubbing inclusive of CO2 extraction section from exhaust gases

The use of amines is quite common in refineries, for applications such as H2S removal and gas purification (LPG production). High removal efficiencies (80-85%) are achievable and have been demonstarated in large-scale prototype applications (e.g., the STATOIL Sleipner-T project; in this case, CO2 coming from a sub-sea oil/gas reservoir is removed at the well). There is a large expertise and relatively large units have been built (anyway, much smaller of those which would be needed by a large power plant). However, amines are not well seen in many industrial environments (e.g. textile industry), because of their polluting nature and toxicity. Their cost, as that of a specialised (at present) chemical compound, is relatively large, and the heat loads required consistent. The size of the equipment – as for all absorption solutions – is basically proportional to the volume flow rate, which is large by power plants, with special reference to conventional, post-combustion applications (for pre-combustion removal, one can consider absorbing/desorbing in a pressurized loop). These are the reasons why there is still interest on other substances usable for chemical absorption.

As an alternative to the use of amines, other alkaline solvents can be considered for capture of CO2. Among these, Alkali scrubbing seems to be a promising technique; the basic, non-regenerative scheme for Na2CO3 (a naturally existing alkali salt), is shown in Figure 7. The basic equations are the following:

1 $\mathrm{CO2} + 2\,\mathrm{H2O} <\!\!-\!\!-\!\!> \mathrm{H3O}^{+} + \mathrm{HCO3}^{-}$ (Equilibrium reaction)

2 $\mathrm{HCO3}^{-} + \mathrm{H2O} <\!\!-\!\!-\!\!> \mathrm{H3O}^{+} + \mathrm{CO3}$— (Equilibrium reaction)

3 $\mathrm{NA2CO3.H2O} <\!\!-\!\!-\!\!> 2\,\mathrm{NA}^{+} + \mathrm{CO3}^{--} + \mathrm{H2O}$ (Salt reaction)

4 $\mathrm{NAHCO3} <\!\!-\!\!-\!\!> \mathrm{NA}^{+} + \mathrm{HCO3}^{-}$ (Salt reaction)

Some results, referred to a commercial 5MWe gas turbine application, and showing the expected CO2 removal efficiency as a function of scrubbing mixture flow rate and reactant concentration in the mixture, are shown in Figure 8.

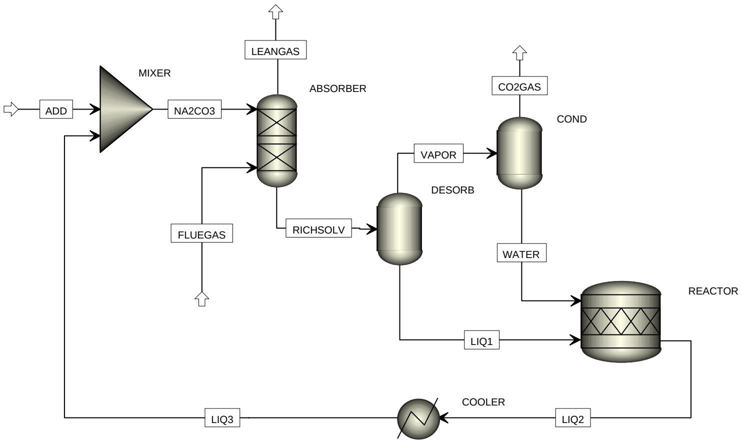


Figure 7 – ASPEN sheet simulation for a CO2 removal case by scrubbing with a a water solution of Na2CO3

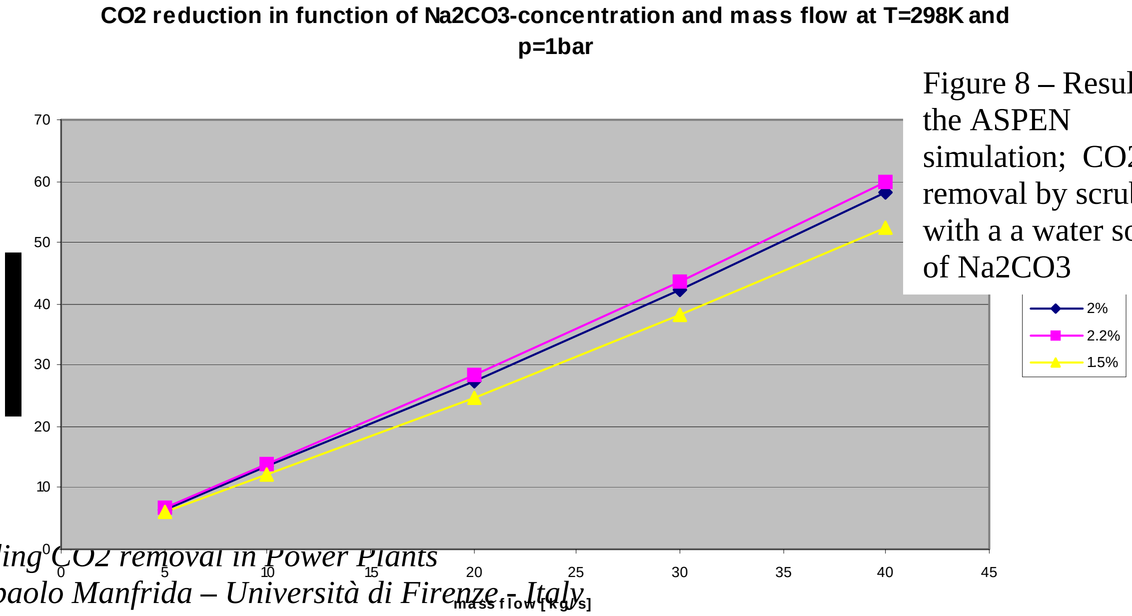


Figure 8 – Results of the ASPEN simulation; CO2 removal by scrubbing with a a water solution of Na2CO3

Looking for cheap alkaline reactants, which could be used – even if with limited CO2 removal efficiency – in a regenerative way, Phosphates can represent an interesting option. They are available in large quantities at moderate price, as they are commonly used in water purification. A recent study on K3PO4 in aqueous solution, including modelling and small-scale chemical laboratory experiments, has provided interesting results. The capture reactions within the solution are the following:

(1) $PO_4^{3-} + CO_2 + H_2O \leftrightarrow HCO_3^- + HPO_4^{2-}$

(2) $HPO_4^{2-} + CO_2 + H_2O \leftrightarrow HCO_3^- + H_2PO_4^-$

A low temperature favours absorption, displacing equilibrium to the right; providing heat, it is possible to move equilibrium to the left (desorption), regenerating the solution and releasing CO2 at high concentration. The reference case (Pellegrini, 2004; Fiaschi, Manfrida, Pellegrini, 2004) is the same considered in the following for ammonia scrubbing, that is, a commercial gas turbine unit of 5MWe. The 20 kg/s of gas (6,7% CO2 in mass) enter the absorbing tower at 80°C, where they are scrubbed by a solution containing 4% in mass of potassium phosphate. Figure 9 shows that the CO2 capture efficiency is a linear function of the solution flow rate.

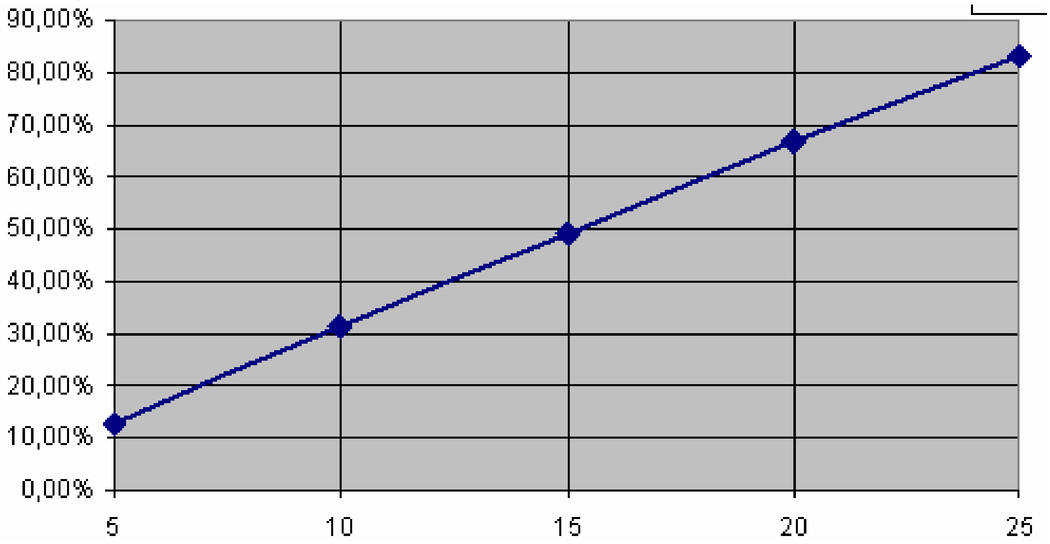


Figure 9 –CO2 capture by scrubbing with a water solution of K3PO4 (5 MWe gas turbine exhaust).

A relevant point is the possibility of reactant regeneration. The model predicts that with adequate desorption temperatures (higher than 450K, Figure 10) regeneration of phosphate is larger than 98%. As there is no published experience on the use of these reactants, a simple, laboratory-scale experiment has been arranged (Figure 11). The complete experiment setup is composed of an absorption unit, followed by a weight scale allowing to measure CO2 removal, and by a heated desorption unit. The absorption and desorption columns can be used with different solutions and equipped with mass transfer enhancement devices (e.g., glass spheres, zeolites,…). During the experiment, a constant flowrate of 0,94 l/h of CO2 was passed (diluted into a 10 l/h Argon carrier flow rate) through a solution containing 1,5% in mass of K3PO4. Allowing sufficient time, a removal efficiency of 58% has been achieved (corresponding to about 1000 mg of CO2 captured, Figure 12). Figure 13 shows that the reactant recovered after desorption can be re-used with a limited drawback on the CO2 removal efficiency. On the whole, the use of phosphates in a regenerative mode seems to deserve further investigation, with special reference to low-cost, low-CO2-capture-efficiency potential applications.

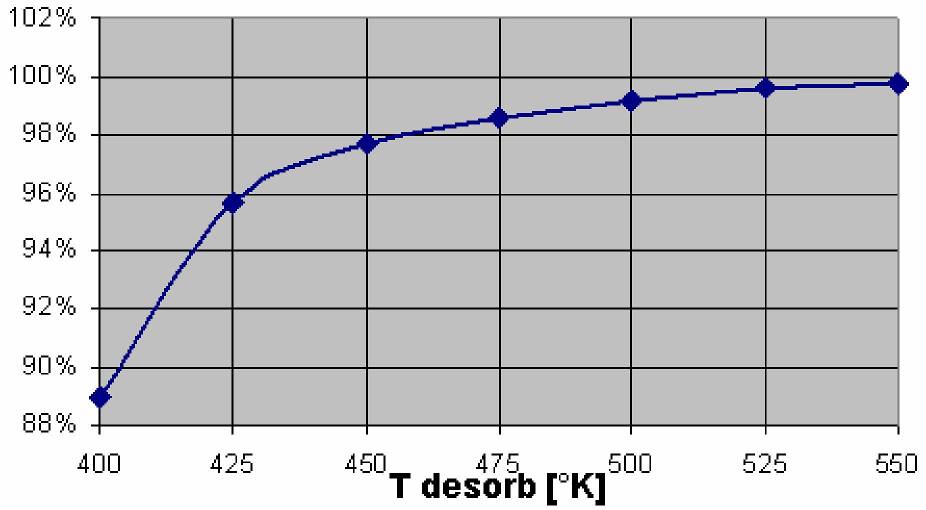


Figure 10 – Regeneration of phosphate through desorption as a function of temperature (ASPEN+ model)

Figure 11 – Laboratory experiment on the use of phosphate for CO2 removal. Left, absorption bottle; right, close-up of desorber.

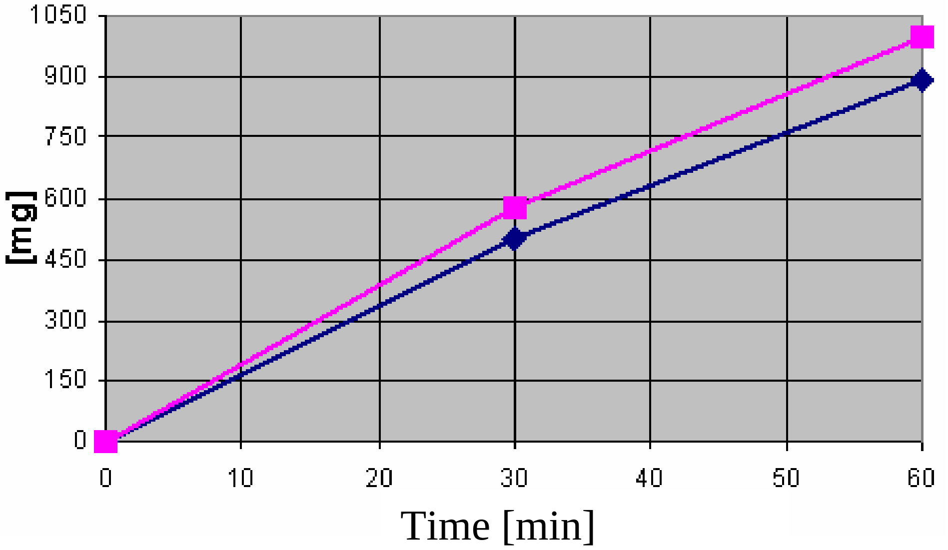


Figure 12 – CO2 removed (mg) as a function of time. 1,5% K3PO4 solution. Squares = with glass beads. Circles = without glass beads.

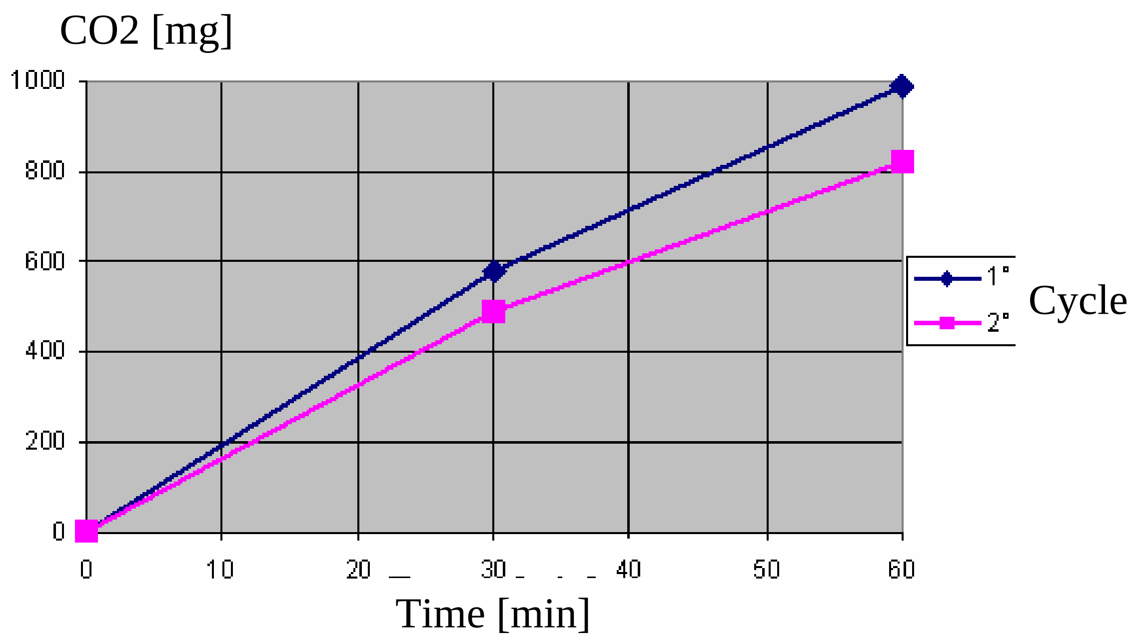
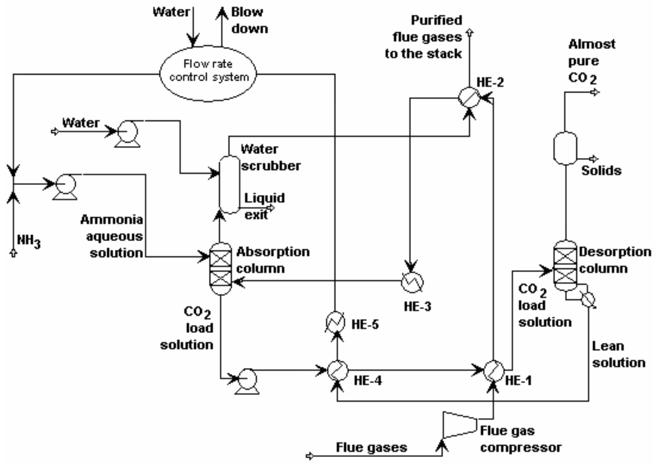


Figure 13 – Re-use of recovered reactant K3PO4

The regenerative use of Ammonia is possible in principle for post-combustion removal of CO2, with a flue gas treatment scheme as depicted in Figure 14 [Corti and Lombardi, 2003; Yeh and Bai, 1999].



The chain of reactions is the following:

$2H_2O \leftrightarrow H_3O^+ + OH^-$ (7)

$CO_2 + 2\,H_2O \leftrightarrow H_3O^+ + HCO_3^-$ (8)

$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$ (9)

$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$ (10)

$NH_3 + HCO_3^- \leftrightarrow NH_2COO^- + H_2O$ (11)

$NH_4^+ + HCO_3^- \leftrightarrow NH_4HCO_3\ (s)$ (12)

Figure 14 – Schematic of CO2 capture by Ammonia scrubbing

The potential of ammonia scrubbing is quite interesting: as a case study, a 5 MWe gas turbine is considered, with an exhaust stream of about 20 kg/s and a CO2 content of 6,7% in mass (from Pellegrini, 2004). The exhaust, cooled to 175°C, was treated through scrubbing with a water solution (5 to 50 kg/s) containing from 2 to 10% in mass of NH3. The results shown in Figure 15 show that in order to achieve a satisfactory capture level one should use large solution flow rates and/or high ammonia concentrations. A problem is represented by the concentration of ammonia in the “clean” gas stream at absorber exit, which is shown for the same test case in Figure 16. Considering current emission limits for ammonia (100 mg/Nm3), a further water scrubbing tower should be added to the process, with large water flowrates. The final results are synthesized in Figure 17.

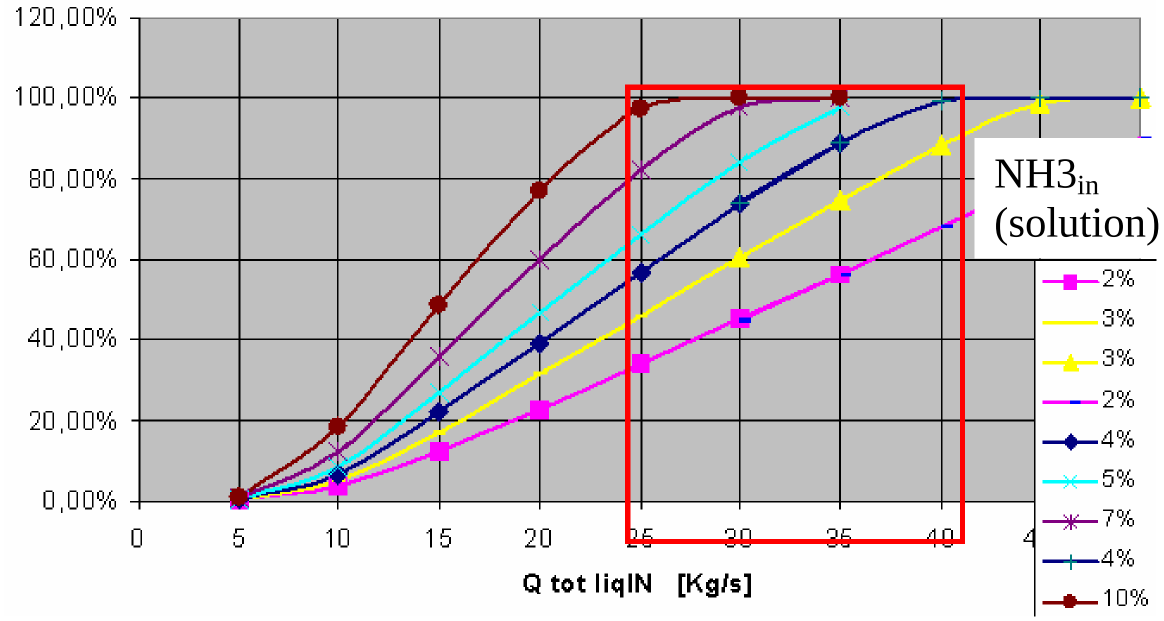


Figure 15 – Results for ammonia scrubbing of a 5 MWe gas turbine exhaust. (the most interesting ranges of scrubbing flow rate and NH3 concentration are outlined in a rectangle)

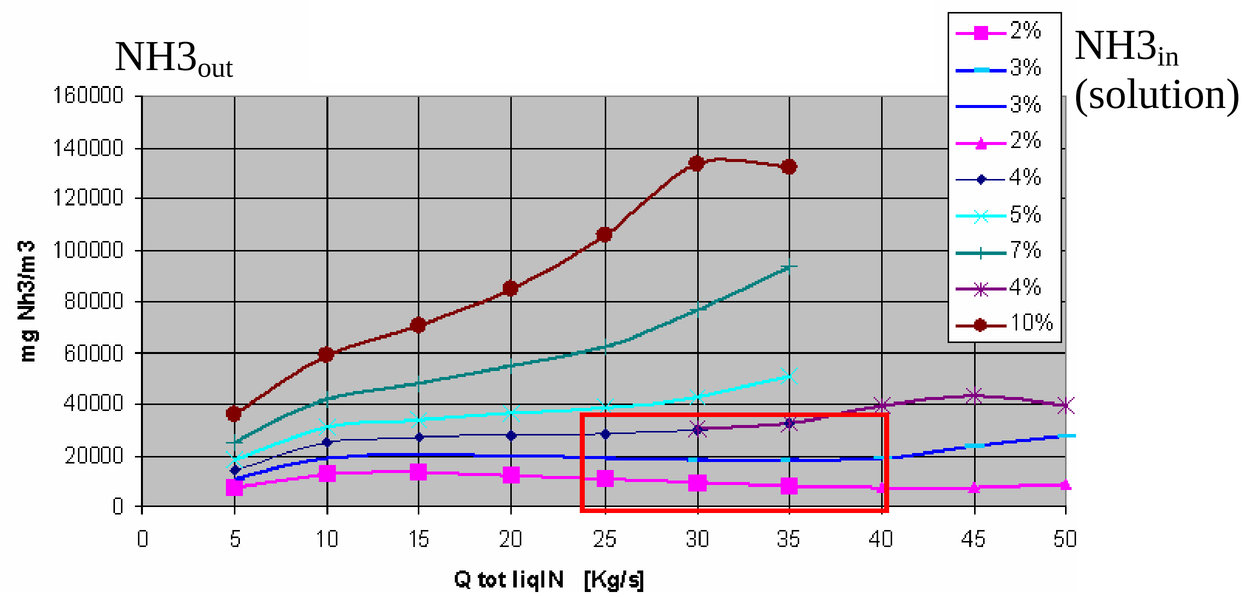


Figure 16 – NH3 concentration in the absorber exit stream (5 MWe gas turbine exhaust)

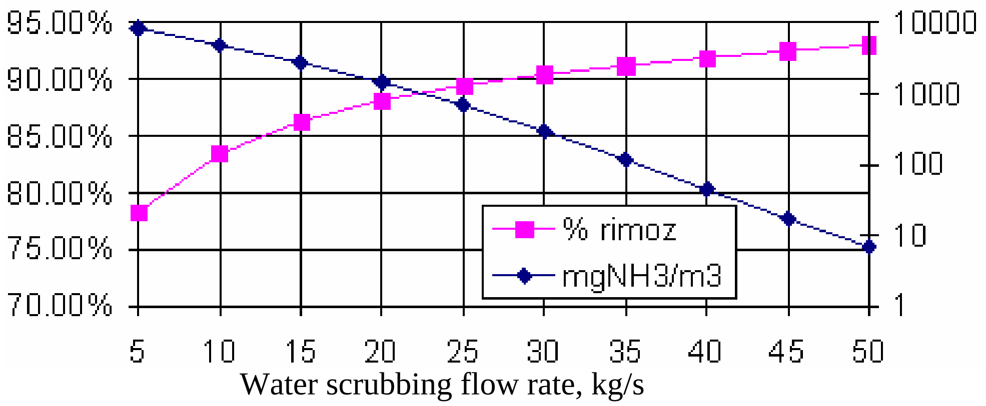


Figure 17 – CO2 removal and remnant NH3 concentration in the clean exhaust stream as a function of the final stage water scrubbing flow rate (ammonia scrubbing of a 5 MWe gas turbine exhaust)

On the whole, ammonia scrubbing looks promising but the water flowrates are impressive and the sizing and economics of the exhaust treatment system appear prohibitive. Moreover, the heat load for desorption is quite large (even if it is regeneratively provided by a low-pressure steam extraction). In order to improve the performance of ammonia scrubbing, achieving also a satisfying recovery of NH_3 through the lean solution, relatively high absorber (3 bars) and desorber (16 bars) pressures should be consdered. This means that the flue gases need to be compressed to 3 bars, which implies the expense of significant power. It is also attractive to consider advanced cycle solutions, allowing to increase the concentration of CO2 in the exhaust, such as a Semi-Closed Gat Turbine arrangement (Facchini et al., 1996; Fiaschi and Manfrida, 1997). On the whole, the estimated performance – shown synthetically in Table 2 - is anyway far from that of amine scrubbing.

GT power [MW]	151.
ST power [MW]	82.
CC power [MW]	233.
Flue gas compressor + pump powers [MW]	37.5
CO_2 compression power [kW]	6,700
CC net power [MW]	189.
Efficiency [%]	41
CO_2 specific emission [kg_{CO2}/MWh]	57

Table 2 – Performance of a new-generation Power Plant (SCGT/CC) with regenerative Ammonia CO2 absorption system

4.2 Physical absorption

Physical absorption is also possible with high removal efficiency with a number of proprietary solutions (e.g. Selexol, Purisol,…) which are however more suitably applied to the refinery industry, where higher concentrations of CO2 and pressurized conditions can be met. It is not surprising that proposals for use of physical solvents for pre-combustion Carbon removal have been issued in Integrated Gassifier/Combined Cycles, where pressurized conditions of the syngas exist at gassifier exit (Lozza and Chiesa, 2002). In Physical Absorption (Figure 18), regeneration of the absorbing solution is obtained through multiple-flash expansions, where CO2 streams are released at progressively diminishing pressures from each flash drum; the CO2 stream needs then to be separately compressed up to the delivery/liquefaction pressure level. The possibility of recovering power through the use of hydraulic turbines working on the liquid solution at exit of each drum must be discarded as leading to complicated and unreliable plant schemes, so that this energy is not recovered. Besides, recycle – through another gas compressor) of vent from at least the first, high-pressure drum is necessary as this stream is not pure CO2. On the whole, the energy balance – considering also that mechanical power for compression is necessary, instead of heat – is not much more attractive than for the case of chemical absorption by Amines.

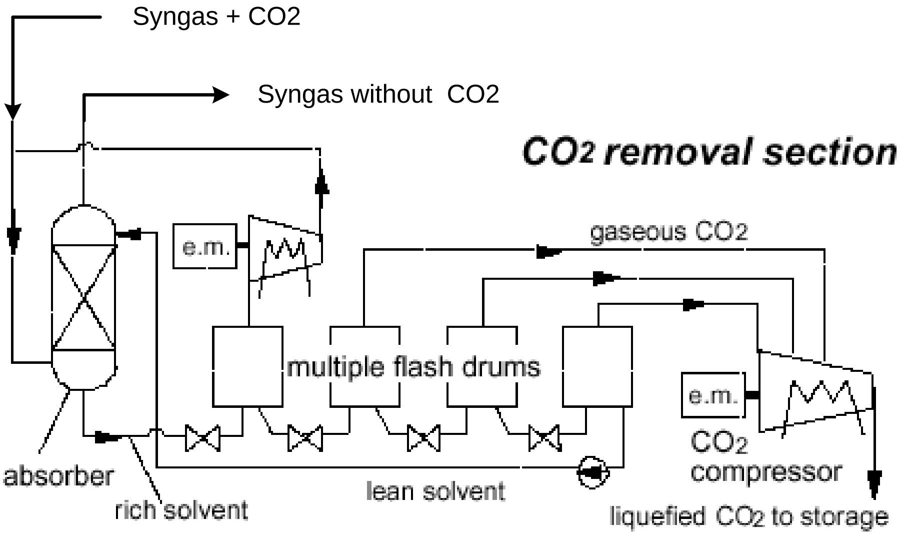


Figure 18 – Schematic of Physical absorption system for IGCC syngas CO2 removal (Lozza and Chiesa, 2002)

Physical absorption can be of interest by power plants when Carbon-rich fuels are considered, giving rise to exhaust streams where the CO2 concentration is relevant (over 15% in mass, typically). Typical cases of this type can be found in metallurgical processes, with special reference to pig iron production. As an attractive application, the innovative COREX process has been studied, as able of producing a synfuel easily adaptable for gas turbine/combined cycle CHP production. The characteristics of the COREX export gas are summarized in Table 3. A C-2000 unit, with a reference production of 800,000 t/yr of pig iron, and a coal consumption of about 1000 kg/t of hot metal, is considered in this study.

CO	%	38 - 45
H_2	%	15 - 23
CO_2	%	30 - 35
CH_4	%	1 - 2
N_2, Ar, H_2O	%	Balance
H_2S	ppm (v)	< 100
LHV	kJ/m^3 (STP)	7500 - 8000
Dust	mg/m^3 (STP)	< 5
Temperature	^{o}C	30 - 50
Pressure	kPa g	5 - 150

Table 3 – Characteristic s of the COREX export gas (composition in volume fraction)

Considering the high CO2 content (over 30% in volume), physical absorption by Selexol was considered. The process diagram is shown in Figure 19 (Lampert et al., 2004). The system is quite similar to that of Figure 12 (including recycle from the first flash drum), however detailed models of compressors is included so that power consumption can be assessed with good precision. Intercooled compression is always used in order to achieve a lower mechanical power consumption.

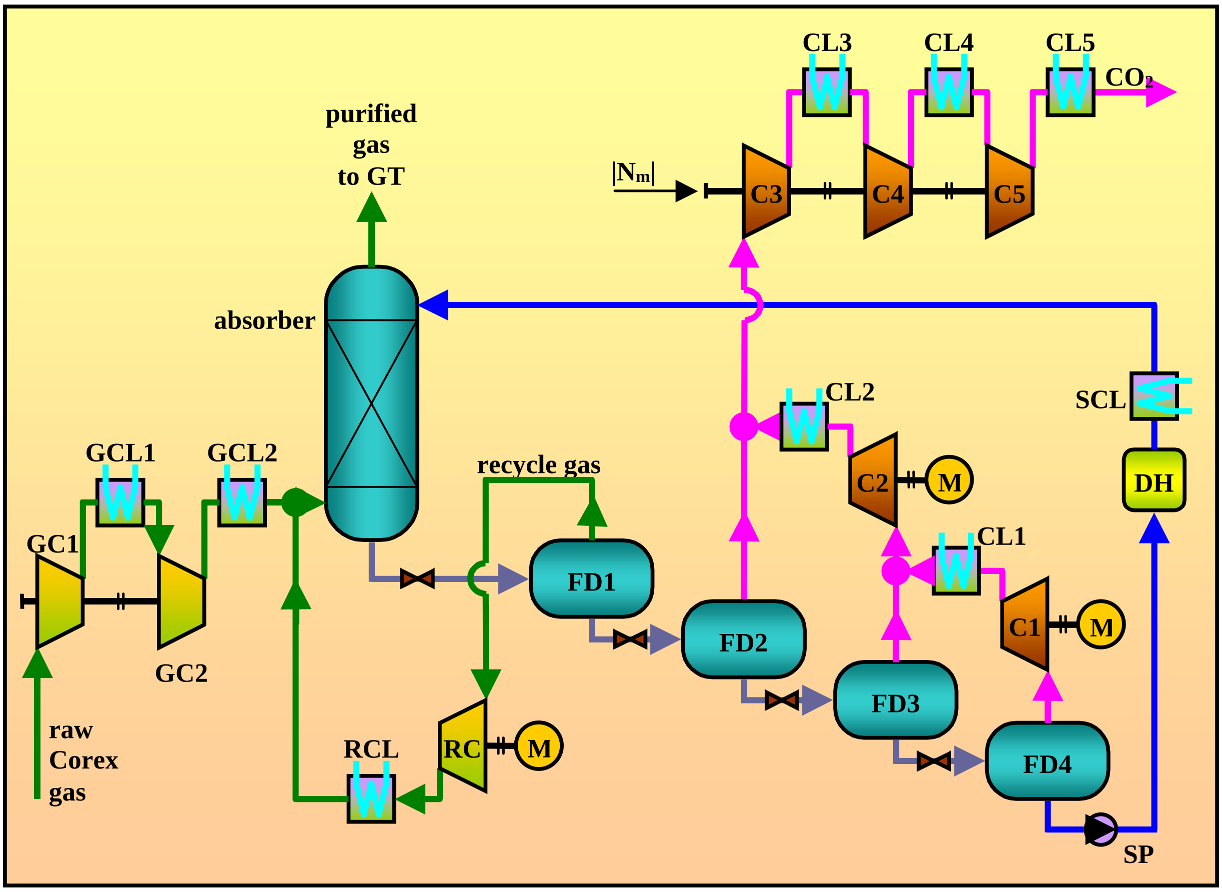


Figure 19 – Schematic of physical absorption model (COREX gas cleaning).

The physical absorption process is modeled through the solvent equilibrium equation, synthesized by the absorption constant AF (Chiesa, 2003):

$$AF = \frac{p_{CO_2}}{\left(\dfrac{n_{CO_2}}{m_{solv}}\right)}$$

where:

$AF = 6447.5$ [bar/(kmol CO_2/kg solv.)] - (at 25°C)

p_{CO_2}	- partial CO_2 pressure in the gas	[bar]
n_{CO_2}	- amount of absorbed CO_2	[kmol], [kmol/s]
m_{solv}	- amount of the solvent	[kg], [kg/s]

The temperature dependency of the AF coefficient is described by the following equation (T in °C):

$$AF(T) = \frac{AF(T = 25)}{9.433 \cdot T^{(-0.6972)}}$$

The solution leaving the absorber contains also small amounts of CO and H_2. The relative solubility of CO, H_2 and CO_2 is given by the following factors:

$$\frac{\text{solubility of } H_2}{\text{solubility of } CO_2} = 1.3 \cdot 10^{-2}$$

$$\frac{\text{solubility of CO}}{\text{solubility of CO}_2} = 2.8 \cdot 10^{-2}$$

Finally, the liquid stream at absorber exit also contains H2O vapour: in this analysis it is assumed that 50% of vapour in the gas is absorbed and then removed in solvent dehydrator. As the water content in the raw gas is not high (2% molar fract.), accurate prediction of water behaviour is not essential for process calculations.

Table 4 shows the parameters of gas flows at different points of the process. It can be noticed that the CO2 removal is very effective, and that the purified exit gas stream is mainly CO and H2, with a LHV of 11,700 kJ/kg (to be compared to the about 6,000 kJ/kg of the raw syngas), suitable for gas turbine combustion.

Parameter		**Unit**	**Raw Corex gas**	**Gas entering the absorber (after mixing)**	**Recycle gas**	**Purified gas**
Gas flow rate		kg/s	50	53.75	3.75	25.46
Gas composition (molar)	CO_2	%	35.0	37.0	70.5	5.2
	CO	%	42.0	40.8	20.1	62.2
	H_2	%	18.0	17.5	9.4	26.7
	CH_4	%	1.0	0.9	-	1.5
	N_2	%	2.0	1.9	-	3.0
	H_2O	%	2.0	1.9	-	1.5

Table 4 – Selexol purification of COREX gas

The model has allowed a detailed calculation of compressor power and cooling loads, which is summarized in Table 5. Compressor isentropic efficiencies where 0,88 for the large GC1 and GC2 units, and 0,88 for the smaller ones. On the whole, the power consumption exceeds 21,500 MWe, with a cooling load of nearly 30 MWt. It is worth to remind that this COREX unit is able to produce about 153 MWe in a combined-cycle power plant (103 MW GT and 50 MW ST), as well as 57 MWt of heat for district heating.

Parameter	**Unit**	**GC1**	**GC2**	**RC**	**C1**	**C2**	**C3**	**C4**	**C5**
Pressure at inlet	MPa	0,15	0,47	0,6	0,1	0,2	0,4	1,2	3,4
Pressure at outlet	MPa	0,47	1,8	1,8	0,2	0,4	1,2	3,4	8
Power consumption	kW	7010	8030	380	248	740	2021	1825	1278
Cooling power in appropriate cooler	kW	8998	8012	395	245	744	2145	2365	5878

Table 5 – Power and cooling loads for Selexol purification of COREX gas

4.3 Cryogenic separation of CO2

Streams with high CO2 contents (as that considered in the COREX CHP case study, discussed in the Physical absorption section) have some interest also for another physical technology for CO2 removal, that is, cryogenic separation. This technique separates the different components from the gas mixture, working on their different condensation temperature. CO_2 has the highest condensation temperature among the fuel gas components (excluding water, which has to be liquefied and removed at the first stage). The condensation temperature of each component of the gas mixture depends on its partial pressure and thus the liquefaction temperature decreases as the partial pressure of the component isw decreased.

The cooling process layout is similar to that used in natural gas liquefaction (Figure 20); however, in LNG production the whole gas flux has to be liquefied, while in the case of the CO_2 removal process, there are two products: the purified, CO_2 lean gas and the liquid carbon dioxide. Both these products are obtained at very low temperature (150 – 160 K, depending on the amount of CO_2 to be removed). The cooling process includes three different loops, with cascaded copressor-driven cooling machines working on different refrigerants according to appropriate the temperature level (R32, Ethylene, Methane). At the first stage removal of H2O in order to prevent icing in further cooling is provided. The operating parameters of the cooling system are summarized in Table 6, and correspond to approximately optimized conditions, investigated by a parametric analysis.

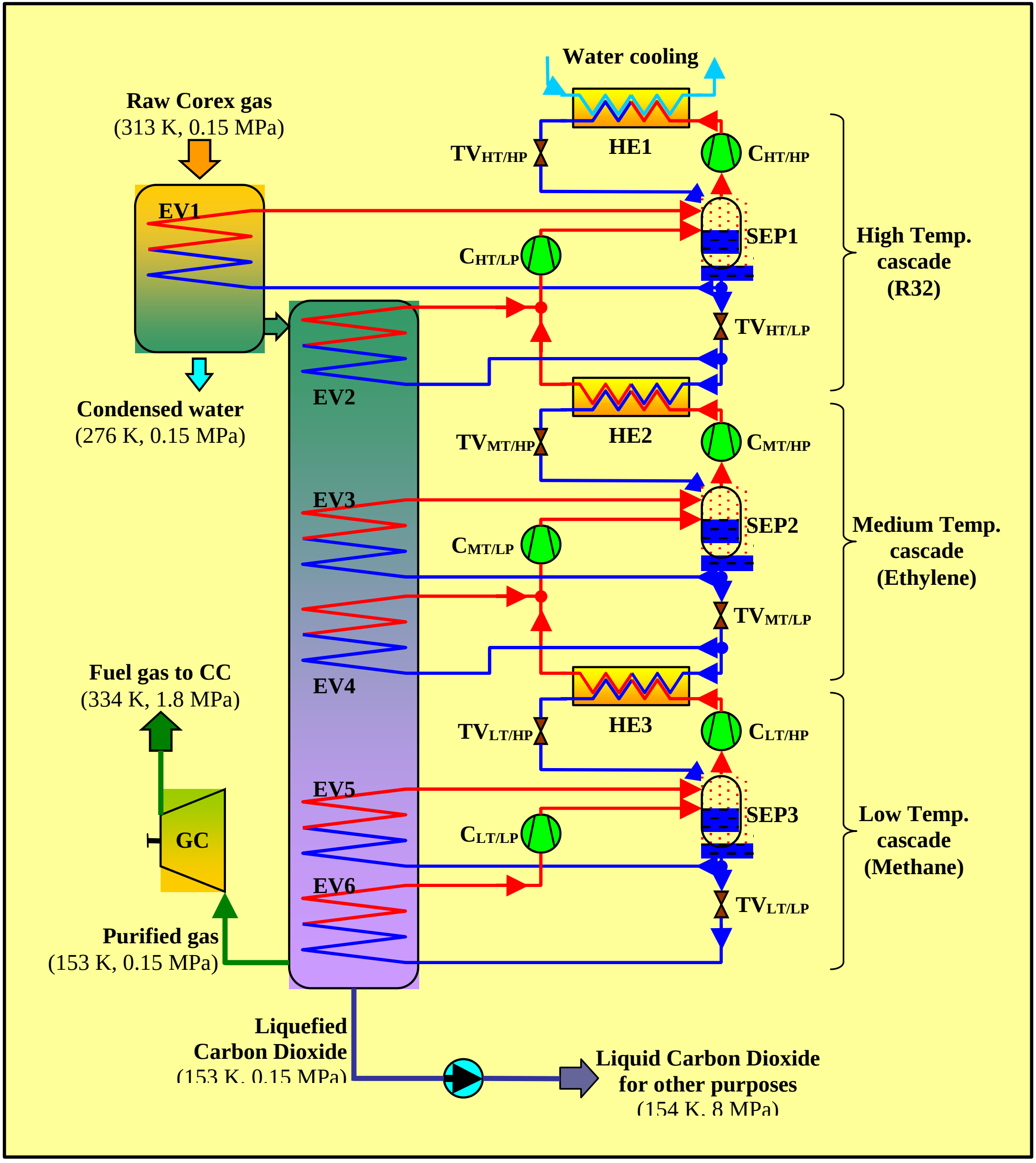
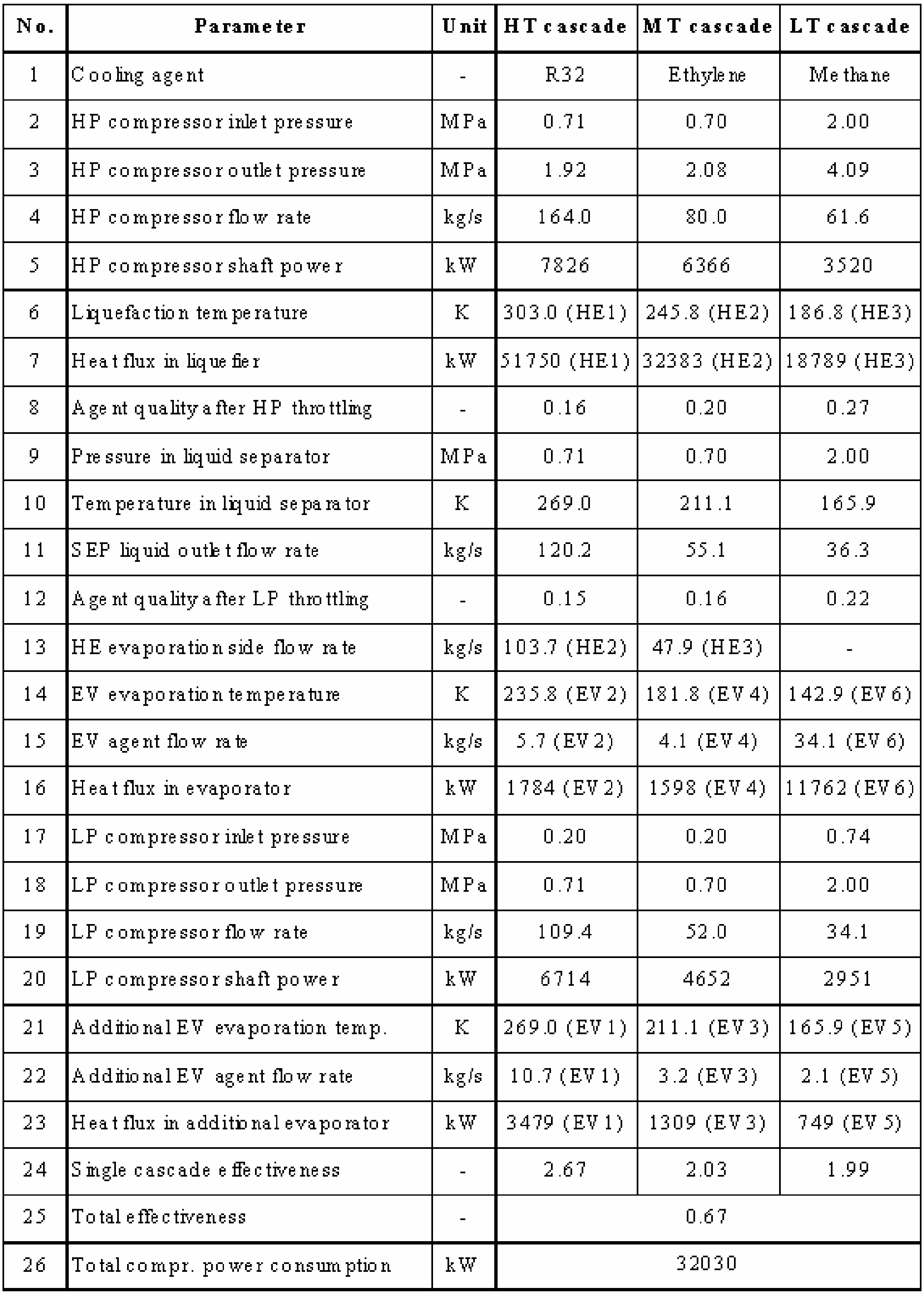


Figure 20 – Cryogenic system for CO2 removal from COREX gas stream



No.	Parameter	Unit	HT cascade	MT cascade	LT cascade
1	Cooling agent	-	R32	Ethylene	Methane
2	HP compressor inlet pressure	MPa	0.71	0.70	2.00
3	HP compressor outlet pressure	MPa	1.92	2.08	4.09
4	HP compressor flow rate	kg/s	164.0	80.0	61.6
5	HP compressor shaft power	kW	7826	6366	3520
6	Liquefaction temperature	K	303.0 (HE1)	245.8 (HE2)	186.8 (HE3)
7	Heat flux in liquefier	kW	51750 (HE1)	32383 (HE2)	18789 (HE3)
8	Agent quality after HP throttling	-	0.16	0.20	0.27
9	Pressure in liquid separator	MPa	0.71	0.70	2.00
10	Temperature in liquid separator	K	269.0	211.1	165.9
11	SEP liquid outlet flow rate	kg/s	120.2	55.1	36.3
12	Agent quality after LP throttling	-	0.15	0.16	0.22
13	HE evaporation side flow rate	kg/s	103.7 (HE2)	47.9 (HE3)	-
14	EV evaporation temperature	K	235.8 (EV2)	181.8 (EV4)	142.9 (EV6)
15	EV agent flow rate	kg/s	5.7 (EV2)	4.1 (EV4)	34.1 (EV6)
16	Heat flux in evaporator	kW	1784 (EV2)	1598 (EV4)	11762 (EV6)
17	LP compressor inlet pressure	MPa	0.20	0.20	0.74
18	LP compressor outlet pressure	MPa	0.71	0.70	2.00
19	LP compressor flow rate	kg/s	109.4	52.0	34.1
20	LP compressor shaft power	kW	6714	4652	2951
21	Additional EV evaporation temp.	K	269.0 (EV1)	211.1 (EV3)	165.9 (EV5)
22	Additional EV agent flow rate	kg/s	10.7 (EV1)	3.2 (EV3)	2.1 (EV5)
23	Heat flux in additional evaporator	kW	3479 (EV1)	1309 (EV3)	749 (EV5)
24	Single cascade effectiveness	-	2.67	2.03	1.99
25	Total effectiveness	-	0.67		
26	Total compr. power consumption	kW	32030		

Table 6 – Operating parameters of the cryogenic CO2 removal process for COREX gas

The appeal of CO2 removal by cryogenic separation/liquefaction is limited, due to the large power requirements, to streams containing relevant amounts of CO2 (in the case considered, more than 30% in volume). However, it should be noticed that liquid CO2 is produced, and at very low temperature. This could offer interesting developments in the view of sequestration/disposal and of availability of a low temperature sink, to be potentially employed in a process integration perspective.

4.4 Semi-permeable membrane technology

Several different types of membranes can be considered for application to gas purification: among these, polymeric membranes (low cost, low gas transport flux, high degradation), palladium (high cost, very low gas transport flux, little degradation), synthetic zeolites,…. In general, the permeability to different gases – which should be exploited for CO2 removal – depends on the molecule size (e.g., it is relatively easier to separate Hydrogen from CO2, than CO2 from an exhaust stream), which calls for a high process integration in order to be able to work on the correct stream compositions. A possible, simplified use of a membrane reactor is represented in Figure 21, with reference to an H2-permeable membrane application. The figure shows also the basic mass-transfer driving equation, that is, the difference of partial pressures between the two sides of the mebrane.

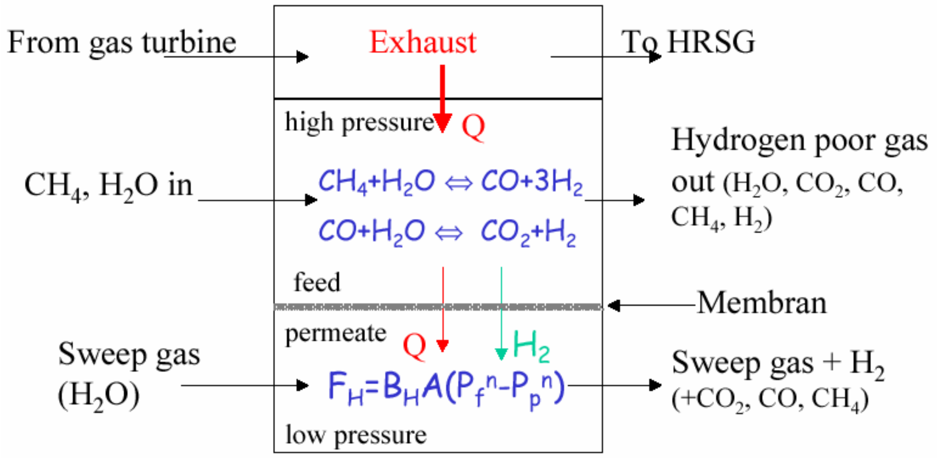


Figure 21 – Example of use of an H2-permeable membrane device to improve the performance of a methane reforming reactor (Bolland, 2003).

Promising developments are presently expected in oxygen-permeable membranes, currently under development under the pressure for effective and economic alternatives to the current cryogenic technology of Oxygen production (which has many applications, from metallurgical to glass production and coal gasification). ALSTOM has proposed a power cycle (AZEP) operating with these new, high-temperature membranes (Figure 22).

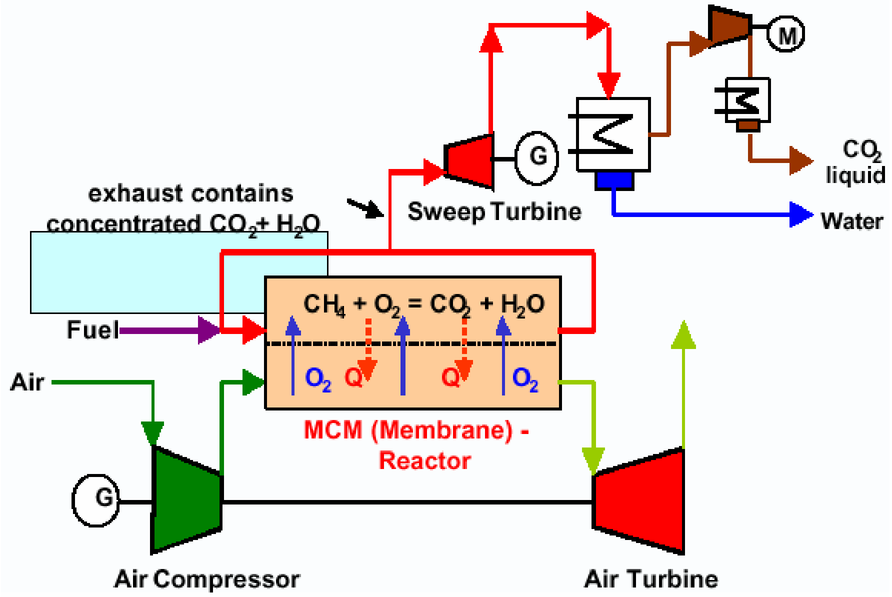


Figure 22 – Schematic of the AZEP cycle concept (Soothill and Griffin, 2003).

The cycle uses a vitiated-air turbine (working on a heated air stream with reduced O2 content), in this case coupled to the air compressor; power is produced by a sweep gas turbine, operating on a CO2+H2O stream; vapour is removed after condensation, while CO2 is compressed and directed to sequestration. This simple concept would not lead to a high performance in terms of efficiency, so that more regenerative – and complicated – schemes are being proposed by several researchers (Fiaschi, 2004); however, the present state of the art depends a lot on the performance of the high-temperature O2-permeable membrane, which in such cycles fulfils several different – and demanding – tasks: gas separator, chemical energy recuperator, and combustion chamber.

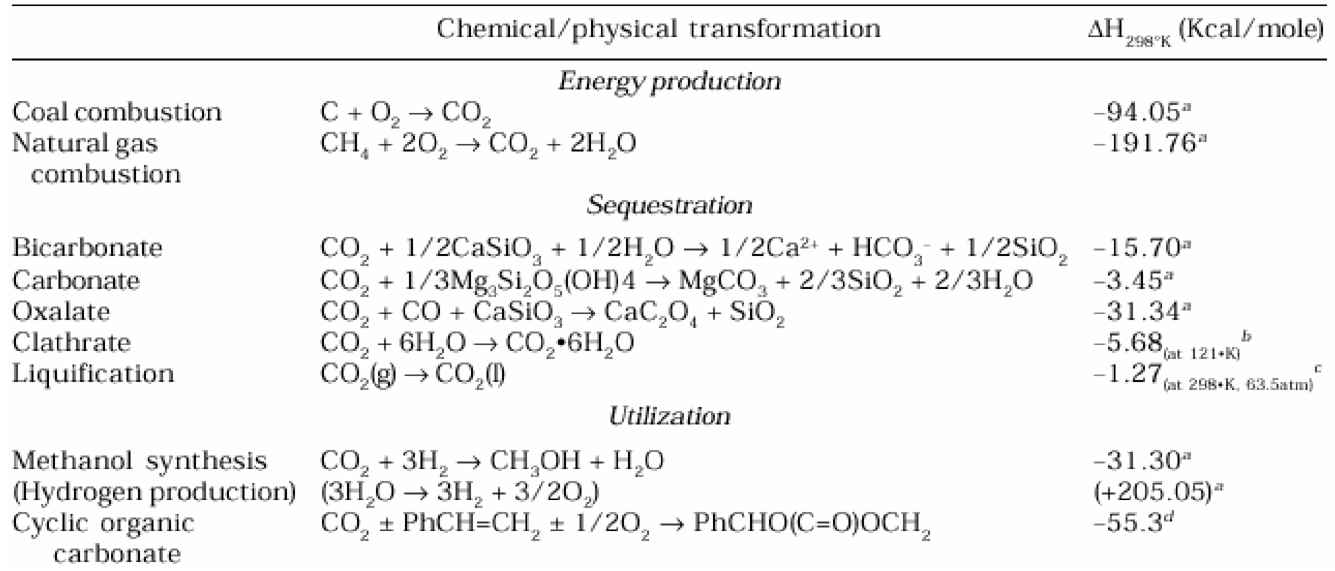
Presently, there is much interest in membrane applications for CO2 separation, as an alternative to chemical or physical absorption. However, published information about the performance indicates that the design goals are still far away, both in terms of required surfaces, functional performance (with special reference to high temperatures), and reliability.

4.5 Chemical sequestration and final solutions - Niche applications

Considering the huge amount of industrial emissions of carbon dioxide into the atmosphere, a relevant obstacle to the spreading of CO2 capture applications is certainly the uncertainty about the final sequestration options. All solutions considered (e.g., deep ocean injection; depleted oil/gas wells; saline formations, deep aquifers,….) have raised objections of different nature (e.g. biology, geology, ….) and there is still much uncertainty about local and global effects if these sequestration technologies should be applied on the required, very large scale. The possibility of capturing carbon and fixing it as a solid (to be disposed of at low cost), or use it as a secondary product of commercial value, is particularly attractive. The Doe study of 2000 reports that the whole world's carbon production of 1990 could be stored as MgCO3 into a volume of 10km*10km*150m, or as Clathrate (an ice-like substance achievable at very high pressure injection in the deep ocean) into a volume of 80km^3. In some way these ways of chemically fixing CO2 into solids reproduce the natural carbon cycle: the relevant problem is how to effectively accelerate it, as natural transformations leading to these species as final solutions take geological times.

A niche application is the use of CO2 – or directly carbon in a pre-combustion fuel processing view – to produce valuable chemical substances through organic chemistry. On the whole, the impact of such technology is limited (the DOE estimate is that the whole worldwide production of plastics and rubber could be produced by recovery of 3,5% of the anthropogenic emissions of CO2); however, these niche applications represent a good opportunity for some users (e.g., refineries, chemical plants,….). The problem is that usually, these paths to chemical sequestration require strong reducing agents: the best option being represented by Hydrogen (allowing for example the synthesis of Methanol). However, large-scale availability of Hydrogen (e.g. from nuclear+renewables) would solve the CO2 emissions problem at its roots, so that there would be marginal need for fuel processing or flue gas decarbonization; on the other hand, if Hydrogen is produced from hydrocarbon sources, the global CO2 cycle of the process should be investigated and it is very likely that the carbon balance would prove that use of Hydrogen is not a valid option in most cases. Table 7 (from DOE, 1999) summarizes some of the processes that can be considered, and indicates through the required energy of reaction the relative difficulty in activating them.

Figure 23 presents an original idea of using carbon – obtained by biomass pyrolisis – as a reducing agent for the production of CO from CO2, coupled to a gas turbine and integrating heat recovery from the hot gas stream (providing heat for the pyrolisis reactions). The system is currently under study, and it could achieve 15-25% CO2 reduction with respect to natural gas firing through substitution of this fuel with biomass. With respect to a biomass gassifier coupled to a gas turbine (an option which is well known, but finds at present no commercial applications, on account of the large modifications needed for the engine), this proposal has the attractive of being proposed as an add-on to a commercial gas turbine unit, with limited modifications.



	Chemical/physical transformation	$\Delta H_{298°K}$ (Kcal/mole)
	Energy production	
Coal combustion	$C + O_2 \rightarrow CO_2$	–94.05[a]
Natural gas combustion	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	–191.76[a]
	Sequestration	
Bicarbonate	$CO_2 + 1/2CaSiO_3 + 1/2H_2O \rightarrow 1/2Ca^{2+} + HCO_3^- + 1/2SiO_2$	–15.70[a]
Carbonate	$CO_2 + 1/3Mg_3Si_2O_5(OH)4 \rightarrow MgCO_3 + 2/3SiO_2 + 2/3H_2O$	–3.45[a]
Oxalate	$CO_2 + CO + CaSiO_3 \rightarrow CaC_2O_4 + SiO_2$	–31.34[a]
Clathrate	$CO_2 + 6H_2O \rightarrow CO_2{\bullet}6H_2O$	$-5.68_{(at\ 121{\bullet}K)}$[b]
Liquification	$CO_2(g) \rightarrow CO_2(l)$	$-1.27_{(at\ 298{\bullet}K,\ 63.5atm)}$[c]
	Utilization	
Methanol synthesis	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	–31.30[a]
(Hydrogen production)	$(3H_2O \rightarrow 3H_2 + 3/2O_2)$	(+205.05)[a]
Cyclic organic carbonate	$CO_2 \pm PhCH{=}CH_2 \pm 1/2O_2 \rightarrow PhCHO(C{=}O)OCH_2$	–55.3[d]

Table 7 – Some Chemical/Physical transformations options for CO2 capture (DOE, 1999)

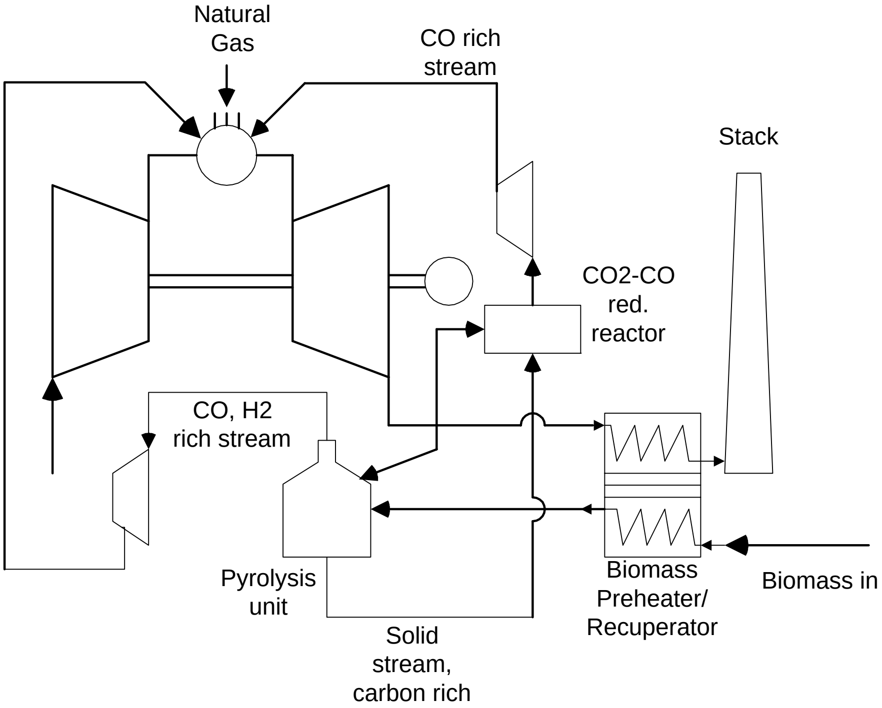


Figure 23 – Proposal for biomass-assisted CO2 removal from gas turbine power plant

5. Proposals for Power Plants including CO2 Removal

There is presently much debate about the integration of CO2 capture emissions in power plants; basically, three are the possible categories:

-Pre-combustion Carbon removal. Carbon is removed from a synfuel, usually in form of CO and CO2, through some physical or chemical process.

-Post-Combustion removal. CO2 is separated from the flue gases before their introduction in the atmosphere

-Oxygen-enriched combustion. Achieving combustion in Oxygen rather than air, only CO2 and H2O can be present in the exhaust. H2O can be removed by condensation (cooling), so that almost pure CO2 can be obtained.

Among these three categories there are several contact points. Basically, the removal technologies fall in one of the cases examined, and depending on the specific case one technology can be more or less adaptable in a near, mid or long-term future perspective.

The current technology offers the separation of CO2 in post-combustion (end-of-pipe) applications in a cost range from about 35€ to 250€ per ton of CO2 captured; accordingly, the increase in the cost of electricity is estimated from 2,5 to over 20 €cents/kWh (IEA, 2003). The wide cost brackets reflect different technologies, but also size, plant- and fuel-type related arguments: the lowest additional prices being achievable by large coal-fired power plants with amine gas scrubbing.

6. Transit generation Power Plants - Atmospheric Semi-Closed Gas Turbine Cycles with combustion in air – Basic idea and advanced solutions.

The increase of the CO_2 concentration in the exhaust, and the reduction of the flow rate of flue gases to be treated in the post-combustion CO_2 separation equipment, is a key issue in developing cost-effective separation of CO_2 for power plants applications. This is especially true for gas turbines, where the high overall excess air in the traditional, open-cycle layout determines large flow rates and CO_2 concentrations lower than 5%, rendering post-combustion carbon separation a difficult task.

Among the many advanced proposals which can be considered to improve the situation, the one probably most close to present-day (gas/steam combined cycle, GTCC) technology is that of Atmospheric Semi-Closed Gas Turbine Cycles. The basic idea is shown schematically in Figure 24.

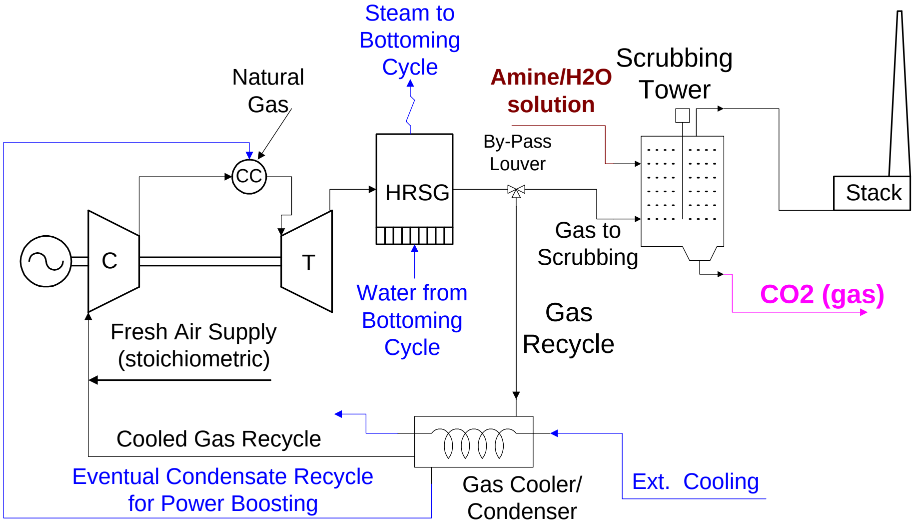


Figure 24 – Schematic of SCGT/CC power plant

Referring to Figure 24, the gas turbine exhaust (which can be as cold as 80 °C by modern gas-fired GTCC) is split in two streams, one of which (the larger) is further cooled down to 30-35°C (depending on the climate and availability of external cooling; during the cooling process water – coming from combustion of hydrogen – is recovered); this cooled stream is then re-circulated to the compressor inlet, mixed with a secondary fresh air stream (necessary for combustion), in what is called a Semi-Closed Cycle arrangement (Facchini et al., 1996; Fiaschi and Manfrida, 1997). The waste-gate system at turbine exhaust can be designed by a set of large louvers/dampers, or incorporated within the gas turbine housing. The concentration of CO2 at the stack can be thus increased to about 15% in mass, and the flow rate to be treated is reduced to about one third of that of the gas turbine. It is important to notice that the amount of CO2 in the GT working fluid is anyway limited to 15%: this value should affect in a very limited way the performance of turbomachinery, as the working gas properties are not much different from those of air (compressor) or usual combustion gases (turbine).

The performance level of SCGT/CC, with current-technology large GT units, can be estimated at an efficiency of about 52%, with a specific work output exceeding 600 kW/kg, and CO2 emission factors as low as 50 kg_{CO2}/MWh. The water recovered can be used for injection at Combustion Chamber level, producing interesting peak shaving features (in the range of 10% of the nominal power) at the price of a small reduction in efficiency during peak load operation (Figure 25). The semi-closed arrangement implies additional irreversibilities, mainly in the gas cooler/condenser and at the recirculation node; however, these irreversibilities are small with respect to other large contributions typical of gas turbine cycles; and the cold stack conditions attenuate these negative issues (Figure 26).

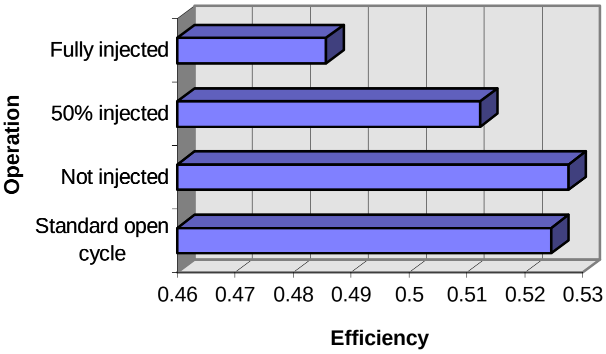


Figure 25 – Efficiency of optimised SCGT/CC cycle (Non-Injected/Injected)

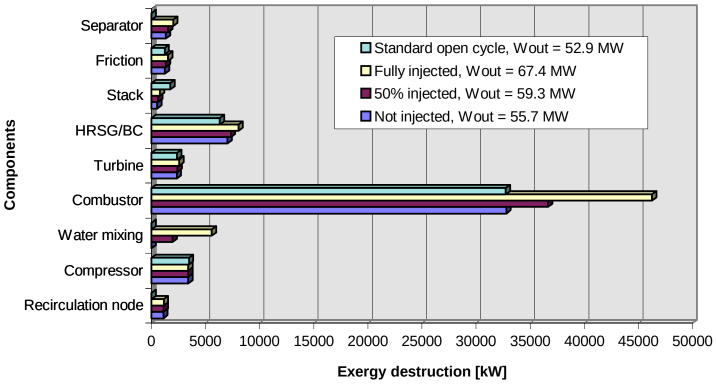


Figure 26 – Irreversibilities in SCGT/CC

With respect to a traditional, equivalent-technology GT/steam combined cycle, a penalty of about 6-7 efficiency points can be realistically expected in the modified SCGT/CC arrangement (inclusive of CO2 capture, which is not considered in Figures 25 and 26). Low-temperature heat for chemical scrubbing can be naturally provided as low-pressure steam from the combined-cycle layout. Modifications to equipment should include the redesign of the combustion chamber, which is anyway quite marginal as the pressure level is unchanged and the CO2 content is limited.

The chemical scrubbing section is energetically connected to the power plant by the heat demand for desorption of the solution; however, it is clear that the cost of this section (both construction costs and operation) is directly proportional to the volumetric flow rate of exhaust gases to be treated, and inversely to the concentration of CO2 at the stack: therefore, any measure reducing the flow rate, and increasing the CO2 concentration, is very beneficial for the applicability of this technology. Such modifications, however, require a redesign of the power plant with this specific goal, and are not usually applicable as retrofit options.

A scheme suitable for building a small-size demonstration plant, developed around a regenerative gas turbine layout, is shown in Figure 27. The SCGT/RE (Regenerative) cycle option (Corti et al., 1998) provides the heat needed for amine regeneration through low-temperature heat recovery from the gas turbine exhaust, after the gas/gas regenerator; the cycle includes compressor intercooling (and possibly aftercooling) and injection of the water condensed in the low-temperature recycle loop. The performance level is of course worse than a large-size, SCGT/CC layout; however efficiency levels of about 48% (with 80% CO2 removal) and specific work levels exceeding 500 kJ/kg appear possible for a reference size of 25-35 MWe (Figure 28). As for most regenerative GT cycles, the SCGT achieves its best performance levels for moderate pressure ratios ($\beta = 10$ to 12).

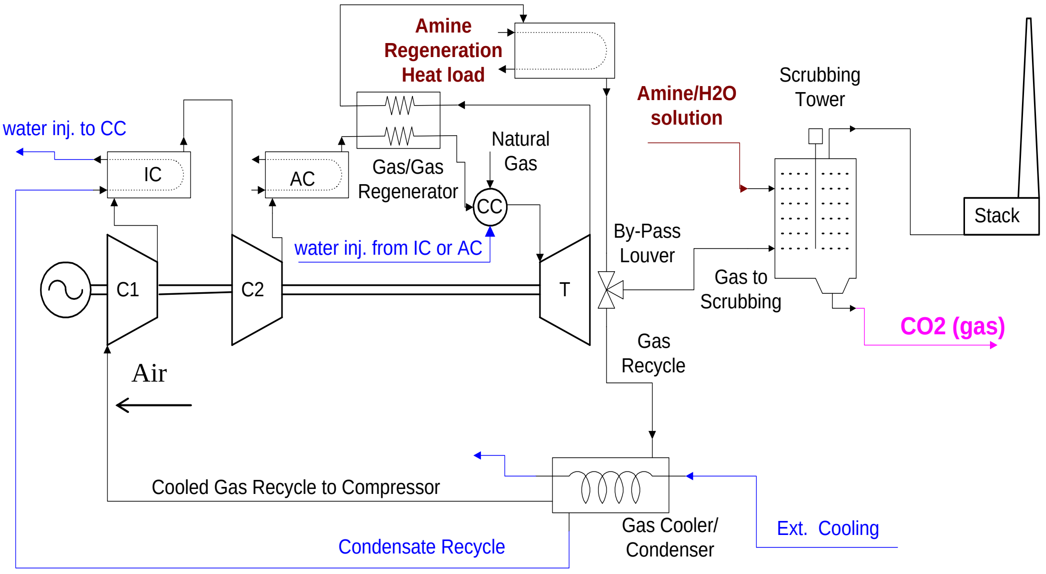


Figure 27 – Schematic of SCGT/RE power plant

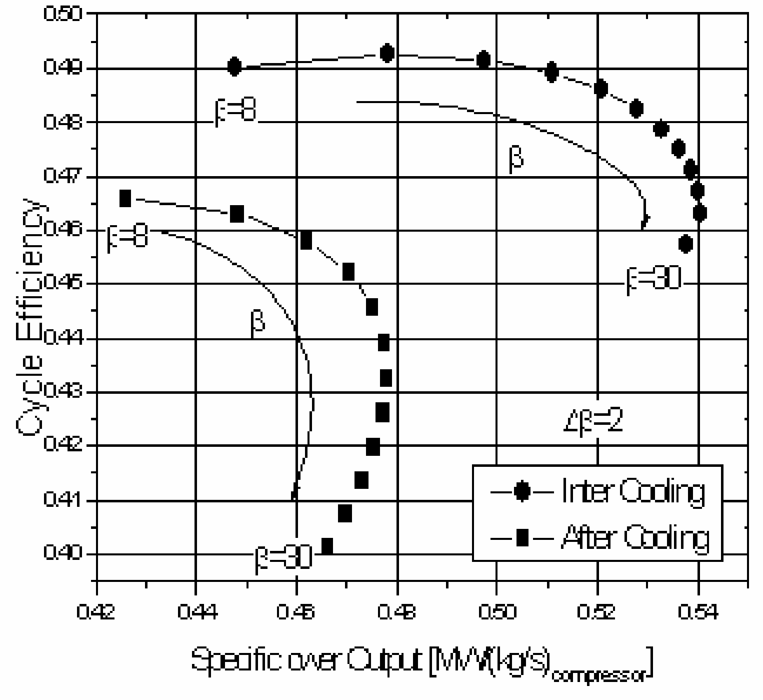


Figure 28 – Performance map of SCGT/RE

If one wishes to apply SCGT cycle concepts to aero-derivative GT engines, having large pressure ratios, the coupling the Semi-Closed Gas Turbine principle to that of Humid Air Turbine (SCGT/HAT; Carcasci et al., 2000) can offer extreme levels of performance combining the advantages of wet GT cycles with CO2 removal. At the price of an evident plant layout complication (Figure 29, SCGT/HAT tries to offer the high performance typical of advanced humidified GT cycles (which already are characterized by a very low stack temperature) with CO2 removal and suppression of the huge water consumption typical of wet GT solutions. The water required for extensive humidification of the stream at CC entry is entirely recovered in the cooler/separator of the low temperature recycle loop, so that the cycle is completely self-sufficient from the point of view of water consumption when running on natural gas.

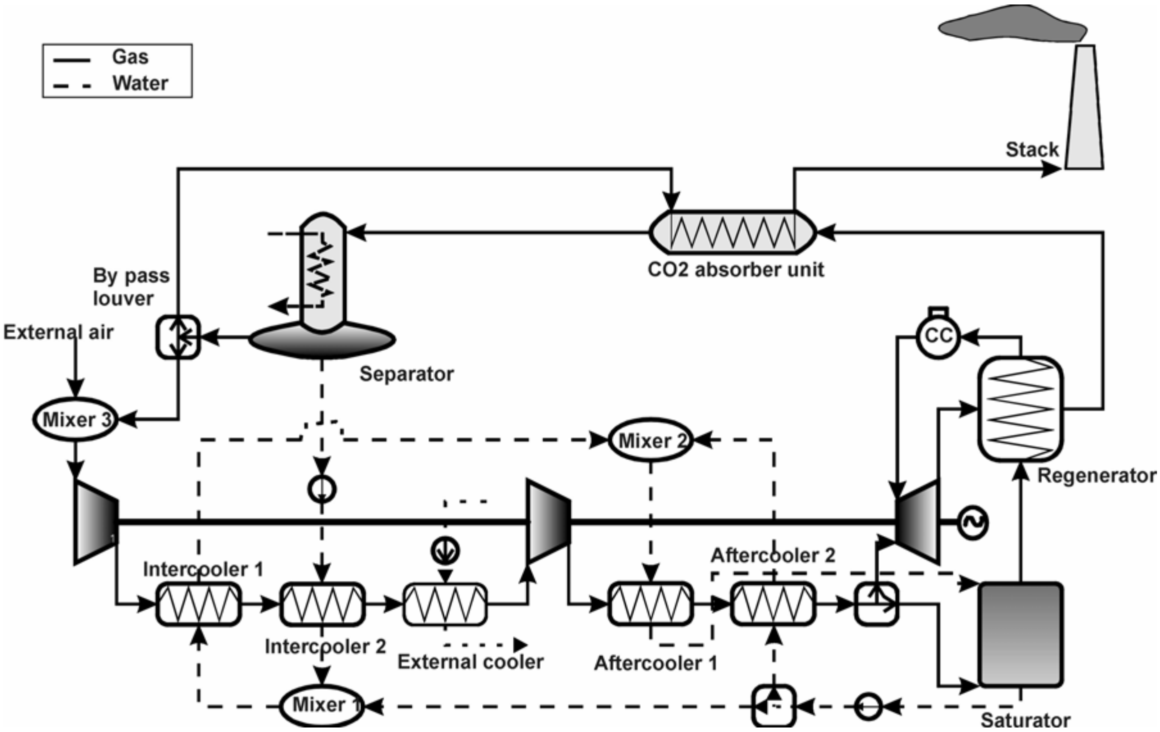
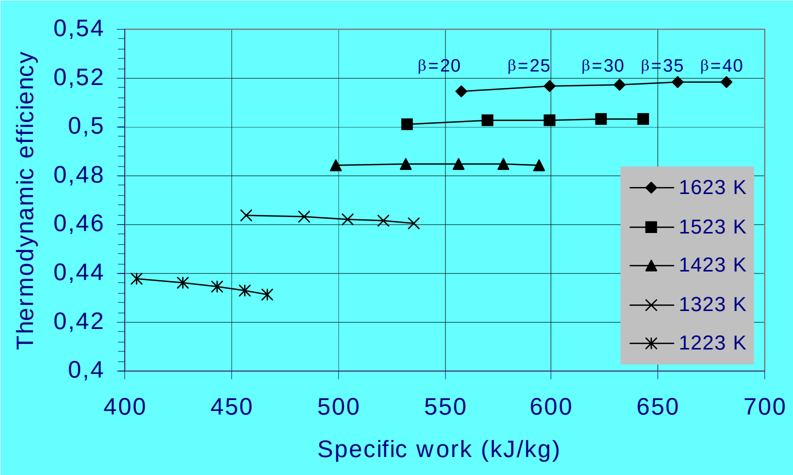


Figure 29 – Schematic of SCGT/HAT power plant



The performance level of SCGT/HAT approaches that of a large-size SCGT/CC plant (Figure 30), with a rather flat optimisation curve for relatively high GT pressure ratios (aero-derivative engines). The reference size should be considered between 30 and 50 MWe.

Figure 30 – Performance map of SCGT/HAT

Another interesting possibility is offered by chemically recuperated gas turbine cycles. This solution includes usually some kind of reformer, promoting transformation of natural gas into hydrogen through the use of a suitable catalytical reactor, with the addition of steam and heat. The reformer can be integrated within a gas turbine-based power plant in several ways, and pre-combustion fuel decarbonization can be added either through chemical/physical absorption, or by the use of semi-permeable membranes (Bolland, 2003; Fiaschi and Tapinassi, 2002). A schematic of the plant layout of such a solution, including an Auto-Thermal Reformer (ATR), is shown in Figure 31. The calculated performance, with present-day gas turbine technology, is shown in Figure 32.

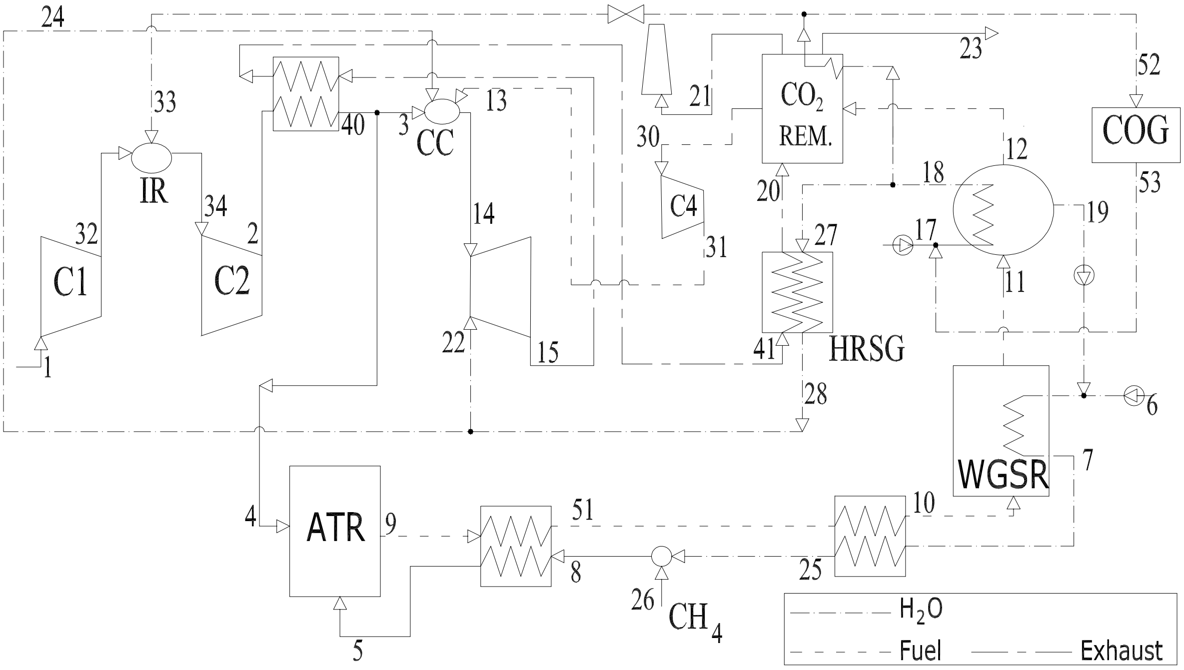


Figure 31 – Plant schematic layout for an ATR gas turbine cycle with pre-combustion fuel decarbonization.

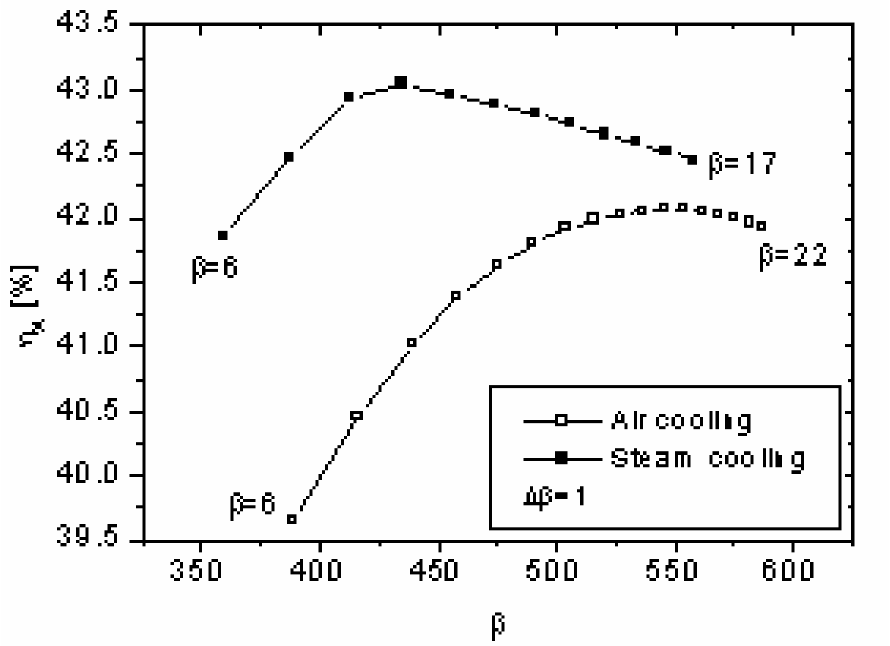
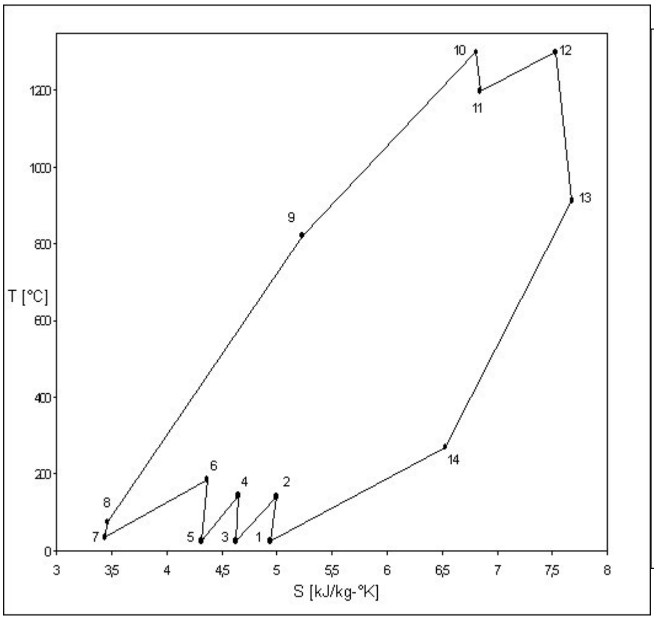


Figure 32 – Calculated performance of an ATR gas turbine cycle with pre-combustion fuel decarbonization

7. Advanced proposals – Oxy-combustion supercritical CO2 cycles

Advanced proposals for innovative power cycles include supercritical CO2 cycles (MATIANT), operating with oxygen-enriched combustion at high pressure, and producing liquid CO2 for direct disposal/sequestration (Iantovski and Mathieu, 1996; Mathieu, 1998; Fioravanti et al., 2000). The cycle diagram and layout are presented in Figures 33 and 34. An example of calculated performances is shown in Figure 35.



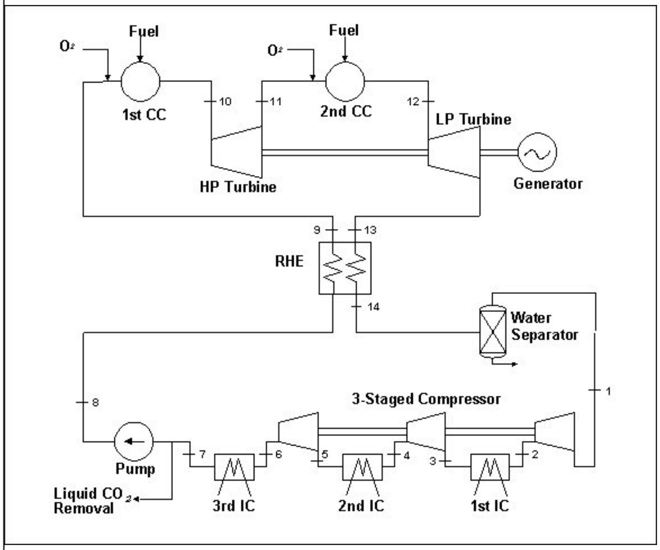


Figure 33 – MATIANT Cycle

Figure 34 – MATIANT cycle schematic layout

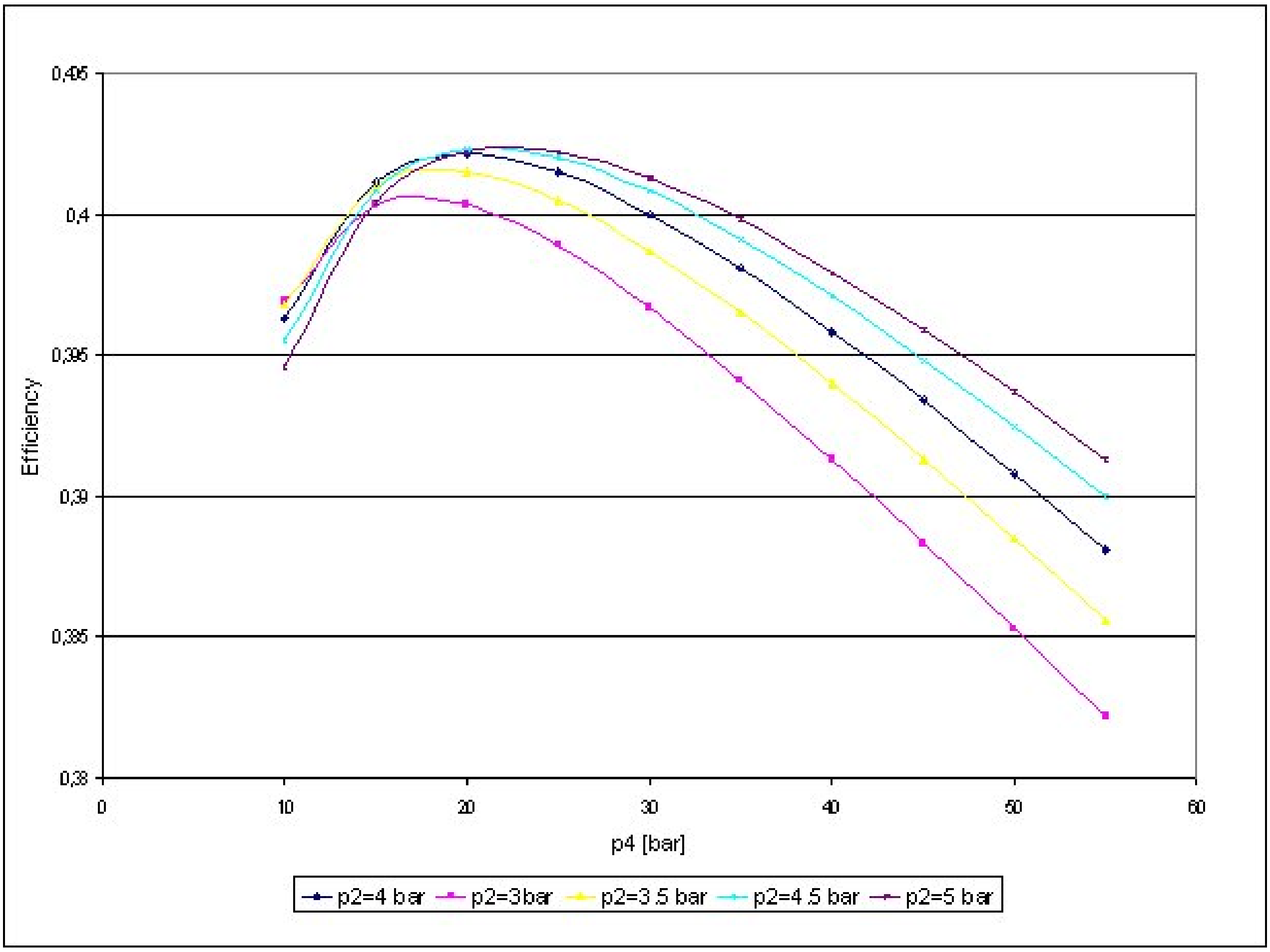


Figure 35 – Calculated performance of MATIANT cycle (sensitivity to p2 and p4; Fioravanti et al., 2000)

The performance of the MATIANT cycle is relevant, considering that CO2 is produced in hypercritical, liquid conditions; the cycle requires dedicated equipment, such as expanders/compressors working on CO2-H2O, and a high-pressure, high-temperature combustor. These requirements put this type of cycles in a mid-term future perspectve, in comparison to the other options previously examined which refer closely to the existing technological level of available equipment, at least for the turbomachinery/combustion/heat exchangers.

8. LCA as a synthesis tool for final evaluation - Conclusions

Cost estimates for R&D, investment and maintenance are subject to large uncertainties when comparing options for innovative advanced power cycles inclusive of CO2 recovery, especially if solutions close to present-day technology (such as SCGT) are compared with more advanced options requiring more substantial R&D (e.g., chemically recuperated or supercritical CO2 cycles with Liquid-CO2 removal). Life Cycle Analysis is a modern tool for the evaluation of the environmental costs of products, services and goods; it is an ISO-14000 guideline (ISO, 1998), and its use will thus become every day more common and widely accepted. Figure 36 (Lombardi, 2000; Lombardi and Manfrida, 2000) shows a comparison in terms of Greenhouse effect for three options: SCGT/CC; IGCC (Coal Gassifier)+Carbon removal; E-Matiant. LCA shows that the environmental advantages introduced by SCGT are valuable and better or comparable with respect to those obtainable by more complex or futuristic technologies.

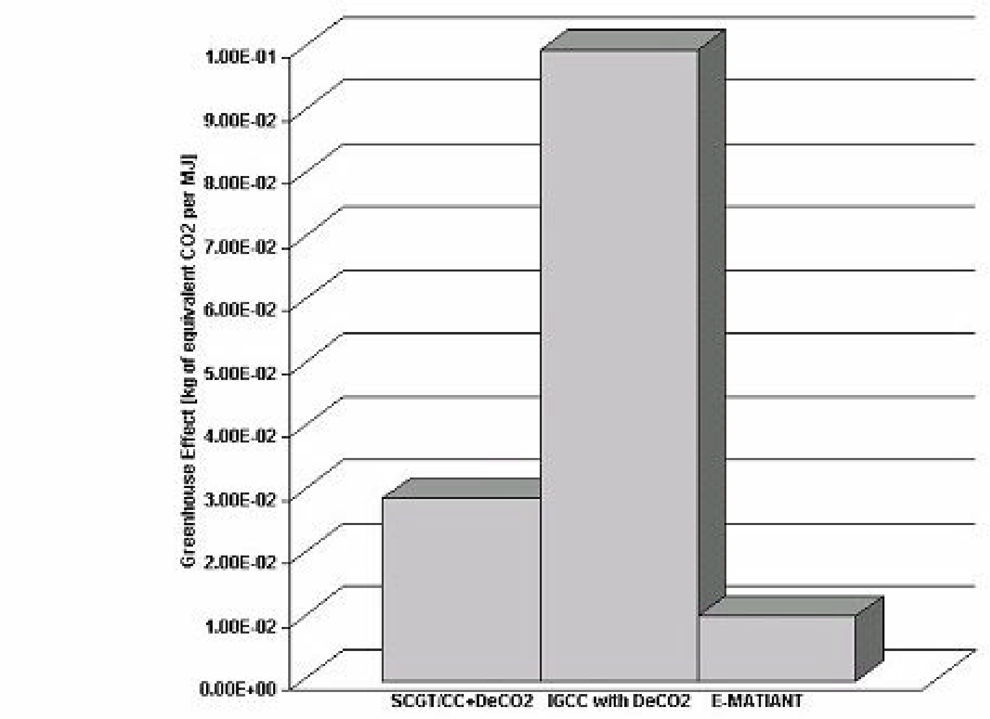


Figure 36 – LCA comparison of three CO2-spearating alternatives: Post-combustion in a SCGT/CC with optimised Amine chemical scrubbing; pre-combustion IGCC with optimised Amine chemical scrubbing; oxy-combustion (MATIANT cycle) (Lombardi, 2000)

Acknowledgments

In preparing this review lecture I took material extensively from my co-workers: Andrea Corti, Daniele Fiaschi, and Lidia Lombardi. Other sources were found in the published work of several friends in the academic community. I am grateful to my co-workers for their contribution to this research through several years, and to friends for their openness to scientific exchange.

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