Environmental sustainability of CO_2 capture in fossil fuel based power plants

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Abstract

This paper analyzes various possible options for the chemical capture of CO_2 and their energy requirements, focusing attention on the introduction of the devices in well-defined power plant configurations. Capture technologies are proposed and the most suitable technology appears to be chemical absorption. Even if, in principle, this option appears interesting, under an energetic point of view it has a great impact on the thermodynamic performance of the plant, reducing drastically its efficiency.

Keywords: CO_2 capture, chemical absorption technologies, energy analysis.

1 Introduction

Fossil fuels retain the largest market share of the world's electricity generation, but they are a source of CO_2 emissions. These considerations have triggered discussions over the wide use of some fossil fuels, like coal, in order to see if capture and sequestration of CO_2 emissions are possible. The aim of CO_2 capture technologies is to remove the CO_2 presents at the flue gas before it reaches the atmosphere, producing a concentrated stream that can be stored and transported. However, to capture the CO_2 produced, a significant amount of energy is required. This means that power plants with capture technology require much more fuel per kWh generated, reducing net plant efficiency [1]. It also results in an increase in most other environmental emissions per kWh of electricity generated, producing a proportional amount of by-products relative to the same type of plant without capture. In addition, there is an increase in the consumption of chemicals, such as ammonia and limestone in De-NO_x and De-SO_2 technologies. These factors restrict the emissions reduction requirements to a not-always-available thermodynamic performance.

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Different technologies have been proposed in order to reduce the pollutant emissions or energy conversion systems.

1. Removing the source of pollution from the fuel before it is burnt.
2. Avoiding the pollutants during combustion (in-furnace measures).
3. Removing the pollutants from the flue gases by “end of pipe“ methods.

CO_2, SO_x, NO_x and PM are some of the emissions related to power generation that made fossil fuels combustion “unclean”. SO_X, NO_X and PM represent accidental emissions of the power plants, since the level of them is about 0.1-2 mg for each kWh of energy produced, the actual technology permits good possibility of reducing their level without significant energy requirements. CO_2 is a structural emission of power plants. It is well known that recent Pulverized Coal Combustion (PCC) plants are characterized by a level of CO_2 emission in the range between 850 and 900 g/kWh. The level of 750 g/kWh can be reached by Ultra Super Critical power plants (USC) and with Integrated Gasification Combined Cycle power plants (IGCC). However, when using coal it is difficult to break the barrier of 750 g/kWh. Using CH_4, the emissions can be reduced by a factor of two reaching levels of 350-400 g for each KWh of energy produced. Indeed CO_2 emissions are inevitably connected to the energy conversion system and therefore they are not accidental. In a coal based thermoelectric power plant the level of CO_2 emissions is of about 3 kg for each kg of coal. In a natural gas combined cycle power plant the CO_2 emissions level is also of the same order of magnitude. This first consideration is crucial in order to define the possible capture strategies and the environmental sustainability of their utilization. For this reason a preliminary analysis of the CO_2 capture energy requirements is necessary.

2 Main technologies for CO_2 capture

Capture techniques can be retrofitted to existing conventional fossil fuel based power systems or integrated into new power-generation facilities. These technologies can be performed in post- or pre-combustion processes. A summary of the possible pathways and of the technologies is given in Fig. 1.

Post-combustion processes capture CO_2 from flue gases produced by combustion of fossil fuels or biomass. Instead of being discharged directly to the atmosphere, the flue gas is passed through devices, which capture the CO_2, while the remaining flue gas, with a low CO_2 concentration, is discharged to the atmosphere. Flue gas from combustion approaches atmospheric pressure, which indicates that in post-combustion processes, a large volume of gases would be treated, involving the use of large-scale equipments.

Due to the low CO_2 partial pressure, absorption processes based on chemical solvents are currently the preferred options for post-combustion capture. The future of post-combustion methods is based on emerging capture technologies that are not yet in such an advanced stage of development. The energy required in CO_2 post-combustion capture is, in general, quite large. This energy requirement reduces significantly the overall efficiency of the process (Fig. 2).

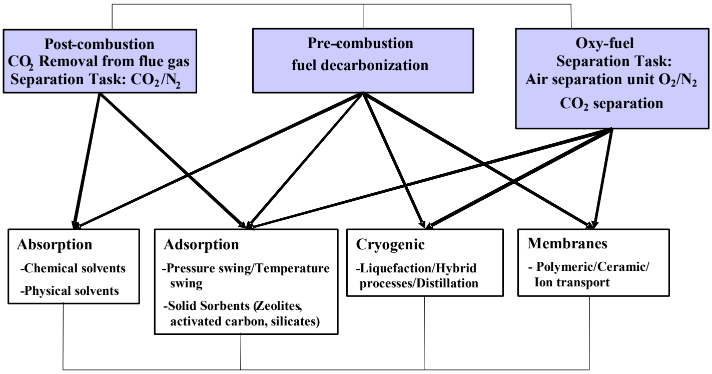

Figure 1: CO_2 capture pathways.

2.1 Absorption

Three different absorption processes can be distinguished: chemical, physical and dry solid absorption. Chemical absorption processes make use of the reversible nature of the chemical reaction of an aqueous alkaline solvent with CO_2. A by-product is originated, which afterwards will be heated, to break the bound between the chemical solvent and the CO_2, producing a CO_2-rich stream and a regenerated chemical solvent. Fig. 3 illustrates an absorption process. The main absorption parameters are the flue gas flow rate, the CO_2 content in the flue gas, the CO_2 removal rate and energy requirements. The energy consumption of the process is the sum of the thermal energy needed to regenerate the chemical solvent, and the electric energy required to operate pumps, blowers and compressors.

Amine-based chemicals are the principal commercial chemical solvents used to separate CO_2 from exhaust gases including, (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) [4]. Furthermore, salts of strong alkalis with weak acids offer various possibilities for chemical absorption process [5].

CO_2 can be also physically absorbed by a non-reactive solvent according to Henry's law and then regenerated using pressure reduction or heat.

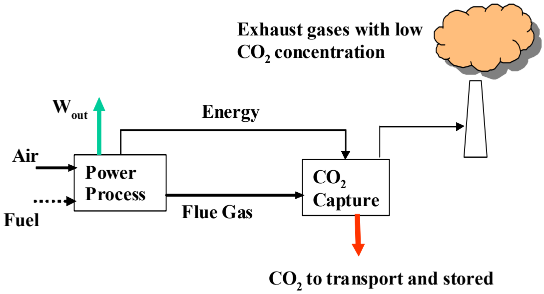

Figure 2: End-of-pipe CO_2 capture.

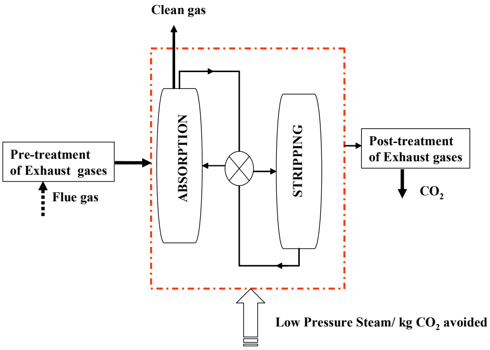

Figure 3: Chemical absorption.

The absorption capacity of organic and inorganic solvents for CO_2 increases with increasing pressure and with decreasing temperatures. Therefore, physical absorption methods are not suitable for flue gas CO_2 capture, since the partial pressure of CO_2 is low. This kind of technology could be very efficient, but only for high-pressure CO_2-rich streams, such as those in pre-combustion processes in IGCC power plants [6]. The physical solvents used are Selexol, Rectisol, and Morphysorb. Another way is represented by dry solid absorption. A solid can be used instead of a liquid as a scrubbing medium for CO_2 capture. In this process, the solid sorbent does not circulate between vessels because the sorption and regeneration are archived by cyclic changes, in pressure or temperature.

2.2 Physical adsorption

An adsorption process consists of two major steps: adsorption and desorption. Strong affinity of an adsorbent for removing the undesired component from a gas mixture is essential for an effective adsorption step. The stronger the affinity the more difficult it is to desorb the gas impurity and the higher the energy consumed for regenerating the adsorbent. Several modes of operation are used to release or regenerate the adsorber gas from the solid. Pressure or temperature changes are used. In Pressure Swing Adsorption (PSA), the gas mixture flows through a packed bed of adsorbent at high pressure, insulating the solid, and then desorbing the sorbed gas by lowering the pressure. In Temperature Swing Adsorption (TSA), the gases are adsorbed at a lower temperature, the solid is isolated and then the temperature is raised during the regeneration step to release the trapped gas. The main advantage of physical adsorption over absorption could be its simple, and energy efficient, operation and regeneration.

2.3 Cryogenic separation

The cryogenic separation separates a gas component from a gas stream. The separation can be made producing a phase change (liquefaction or solidification) of the component that needs to be separated, thereby condensing it and removing it as a liquid/solid from the gas mixture (Fig. 4). The condensation is fulfilled by a series of compression, cooling and expansion steps.

Cryogenic separation for CO_2 is only practical for a high-pressure stream with a high CO_2 concentration, such as in pre-combustion capture or Oxy-fuel combustion. Cryogenic separation produces liquid CO_2 that is ready for transport and storage. Quite a high-energy rate for cooling and compression is necessary.

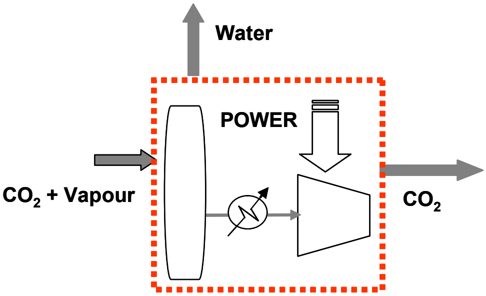

Figure 4: Cryogenic separation.

2.4 Membranes separation

Membranes are special materials that allow either the selective transport (diffusion) or selective exclusion of a desired component [8]. The flow of gas through the membrane is usually driven by the pressure difference across the membrane. Therefore, high-pressure streams are usually preferred for membrane separation. Indeed, the low CO_2 partial pressure difference that characterizes fuel gas provides a low driving force for gas separation membrane. Membranes can separate CO_2 from a gas stream by size exclusion or by chemical affinity. There are many different types of materials (polymeric, metallic, ceramic) that may find application in CO_2 capture. Nowadays, the removal of CO_2 with commercially available membranes results in higher energy penalties on the power generation efficiency compared with standard chemical absorption processes.

3 Energy analysis of CO_2 capture by chemical absorption

Chemical absorption technologies are nowadays the only method that can be proposed to implement large-scale capture of CO_2 from fossil-fuel energy combustion systems. Capture efficiency is higher than 90% and produces CO_2 with a purity of 99%. However, the introduction of CO_2 capture devices represents an important efficiency penalty on the thermodynamic performance of the power plant as well as a remarkable increase of the net cost of power generation with CO_2 capture.

3.1 Thermodynamic model to evaluate the energy required for CO_2 capture

The capture process can be divided in three main stages (Fig. 5): pre-treatment of the flue gas, in order to reach the desirable scrubber conditions, scrubber/stripper processes, and post-treatment of the produced CO_2 stream. Energy consumption of the whole process is the sum of the thermal energy needed to regenerate the solvent and the energy required to deliver a high-pressurized CO_2-pure stream.

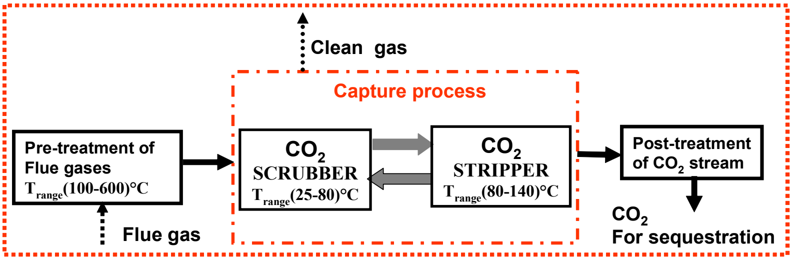

Figure 5: Chemical absorption flowsheet.

Electrical energy for compression, the pumping and blowing of the circulated solvent flow rate, or to operate the flue gas, are not considered in this analysis. The parameters used for the model are; the sorbent absorption capacity, depending on the CO_2 concentration in the flue gas (lower CO_2 concentration will require higher absorption capacity), the scrubber/stripper temperatures, depending of sorbent type, and the desirable CO_2 temperature and pressure for transport and storage. The flue gases from a combustion power plant are usually quite hot, ranging from 60°C to 600°C, depending on the power system. Absorption being an exothermic process is favoured by low temperatures. Thus, it is desirable to cool down the flue gas to scrubber temperatures in order to improve CO_2 absorption and minimize sorbent losses. A direct contact cooler (consisting a packet tower where the cooling fluid is water at 25°C) can be used to reduce the flue gas temperature to acceptable levels, also acts as a flue gas wash with the additional removal of fine particulates. The flue gas temperature directly affects the volumetric flow rate of gas stream. The heat duty, Q, to be removed from the flue gas at the cooler pre-treatment depends on the temperature and the mass flow of the flue gas together with the desirable absorption temperature required for the absorption, is:

$$Q = m_f c_p (T_{scb} - T_f) \tag{1}$$

where m_f is the mass flow of the flue gases, c_p is the heat capacity of the flue gases, T_{scb} is the scrubber temperature and T_f the flue gas temperature. Since CO_2 absorption might be a spontaneous reaction in order to facilitate the CO_2 capture, at the scrubbing an exothermic reaction is fulfilled, thus no energy is demanded. The stripper process is the desorption process, where a high concentrate CO_2

stream is produced, the energy required for the sorbent regeneration is quite high and one of the most relevant energy consumption in the whole process. This energy is usually supplied by the low/medium pressure steam flow produced in a steam turbine and supplied by a reboiler. In any case, this required heat can be divided in three main contributions [7]. The sensible heat is the energy used for heating the scrubber solution to the stripper temperature is given by

$$V_{\mathrm{sen}} = \frac{m_{\mathrm{sol}} c_{\mathrm{p}} (T_{\mathrm{sol}} - T_{\mathrm{strp}})}{m_{\mathrm{CO_2}} \Delta H_{\mathrm{v}}} \tag{2}$$

where V_{sen} is the ratio between the steam mass flow rate required and the mass flow rate of CO_2, m_{sol} is the solution mass flow, c_{p} is the specific heat of the solution, T_{sol} is the rich solvent hot solution temperature, T_{strp} is the stripper temperature, m_{CO2} is the CO_2 mass flow recovered and ΔH_{v} is the steam reboiler vaporization heat coming into the stripper at a given temperature. The recovery of CO_2 from the chemical solvent needs energy to reverse the adsorption reaction. This energy reaction includes the enthalpy reaction and in the solution case, also the solution reaction of the dissolution in water, is given in eqn (3).

$$V_{\mathrm{des}} = \frac{\Delta H_{\mathrm{r}}}{\Delta H_{\mathrm{v}}} + \frac{\Delta H_{\mathrm{sol}}}{\Delta H_{\mathrm{v}}} \tag{3}$$

where V_{des} is the desorption ratio (kg of steam/kg CO_2), ΔH_{r} is the reaction enthalpy, ΔH_{sol} is the solution reaction and ΔH_{v} is the steam reboiler vaporization heat coming in to the stripper at imposed temperature (all in kJ/kg steam). The CO_2 recovered in the stripper must come out along with the help of a vapour stream. The mixture is composed of 1 mol vapour/mol CO_2 and that the whole process occurs at constant temperature and pressure. Steam goes from the saturated vapour to the saturated liquid point at the stripper temperature, the vapour required for stripping is:

$$V_{\mathrm{strp}} = \frac{m_{\mathrm{steam}}}{m_{\mathrm{co_2}}} \tag{4}$$

where V_{strp} is the steam supplied for CO_2 stripping (kg steam/kg CO_2), m_{steam} is the steam mass flow required from the reboiler at the stripper temperature, and m_{CO2} is the CO_2 mass flow recovered. The total vapour required in the stripper is:

$$V_{\mathrm{T}} = V_{\mathrm{sen}} + V_{\mathrm{des}} + V_{\mathrm{strp}} \tag{5}$$

In order to obtain CO_2 ready for transport, in the model a post-treatment at ambient temperature and 140 bar pressure is considered. After the stripper, the vapour-CO_2 mixture is cooled down to 25 °C in order to separate water from the

CO_2 before the liquefaction plant. For the model proposed here, it is considered that the vapour condensation occurs in a direct contact cooler with water at 25°C. In order to liquefy the pure CO_2 stream produced, a three-stage intercooler compression is used. The energy required to compress the produced CO_2 to sequestration parameters for efficient transport and storage, can be estimated as:

$$W_c = \frac{m_{CO_2} c_p \Delta T}{\eta_c} \tag{6}$$

where W_c is the compression energy, m_{CO2} is the CO_2 mass flow recovered, c_p is the CO_2 specific heat, ΔT is the temperature difference in each stage, η_c is the compression efficiency in the different stages.

3.2 Energy analysis

In Table 1, the energy requirements for the different CO_2 chemical absorption technologies are displayed. The high energy consumption needed to capture the CO_2 emissions is pointed out. Using coal as fuel, the energy requirement is of the order of 1/5-1/6 of the calorific value of the fuel. Considering a general thermoelectric plant configuration based on coal, for each kg of coal 3 kg of CO_2 is produced, the energy required to remove CO_2 corresponds more or less to the electric energy produced by the plant, reaching pointless solutions. This result emphasizes the perspective of CO_2 capture only in case of integrated configurations. From this, we can see the necessity to promote solutions in which the capture process uses the marginal energy of the plant. Indeed, the conclusion is that the strategy cannot be applied in the same way to all the plants. Figs 7 and 8 describe two different situations. In the first, a CGAM power plant, the integration between the plant and the capture is possible without a particular penalty (mainly in terms of second law analysis). Low steam pressure coming out from the heat recovery steam generator is used for capturing the CO_2 without subtracting output power to the plant. In the second case, the capture is possible only by subtracting a consistent amount of the low-pressure steam from the boiler; the result is a strong reduction of the plant output power. Under this perspective, solutions like IGCC coal based power plants can be interesting.

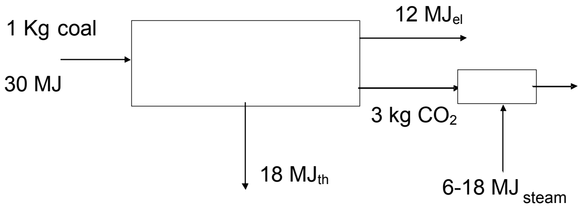

Figure 6: CO_2 capture energy balance.

Table 1: Energy required for chemical absorption CO_2 capture.

		MEA	MDEA	Na_2CO_3	K_2CO_3	$NH_{3(aq.)}$	CaO
Molar concentration	[%w]	30	50	-	-	30	-
	[mol CO_2 /mol sorbent]	0.5	1	1	1	1	1
	[gr CO_2 /gr sorbent]	0.36	0.36	0.42	0.32	2.58	0.78
Energy consumption							
Pre-treatment							
Heat duty	[kW]	-140	-140	-114	-88	-156	-
Scrubber/stripper							
Sensible heat	[kJ/kg CO_2]	331.7	144.9	278.3	92.8	229.9	1177
Reaction heat	[kJ/kg CO_2]	1920.	1105	2920	3210	1455	4587
Stripping heat	[kJ/kg CO_2]	1106	1094.7	-	-	-	-
Post-treatment							
CO_2 compressed	[kJ/kg CO_2]	340	340	340	340	340	340
Heat duty	[kW]	-420	-420	-384	-384	-384	-384
TOTAL Energy consumption [kJ/kg CO_2]		**3460**	**2440**	**3540**	**3640**	**2025**	**6000**

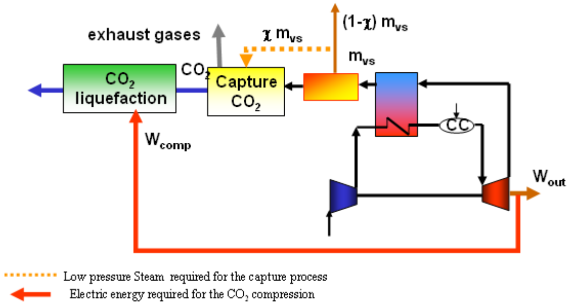

Figure 7: CGAM plant with CO_2 capture.

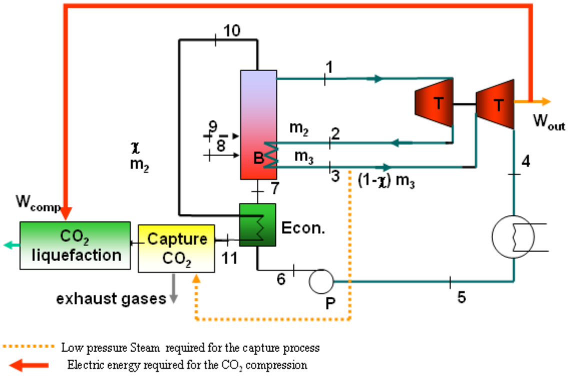

Figure 8: Coal plant with CO_2 capture.

Table 2: Effect of CO_2 capture on the overall plant performance.

	Coal fired power plant				CGAM power plant			
χ	χm_2 [kg/s]	$(1-\chi)m_2$ [kg/s]	η_{II}	W_{out} [MW]	χm_{vs} [kg/s]	$(1-\chi m_{vs})$ [kg/s]	η_{II}	W_{out} [MW]
0	0	21.7	0.41	30	0	14	0.50	30
0.2	1.89	19.8	0.38	27.8	1.50	12.4	0.48	29.68
0.4	3.79	17.9	0.35	25.7	3.00	10.9	0.46	29.36
0.6	5.69	16.0	0.32	23.5	4.51	9.48	0.44	29.04
0.8	7.59	14.1	0.29	21.40	6.01	7.98	0.42	28.72
1	9.49	12.3	0.26	19.25	7.51	6.48	0.40	28.40

The results shown in Table 2, where a link between the amounts of CO_2 captured (χ) and the required kg of steam for each kg of CO_2 recovered (m_s) is reported, demonstrate that the most significant reduction takes place in the electrical output of the steam turbine. This is due to the different points where the low-pressure steam used for the CO_2 recovery is taken into the energy generation process. While for the gas turbine, the low-pressure steam used for the CO_2 capture process does not affect the energy generation process of CGAM plant.

Considering the results discussed in this section, it is clear that the future of CO_2 capture should not only be based on overcoming the limitations of the existing solvents [9], and on the reduction of energy consumption for solvent regeneration and of equipment sizes, but also on the development of particular plant configurations where the marginal energy of the plant can be used for capture.

4 Conclusions

In spite of great research efforts and the great emphasis connected with the development of pollutant emission control, the concept of CO_2 capture in power generation and heating processes is still in a development phase. The paper focuses attention on the connection between the capture technologies (mainly chemical absorption technologies) and the thermodynamic performance of the power plant. It is shown that the energy consumption required to capture the CO_2 emissions is quite high varying from 2 to 6 MJ for each kg of CO_2 emitted. Depending of the fuel used and the power plant configuration, the energy required for CO_2 capture and separation processes causes a significant power plant efficiency reduction, which necessitates an agreement between the desirable amount of CO_2 to be captured and the permitted energy consumption for maintaining acceptable performance of the plant. In general, it is possible to conclude that CO_2 capture strategy is sustainable only if the marginal waste energy of the plant can be used; but this is not always possible.

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