

Post-combustion CO₂: separation and stocking

M. Mariani

ISPESL-DIPIA, Italy

Abstract

Safeguarding the environment is one of main duties that industrial countries have to respect. Specifically, there is the problem of the greenhouse effect caused by CO₂ emissions in the atmosphere from human activities. The CO₂ is the main greenhouse gas emitted by fossil fuel combustion and causes global warming. With regard to this important environmental problem, the present paper has the main purpose of showing that it is possible to get “clean-work” from power plants if the post-combustion CO₂ separation process from the exhaust flow is made before that same exhaust flow is emitted into the atmosphere. Also, the paper shows that the post-combustion CO₂ separation process is beneficial as the additional CO₂ emissions caused by the separation process is compensated by the capture of a lot of post-combustion CO₂ from the exhaust flow. Furthermore, the paper shows the main problems of the CO₂ (gas, liquid, solid) stocking in full safety with respect to human health and environment.

Keywords: CO₂ emissions, separation process, stocking, human health safety.

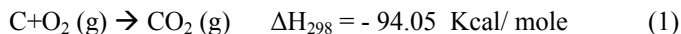
1 Introduction

Many industrial combustion processes are concerned with gas emissions in the atmosphere. Among these gases, CO₂ is a greenhouse gas having an estimated radiative forcing equal to 4.37 (W/m²) for a CO₂ doubling and it causes 60 % of the earth's global warming [1]. To reducing this environmental problem we need to minimize CO₂ emissions into atmosphere. This is achievable if there are plant solutions that involve the post-combustion CO₂ separation process and its subsequent stocking in full safety with respect to human health.



2 Carbon oxidation and combustion temperature

Carbon stoichiometric oxidation is given by:



where (g) is gas and ΔH_{298} is standard enthalpy at 25°C. The relation (1) shows that 1 C mole need 1 O₂ mole, 3.762 N₂ moles or 4.762 dry-air moles from a mixture 21% O₂ – 79%N₂ [2]. In short, because the dry-air is constituted by 23% O₂ – 77% N₂ in weight, the combustion of 1 C Kg need 2.67 O₂ Kg, 8.93 N₂ Kg and then 11.60 dry-air Kg or 9.70 dry-air m³ with specific weight 1.2 Kg / m³. In order to determine the combustion temperature the equation is [2]:

$$\sum (N_i C_{pi})_p dT + \Delta H_{298} = 0 \quad (2)$$

where subscript p is product, N_i is the i -mole number, C_{pi} is constant pressure specific heat (cal/gmole K), ε reaction velocity (gmole/s). The constant pressure specific heat is [2]:

$$C_p (\text{N}_2) = 6.66 + 1.02 \cdot 10^{-3} T ; C_p (\text{CO}_2) = 10.55 + 2.16 \cdot 10^{-3} T \quad (3)$$

The ε value is 1 CO₂ gmole/s. Substituting the above values into (2) it has the absolute combustion temperature T = 2444 K (2171°C) starting from T = 298 K (25°C) the absolute room temperature. It's only too natural that the practice combustion temperature is less than stoichiometric combustion temperature. Because the combustion products have high heat content at high temperature they are used in many technological appliances.

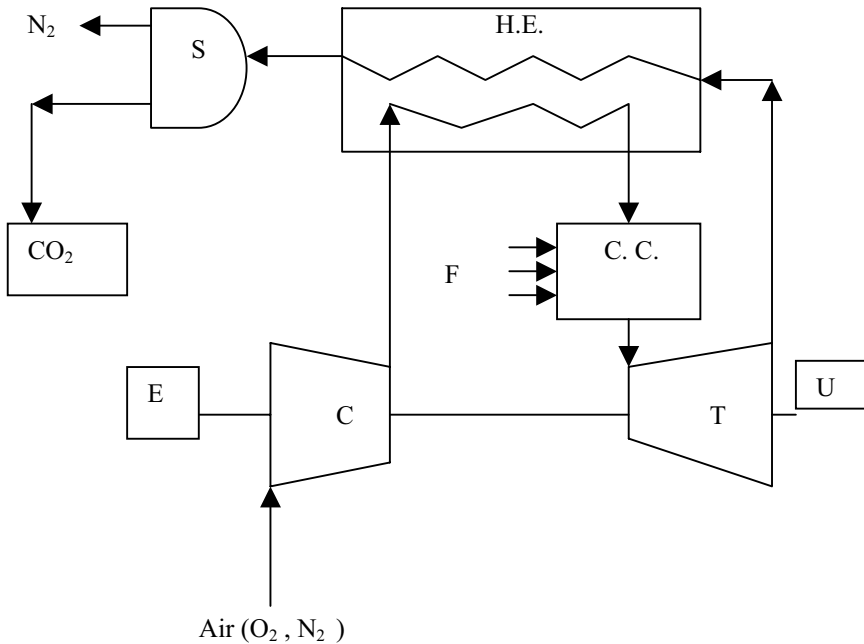
3 Technological appliances

The post combustion gases are used as fluid in gas turbines or as a convector fluid in heat exchangers. In order to obtain “clean work” with respect to CO₂ it is necessary to separate the post combustion CO₂ from the exhaust flow and then to stock it.

3.1 CO₂ separation - Gas turbine plant

Figure 1 shows CO₂ separation - gas turbine plant. It gives the maximum efficiency and the maximum work at a parity of circulating fluid [3]. In reality, the main problem of gas turbine is the emission of many exhaust gases such as NO_x, SO_x, CO, UHC (unburnt hydrocarbons), smoke and solid particulate material. In many countries, there are restrictions on exhaust gas emissions.

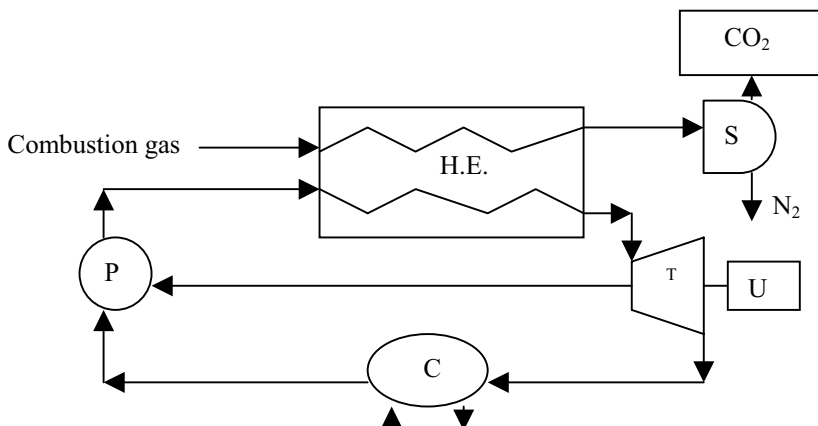




Keywords: E = Diesel engine; C = compressor; F = Fuel; C.C. = Combustion chamber; T = gas-turbine; U = User; H.E. = Heat exchanger; S = Separator; CO_2 Stocking.

Figure 1: CO_2 separation - gas turbine plant.

3.1.1 CO_2 separation - Water turbine plant [2]



Keywords: H.E. = Heat exchanger; S = Separator; CO_2 Stocking; T = water-turbine; U = User; C = condenser; P = pump.

Figure 2: CO_2 separation - water turbine plant.

4 CO₂ separation work

The equations of the ideal gas-flow separation process is given by[2]:

$$\Delta H = 0 \quad \Delta S = R \sum (Y_i \ln Y_i) \quad (\text{cal/gmole K}) \quad (4)$$

where ΔH is enthalpy, ΔS is total molar entropy, R is ideal gas constant (1.987 cal/gmole K) and Y_i is the gas-flow i -component molar fraction. As shown, the separation process gives environmental thermal pollution equal to:

$$\Delta Q = 0.24 N T_{\text{amb}} \Delta S \quad (\text{J}) \quad (5)$$

where N is gas-flow total number moles and T_{amb} is absolute room temperature. In order to estimate the environmental thermal pollution of a gas flow with two components CO₂ + N₂ at room temperature (300 K) the following scheme is considered:

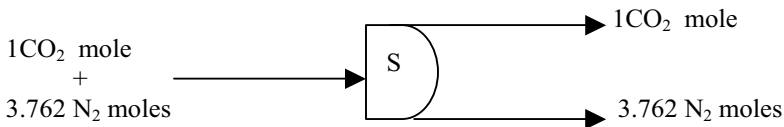


Figure 3: Gas-flow separation process with two components CO₂ + N₂

The number of moles involved in Figure 3 is equal to the number moles of combustion products from carbon stoichiometric oxidation. In the present case it has:

$$\Delta S = 1.987 \left[(1/4.762 \ln (1/4.762) + (3.762/4.762) \ln (3.762/4.762)) \right] = -1.021 \quad (6)$$

$$\Delta S_{\text{Tot}} = 4.762 (-1.021) = -4.8635 \quad (\text{cal/ K}) \quad (7)$$

$$\Delta Q_{\text{Tot}} = 0.24 (300) (-4.8635) = -350.17 \quad (\text{J}) \quad (8)$$

The 63.81% of ΔQ_{Tot} or 223.46 (J) are required for 1 CO₂ mole separation. The CO₂ separation energy L certainly is greater than 223.46 (J) because it depends on η -efficiency of the real separation process and L can be given approximately by:

$$L = 223.46 / \eta \quad (\text{J / CO}_2 \text{ gmole}) \quad (9)$$

5 Valuations on CO₂ separation process

As a reference parameter, it is assumed that a 800 MW electric power plant emits about $2 \cdot 10^6$ CO₂ t into the atmosphere a year. This means that $6.34 \cdot 10^{-2}$ CO₂ t are

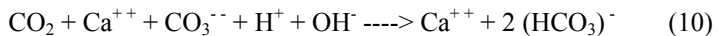
in front of 800 MJ. If η -efficiency is assumed equal to 20% (low efficiency) separation energy L is 1117.30 (J/CO₂ gmole) or 29.39 (MJ) that are equivalent to $2.33 \cdot 10^{-2}$ CO₂ t as additional potential emissions. Therefore, 1 CO₂ t separation and 20% η -efficiency give 23.3 CO₂ Kg as additional potential emissions. This gives a good reason to separate CO₂ from the exhaust gas flow. This need is increased when η -efficiency is greater. For example $2 \cdot 10^6$ CO₂ t separation a year and 20% η -efficiency give $46.6 \cdot 10^3$ CO₂ t a year as additional potential emissions that are equal to 2.33% of $2 \cdot 10^6$ CO₂ t a year. If η -efficiency is 40% then the CO₂ additional potential emissions are $2 \cdot 10^3$ t a year, equal to 0.1% of $2 \cdot 10^6$ CO₂ t a year.

Table 1: Separation energy L as function of η -efficiency.

0	20%	25%	30%	35%	40%	45%
L (J/gmole)	1117.30	893.84	744.87	638.46	558.65	496.58
η	50%	55%	60%	65%	70%	75%
L (J/gmole)	446.92	406.29	372.43	343.78	319.23	297.95

6 CO₂ stocking

The CO₂ separation process gives safety problems relating to CO₂ stocking. CO₂ can be stocked in artificial or in natural containers such as oceanic depths, exhaust gas or oil wells, but not extraction coal deposits or saline deepwater deposits. The problem is to stock the CO₂ within a specific volume which is as small as possible so as to reduce storage space and also to avoid the direct contact between stocked CO₂ and air. In fact, the CO₂ gas has detrimental effects with respect to human health when CO₂ air concentration is greater than 3-4% in volume. Such concentrations can lead to headaches, emesis and heart deficiency. When CO₂ air concentration is greater than 30% in volume death by asphyxia occurs [3]. CO₂ stocking phases are approximately showed in Figure 4. CO₂ phases (vapour, liquid, solid) are a function of pressure and temperature and the three physical phases coexist at the triple point ($516.76 \cdot 10^3$ Pa, -56.5°C) and the CO₂ critical point occurs at 7.6 MPa, +31.3°C. Above the critical temperature (+31.3°C), CO₂ is always in the gas phase whatever the pressure. CO₂ gas reacts with sea water according to the following reaction and in this way it settles:



The CO₂ liquid stocking is possible in the ocean depths because CO₂ liquid is water soluble and its solubility coefficient becomes greater when the pressure increases [4]:

P = 1 atm: solubility coefficient = 1.80 (mg/ml);

P = 5 atm: solubility coefficient = 8.65 (mg/ml);

P = 10 atm: solubility coefficient = 16.03 (mg/ml);

P = 15 atm: solubility coefficient = 21.95 (mg/ml).



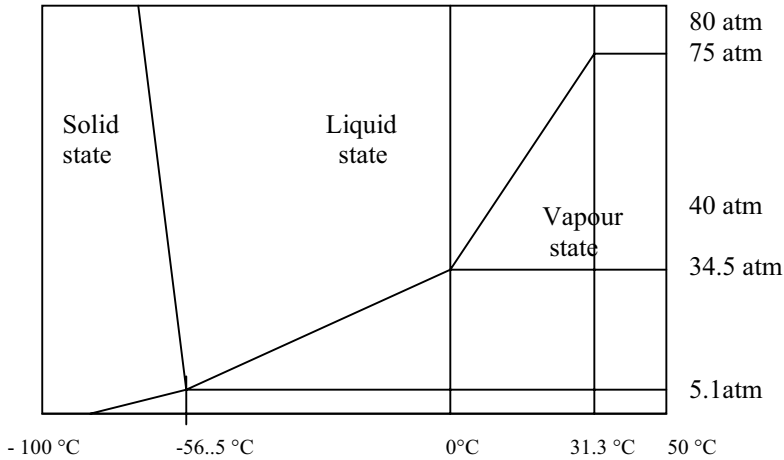


Figure 4: CO₂ state diagram (1 atm = 101.325 KPa).

If the average hydrostatic pressure increases to 10.5 MPa /Km then at the sea depth of about 724 m there is a pressure of 7.6 Mpa (75 atm) equal to the CO₂ critical pressure. Also, at the same depth the sea temperature is certainly less than 20°C and the CO₂ may be stocked in the liquid phase. If the CO₂ liquid is stocked at about 3000 m oceanic depth the CO₂ holder times are about 1000 years; if the CO₂ is stocked at 3700 m there is the possibility to form a “stable” lake of CO₂ liquid and CO₂ solid. It is more appropriate to stock CO₂ in exhaust gas or oil wells rather than extraction coal deposits or in saline deepwater deposits. In those cases, if the average superficial temperature is 10°C and the average geothermal gradient is 30°C/Km [5], the CO₂ critical temperature (31.33°C) will be reached at a depth of 711 m.

That means that it is possible for CO₂ liquid stocking if the geological deposits are at a depth less than 711 m. Alternatively, at depth greater than 711m it is possible to stock CO₂ gas because the temperature is supercritical. The geological deposits with a low superficial temperature, a low geothermal gradient and made by porous rocks with impermeable superficial rock are the better containers. Also, the stratum above geological deposits prevents the direct contact between the CO₂ stocked and the air. The best CO₂ stocking locations are submarine exhaust gas or oil wells that are generally at 800 m sea depth. The CO₂ solid or dry ice stocking is not usual and it is possible when the CO₂ is stocked, as shown, at great oceanic depths. The use of CO₂ dry ice gives safety problems because its vapours have detrimental effects with respect to human health. In fact, it is not possible to stay in a confined space more than 8 hours when the CO₂ air concentration is more than 0.5%. The exposure time without hazards for human health are: CO₂ 0.5% max 8 hours; 2% max 1 hours; 3 % max 15 min.

7 Conclusions

This paper shows that it is possible to get “clean work” from power plants burning gas or oil if the post-combustion CO₂ is separated from the exhaust gas flow and then stocked in geological deposits. That is a good method for reducing the CO₂ emissions into the atmosphere and to mitigate the earth’s global warming. Also, the CO₂ stocking in geological deposits gives full safety with respect to human health: this form of stocking is able to keep the CO₂ stocked for a hundred years and prevents the direct contact between the stocked CO₂ and air. The CO₂ may be injected into geological deposits by well-known industrial technologies used for oil extraction.

References

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