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Innovative Process Cycle with Zeolite (MS13X) for Post Combustion Adsorption

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Abstract

This paper reports the integration of Electric swing adsorption (ESA) Process in a Natural Gas Combined Cycle. This process was investigated in the MATESA FP7 project financed by European Commission. The ESA process is modelled through ASPEN Adsorption using both heat and electricity for regenerating the sorbent. The overall heat duty of the sorbent is 4 MJ/kgCO₂ where half of this is recovered in the regeneration cycle. The resulting CO₂ avoided is around 90% with a net electric efficiency of about 40%. The low efficiency is consequence of the higher energetic value of electricity with respect to the thermal power typically adopted in MEA regeneration. Being the first attempt of simulating this process using multiple heat sources and the recent development of sorbents, significant improvements can be expected by ESA reducing the gap with conventional post-combustion CO₂ capture technologies.

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1. Introduction

Power generation is one of the major stationary sources of CO₂ emissions. The existing power plants, but also the ones available in the near future, will emit CO₂ if no corrective action will be taken. A way is to remove the carbon dioxide out of the atmospheric emissions. In this moment, the available CO₂ removal technologies are still under investigation to decrease the high impact that they have on an equipped power plant. The flue gas of current power plants is a mixture of nitrogen, oxygen, carbon dioxide and water plus other minor contaminants. The post-combustion capture layout can be used for retrofitting the existing power plants. Also greenfield power plants can adopt this kind of technology, especially until other technologies are not available.

The most studied post-combustion technology is the chemical absorption, in particular MEA-based one. Substances that are more promising have been proposed. The piperazine [1] and ammonia [2], [3] are examples of alternative solvents, but the energy penalty of the capture plant is still relevant. Other technologies are studied, as membranes[4] and sorbents [5]. The main focus of these techniques have been in coal-fired flue gases where the content of CO₂ is around 10-15%. On the other side, several technological problems were found when the flue gas comes from a natural gas fired power stations. In this case, the gas contains only 3-5% of CO₂ and large amounts of oxygen. Also, increasing the purity of CO₂ from 3.5% to 95% means an enrichment factor of 27 which is very difficult to achieve without spending large amounts of energy. In this case, adsorption technologies can provide a large and selective surface where the separation can take place efficiently.

When the flue gas has a low CO₂ content, Temperature Swing Adsorption (TSA) process can be adopted as proposed by Merel et al. [6]. The main drawback of TSA process is the longtime required for desorption cycles that can be reduced maximizing the contact area of the hot gas and the adsorbent [7]. A process that can increase very fast the temperature of the adsorbent is Electric Swing Adsorption, where a low voltage electric current is employed to heat the adsorbent by the direct Joule effect [8]–[11]. A review of ESA application for gas separation and purification is available by Ribeiro et al. [12]. One disadvantage of ESA when compared to TSA is that the temperature increase is achieved by using electric power while in the case of TSA waste heat is employed. For the particular case of CO₂ produced in NGCC plants, due to the complex energetic integration already implemented, the amount of waste heat may not be enough to be employed in a TSA process and ESA may be an interesting alternative. Grande et al. [13] propose an application for CO₂ capture with activated carbon honeycomb monolith.

The main objective of this work is to evaluate the Electric swing adsorption (ESA) technology as an innovative second generation technique to capture CO₂ from flue gases. The ESA process is mentioned in several reports as one possible technique to capture CO₂ from flue gases, but so far this process was commercially employed to remove volatile organic compounds.

In this work, particular interest will be given to the modeling of the ESA section applied to natural gas fired power plants carried out in Aspen Adsorption [14]. Starting from the reference NGCC power plant defined in the EBTF document [3], the ESA process which is cyclic and sequential process composed by different steps to use and regenerate the adsorbent in an efficient way is applied. The cyclic configuration able to achieve a high purity CO₂ stream is based on a previous work [4]. The sorbent regeneration is done in the most efficient way by recovering it from during the cooling phase, using steam from the power plant and by electric power.

An adsorbent with good electrical properties (able to conduct electricity) and with high loading of CO₂ at low partial pressures is the (molecular sieve 13X) MS13X. The following section will present the reference power plant, the capture and compression sections and the modeling tool. Finally, the results of the modeling activity will be presented.

Nomenclature

TSA	Temperature Swing Adsorption	MEA	Mono Ethanol Amine
ESA	Electric Swing Adsorption	NGCC	Natural Gas Combine Cycle

2. Process description

2.1. Reference NGCC power plant

The power plant used as reference for the preliminary assessment of ESA technology is based on two identical gas turbines (GT), each equipped with a heat recovery steam generator (HRSG) that share the same single steam turbine.

The net power output is 829.5 MWe and the net electric efficiency is 58.3% [15]. Thermodynamic properties, composition and mass flowrate of one gas turbine exhaust gases are reported in Table 1.

Table 1 Thermodynamic properties, composition and mass flowrate for the gases at the inlet of the capture section. The mass flowrate corresponds to one gas turbine [15]

G [kg/s]	T [°C]	P [Bar]	Composition, %mol					
			Ar	N ₂	O ₂	CO ₂	H ₂ O	NO _x
665.3	100.0	1.04	0.89	74.38	12.39	3.96	8.38	1.4E-03

The overall CO₂ flowrate is around 41 kg/s. When ESA capture section is considered with only electrical duty for the regeneration as in previous works [16], the operating condition of the power plant results unchanged. When the duty for the regeneration is both thermal and electric, the gas turbine operating condition will not change while steam cycle power will reduce because of the steam bleeding. Simultaneously, power consumptions for heat rejection (which have limited impact) will reduce because the latent heat will be used for sorbent regeneration.

2.2. CO₂ capture plant process simulation

The overall process for CO₂ capture is sketched in Fig. 2. Before the ESA process, exhaust gas cooling and water separation section are necessary for drying the exhaust gases.

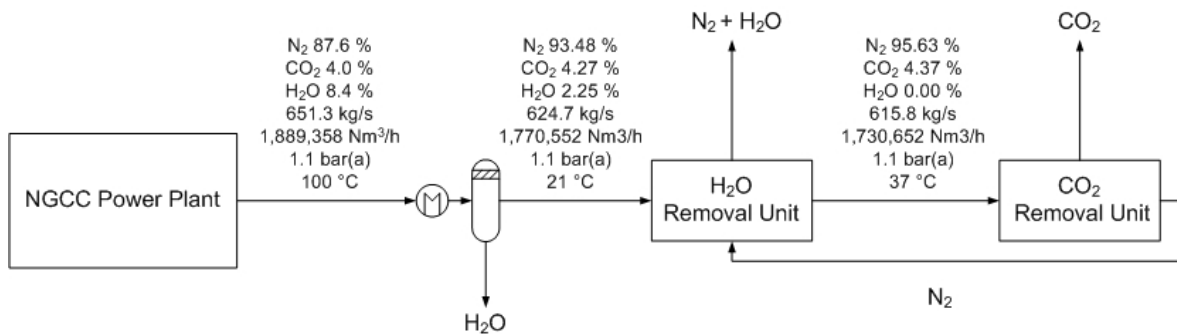


Fig. 1 Scheme of the overall process for CO₂ removal from a NGCC plant.

The reference adsorbent material as well as the advanced MOF adsorbent material exhibits a significant affinity towards water. Therefore, it is required to remove water upstream the carbon dioxide unit to achieve the required carbon dioxide recovery rate and carbon dioxide purity. The pre-cooler is used to lower the flue gas temperature to 21°C. By decreasing the gas temperature, most of the water is condensed and separated by gravity. The final amount of water in the gas phase is reduced to 2.25 mol-%. The exhaust gas cooling is carried out into two steps: from 100°C to 40°C (same temperature assumed in MEA capture plants), a washing section which very limited consumptions is used, while the final cooling up to 21°C is carried out with a chiller whose consumption accounts for 3.5 MWe. Activated alumina is used to adsorb of the remaining water from the flue gas stream. For regeneration of the activated alumina adsorbent, purified flue gases of the carbon dioxide removal unit is used. The alumina regeneration by ESA

process flue gases reduces the energy penalties of the H₂O removal section only to fan power consumption. The flue gases that enters the carbon dioxide removal unit are at an average temperature of 37 °C.

2.2.1. Carbon dioxide removal unit

The investigated ESA process is composed by 3 columns. The conceptual stages of the process are: (i) the adsorption stage in which the flue gas passes the column and the major part of CO₂ is adsorbed; (ii) a regeneration stage where the sorbent is heated so that it releases the CO₂ which can be captured. The heating is divided into three parts: the 1st heating is carried out recovering the heat from the columns in the cooling step, the 2nd heating in which the heat is supplied by the condensing steam bled from the steam turbine and the 3rd heating reaches the maximum temperature of the process is done by electric power. The bed purging is divided into two steps where in the first, an almost pure CO₂ stream is sent to the compression section, while in the second one the diluted CO₂ is recycled at the inlet of the adsorber column. The last step (iv) consists of the cooling where part of the heat is recovered in the heating process.

3. Simulation tools

The ESA process has been investigated using ASPEN Adsorption software. The adopted isotherms for the MS13X materials are reported in the Fig. 2. The isotherms are obtained from experimental measurements carried out in MATESA project by regressing the parameters of the Extended Langmuir of the equation 1 from the general equation 2 and 3:

$$q_i = \frac{q_{m,i}K_iP}{1+\sum K_iP} \quad (1) \quad K_i = K_i^0 \exp\left(\frac{-\Delta H_i}{R_gT}\right) \quad (2) \quad w_i = \frac{IP_{1i}e^{IP_{2i}/T}P_i}{1+\sum_k IP_{3k}e^{IP_{4k}/T}P_k} \quad (3)$$

The values for the regression of the equations are reported in Table 2 and the regressed values are in Table 3.

Table 2 Values for equation 1 and 2

Isotherms parameters	CO ₂	N ₂
R [J/mol/K]	8.31	8.31
$q_{m,i}$ [mol/kg]	3.00	3.00
K_i^0 [1/bar]	4.25E-07	3.33E-05
$(-\Delta H_i)$ [J/mol]	4.50E+04	2.02E+04

Table 3 Values for equation 3

Isotherms parameters	CO ₂	N ₂
IP_1 [mol(kgkPa) ⁻¹]	1.275E-08	1.00E-06
IP_2 [1/K]	5.412E+03	2.425E+03
IP_3 [1/kPa]	4.25E-09	3.46E-07
IP_4 [1/K]	5.412E+03	2.425E+03

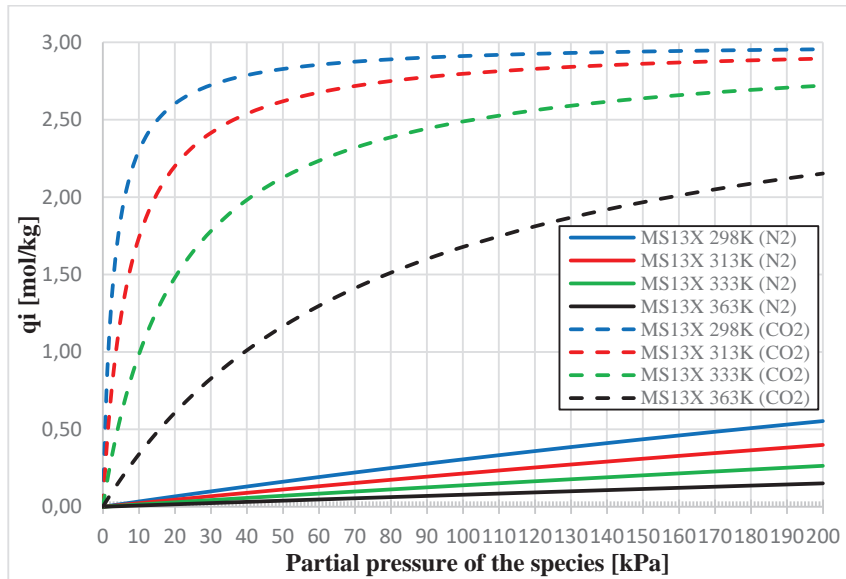


Fig. 2 - Isotherms for MS13X: N₂ solid lines, CO₂ dashed lines

A sketch of the cycle modelled with ASPEN including flow directions and basic equipment of the carbon dioxide removal unit is given in Fig. 3. The implemented process includes the sorbent regeneration by heat recovery, heat from the steam cycle and electric power. It must be outlined that the heating by heat recovery and condensing steam are carried out through a secondary loop to keep the CO₂ purity as high as possible (i.e. during the cooling the exhaust gases are recycled in the column and an external heat exchanger where the heat is transferred to pressurized water). However, the indirect heating increases costs due to additional equipment as well as auxiliary consumptions. The designed timing of the process for the MS13X material is reported on the right of Fig. 3 requiring about 3600 s for one cycle. It must be outlined that the adoption of three heating steps increases the number of problem variables making more difficult to optimize the cycle. Further investigations are necessary to fully optimize the cycle minimizing the consumptions.

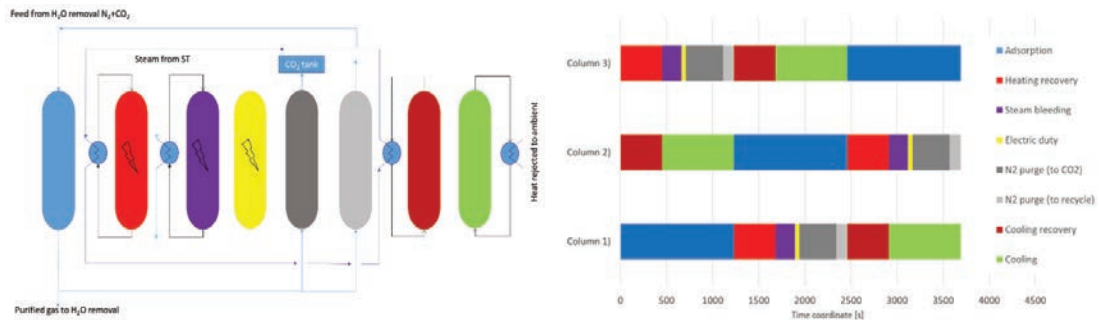


Fig. 3 Scheme of the of the individual cycle steps (colour of the columns corresponds to the ones used in Figure 8 and Figure 9)

The temperature vs. heat transferred graph for the heating and cooling phase are reported in Fig. 4 (left side). In particular, heat recovery from the cooling phase accounts for 59.4% of the total heat duty, the steam bleeding from the steam turbine for 20.2% of the total and the remaining is provided by the electric heating. Fig. 4 right side shows the cooling curve where the final cooling is done through an evaporative tower. A parameter which can be optimized

is the initial adsorption temperature. Higher temperatures lead to lower cyclic capacity but reduce cycle time as well as auxiliary consumptions for heat rejection.

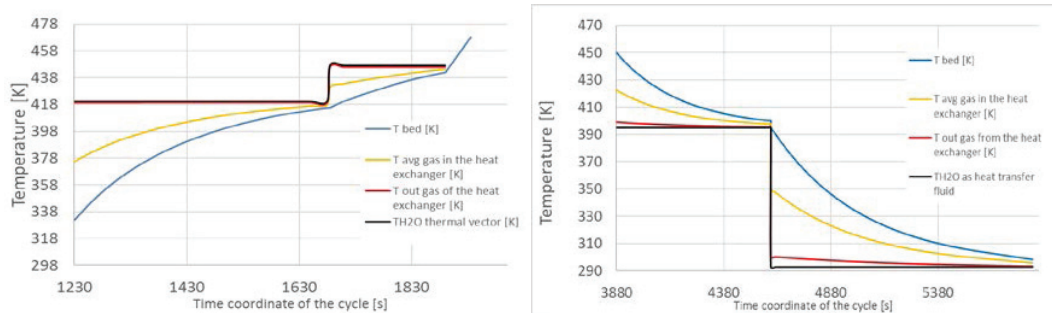


Fig. 4 Heating and cooling steps during the sorbent regeneration process

The overall energy consumptions for the selected ESA process are reported in Table 5.

Table 4 Performance of ESA process

Main results	
Carbon Capture ratio	92.14
CO ₂ purity	95.04
Electric duty for the fans [MJ _{el} /kgCO ₂]	1.43
Heat duty means steam bleeding @ 150°C [MJ _{th} /kgCO ₂]	0.71
Heat duty means electricity [MJ _{el} /kgCO ₂]	1.30
Heat recovered [MJ _{th} /kgCO ₂]	2.90

It can be noted the limited heat duty around 2 MJ/kgCO₂ provided by external sources (electricity and steam). However, the results outline the significant contribution of the fan consumptions to the overall energy requirement. The regeneration, heating and cooling step requires the gas circulation with consequent pressure drops both for the honeycomb and the heat exchanger balanced by fan work. It must be reminded that to preserve CO₂ purity and capture ratio, the heat transfer by pressurized water as heat transfer medium is favored. The significant fan consumption can be reduced by 70% if the gas velocity is reduced, hence the duration of the heating and cooling step are doubled. However, this would result in higher investment costs. These results are not extensible to other adsorption processes but are particular to the nature of ESA.

Beside the thermodynamic results, it is of importance to stress that it is the first time that such complex regeneration system was modeled in ASPEN adsorption. Significant efforts have been dedicated to implement the ESA modeling in ASPEN for the sorbent limiting the possibility of process optimization which is now mandatory to improve the cycle. Moreover, the adoption of heat recovery, steam and electricity as heat sources for sorbent recovery increased the number of degree of freedom, increasing the optimization timing.

4. Results

This section summarizes the overall consumptions adopted for the CO₂ capture section. Compared to the results presented in previous section, the CO₂ compression work is included together with fan consumption upstream the ESA process. The CO₂ compression section was simulated with ASPEN according to the EBTF guidelines [15]. Compression work as well as amount of nitrogen remaining in the liquid CO₂ depends on thermodynamic models used in ASPEN™ (i.e. Peng-Robinson or PC-SAft) as well as binary coefficients adopted. Compression is divided into

two steps: i) the first part, when the CO₂ is in vapour phase, consists of intercooled compressor composed by five stages with four intercoolers and one aftercooler and ii) the second part, when CO₂ is liquid, includes a pump with a final aftercooler. The compressor provides an outlet pressure of 80 bar while the pump provides 110 bar, fixed as delivery pressure. All the water inside the CO₂ stream is removed before the fourth intercooler.

The compressor isentropic efficiency and the pump hydraulic efficiency are fixed and set equal to 0.85 and 0.75 respectively. The resulting overall consumption for CO₂ compression assuming 100% purity, which is the typical value for MEA separation process, is 310 kJ/kgCO₂. The ESA process produces a less pure CO₂, therefore the specific consumption will be slightly higher.

Additional consumption which should be taken into account are related to fans. One fan is needed to overcome the pressure losses in the water removal and CO₂ separation sections (the exhaust gases at the outlet of the adsorbent must be kept at ambient pressure, therefore the fan is necessary to overcome the pressure losses in the capture section). This fan is placed upstream the entire section and is named Main fan (the same component is required in MEA plant). In addition, a fan for the column heating/cooling must be adopted (called ESA fan).

The overall performance of the considered case, together with the MEA reference case and the NGCC without CO₂ capture are reported in Table 8. Significant penalties with respect to the MEA reference case can be noted. These are related to the electricity consumption for sorbent regeneration (up to 96 MW) as well fan consumptions (up to 106 MW). The overall net electric efficiency for the ESA process is 39.8% leading to an efficiency penalty of 19% which is twice the MEA one. The resulting CO₂ avoided and SPECCA are 89.9% and 9.05 MJ/kgCO₂ respectively. It must be outlined that a timing optimization for the heating and cooling should be carried out to evaluate thermodynamic advantages with fan consumptions. For example, increasing the heating/cooling timing will be beneficial for the energy penalties as well as adopting more complex cycle configurations. In addition, the ESA process is at early stage compared to MEA and higher sorbent capacities can significantly reduce the energy penalty.

In general, the sorbent regeneration duty is higher than MEA one and the higher energetic value of electricity with respect to condensing steam @4 bar leads to penalties around 3 times higher.

Table 5

	NGCC	MEA	ESA
N° of gas turbine	2	2	2
Gas Turbine [MW]	272.1	272.1	272.1
Steam Cycle Gross Power, [MW]	292.4	215.67	277.54
Steam Cycle auxiliaries, [MW]	-3.4	-3.4	-3.4
CO ₂ compressor, [MW]	-	-22.6	-26.6
Exhaust gas fans, [MW]	-	-15.0	-15.0
Aux. for heat rejection, [MW]	-3.7	-4.4	-4.1
ESA fan consumptions [MW]	-	-	-106.1
Chiller consumptions [MW]	-	-	-3.6
Electric consumption for sorbent regeneration [MW]	-	-	-96.4
Other auxiliaries [MW]	-	-4.6	-
Net Power Output, [MW]	829.5	709.9	566.7
Thermal Power Input _{LHV} , [MW]	1422.6	1422.6	1422.6
Net Electric Efficiency (LHV base), [%]	58.3	49.90	39.83
Emissions [gCO ₂ /kWh _{el}]	351.8	42.36	35.55
CO ₂ avoided, [%]	-	88.0	89.9
CO ₂ purity, [%]	-	100.0	95.1%
SPECCA (MJ _{LHV} /kgCO ₂)	-	3.36	9.05

5. Conclusions

The thermodynamic assessment of the ESA process when integrated to NGCC power plant was described in this work. The ESA process was modelled using Aspen Adsorption and integrating different heat sources for the sorbent

regeneration. A water removal section upstream the ESA process was considered to avoid the competitive water/CO₂ adsorption in the ESA unit. The efficiency penalty of the ESA technology is 20 percentage points with an overall efficiency of the integrated power plant below 40% and the CO₂ avoidance close to 90%. The energy penalty is significant because of electric regeneration and fan consumptions during the heating/cooling steps of the sorbent regeneration. The energetic value of electric power is about 5 times higher than low temperature heat used in competitive technologies (i.e. amine scrubbing). These results do not want to draw a line on ESA technology because this work represents the first tentative of simulating ESA using different heat sources for sorbent regeneration and the sorbent development is still at early phases, therefore significant improvements (i.e. lower efficiency penalties) are foreseen both for material and modelling point of view.

Acknowledgements

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