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Development of moving bed temperature swing adsorption (MBTSA) process for post-combustion CO₂ capture: Initial benchmarking in a NGCC context

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Abstract

A moving-bed temperature-swing adsorption (MBTSA) process has been evaluated for post-combustion CO₂ capture in a natural-gas combined cycle (NGCC) context using Zeolite 13X as adsorbent. The performance of the different sections of the reactor (adsorption, regeneration and heat exchange) were modelled in gPROMS using real equilibrium and kinetic adsorption data and typical heat transfer parameters. As a consequence of the internal heat transfer between the hot adsorbent powder leaving the regenerator with the cold powder entering the regenerator, a low specific heat requirement for regeneration of 2.3 GJ_{th}/ton CO₂ captured is estimated. When also including the electrical energy needed (also compression of CO₂) a total energy penalty of 6.5 %-points is obtained. For regeneration, flue gas at 222 °C was used for heating and it was assumed that the flue gas was heated after the power plant by using saturated steam condensing at 230°C. A major reduction in the heat requirement for the process can be gained if the heat required for regeneration is provided from more optimal integration with the steam cycle of the power plant.

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1. Introduction

The use of solid adsorbents is an alternative approach that may alleviate many of the problems connected to the liquid absorption processes: On a solid adsorbent the adsorption sites are spatially separated on a carrier, thus avoiding possible chemical degradation through site interaction. The number of adsorption sites is in most cases dependent on the surface area of the carrier, and often a linear relationship exists between the adsorption capacity of an adsorbent and its specific surface area. In addition, a good solid adsorbent will be chemically and physically stable at the operating conditions giving negligible loss of volatiles and good recyclability.

For post-combustion CO₂ capture, both pressure swing adsorption (PSA or VSA) and temperature swing adsorption (TSA) processes have been suggested. However, for post-combustion CO₂ capture in a natural gas fired power plant (NGCC) context, where the partial pressure of CO₂ is small (typically around 4 vol%), regeneration with temperature swing may be more appropriate [1]. In a TSA process, adsorption takes place at the lower temperature of the process, typically around 30-40°C. When the adsorbent is saturated, it is heated to the desorption temperature where CO₂ is released [2]. The amount of CO₂ released depends on the adsorbent employed and on the regeneration temperature used. The adsorbents used in a TSA process for post-combustion CO₂ capture should have a strong affinity (steep adsorption isotherms) to CO₂ at low partial pressures. The main advantage of this process is the utilization of heat as the major energy input of the process. Main disadvantage is related to the productivity of such units since temperature changes (heating and cooling) in large fixed-bed columns can take several hours. However, it has been previously shown that fast-cycle thermal swing processes result in lower energetic demand [3]. Finding the optimal conditions for adsorption and regeneration, it is possible to envisage a process that can remove CO₂ from flue gas stream and in a separate step, desorb it for further storage or utilization.

For conventional fixed bed adsorption processes based on either pressure swing or temperature swing mechanisms one would expect a potentially high pressure drop over the adsorbent bed in addition to the slow heat transfer. The moving bed temperature swing adsorption (MBTSA) concept is one way to overcome the pressure drop challenge. The first moving bed concept is the "Hypersorption" process suggested by Clyde Berg in the late 40-ties [4]. The process included a tower with an adsorption section where a low pressure drop is obtained by "flowing" the adsorbent powder through as quite open structured part of the reactor, and a stripping section where steam was used to remove the last desorbed amount. The process has been thoroughly described by Ruthven in his classic book on Adsorption processes [5].

Later, a slightly modified MBTSA process was suggested by Knaebel in which hot flue gas was used to indirectly heat the adsorbent during regeneration [6]. Indirect heating was necessary since Zeolite 5A, having high water affinity, was used as adsorbent. Recently, SRI has reported results from the development of MBTSA process development using direct heating with steam during regeneration with carbon based adsorbents [7]. Lately, also researchers from Kawasaki in Japan published results from a CO₂ capture test for moving-bed system, however, lacking detailed information about the process details and adsorbent used [8].

Here we present modelling results and benchmarking of a MBTSA process against a standard MEA solvent based capture process in a NGCC context [9]. For the MBTSA process we have chosen to use indirect heating of the powder during regeneration as suggested by Knaebel [6], using conservative assumptions on the heat transfer parameters and regeneration temperature needed.

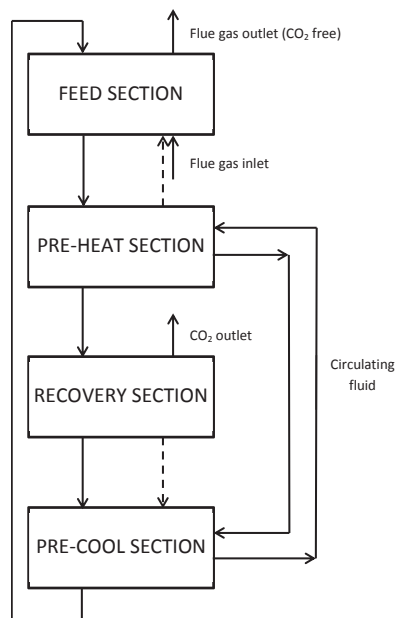


Figure 1. Simplified scheme of the necessary steps in the MBTSA technology for CO₂ capture.

2. Process considerations

The concept of the moving bed temperature swing adsorption (MBTSA) is based in a traditional cyclic adsorption process. Its main difference is that instead of arrangements of fixed beds that switch operation at given time, the system comprise different sections that operate in a continuous basis. A schematic presentation of the MBTSA process is shown in Figure 1.

The MBTSA process for CO₂ capture is thus composed by a feed section where the CO₂ molecules are stripped from the cold flue gas. In this section, the gas is fed counter-currently to the sold adsorbent in a similar manner as in a liquid scrubber (amine process for CO₂ capture). When the adsorbent is loaded with CO₂ it should be regenerated. In the MBTSA process, the regeneration is carried out using heat. Details on the process design and adsorbent to be used are given in Table 1:

Table 1. Summary of process details of the MBTSA process.

Feed section	Structured packing for distribution. Pressure drop assumed to be similar to liquids. Gas hold-up (porosity) equal to 0.8 (at least).
Pre-heater	Perpendicular tubes after the feed section. Utilization of heat-transfer fluid. Good contact between tubes and solid.
Recovery (regeneration)	Heat exchangers are parallel plates (gas-solid heat exchangers). Vacuum (0.95 bar) necessary to remove CO ₂ . Has also been used by Kim et al.[10].
Pre-cooler	Perpendicular tubes located after the heat exchanger. Use of closed circuit heat-transfer liquid. Can act to control solid velocity.
Cooler	More perpendicular tubes across the adsorbent. Cold water is used to speed-up cooling.
Conveyor belt	Not specified. Energy consumption calculated for mechanical belts.
Adsorbent	Zeolite 13X. Short adsorption bed. Tabulated equilibrium data is available [11].

3. Mathematical model of the MBTSA process

The mathematical model of the MBTSA process is based in a set of mass, energy and momentum mass balances in the different sections of the equipment. For simplicity, the equations used in the description of the different sections were the same, except for the momentum balance: the Ergun equation was used in the desorption sections, but cannot be employed in the adsorption section since the porosity is very high. In the adsorption section, the pressure drop was assumed to be 150 Pa/m. The mathematical model was solved using gPROMS (PSE, UK) or COMSOL Multiphysics (COMSOL AB, Sweden) where this is noted. The centered finite different method was used to discretize the equations. Due to the high velocities used and the large scale of the problem, oscillations were always present in the system. Over 800 elements were used to minimize the oscillations.

3.1. Results for the feed section

The modeling study intend to develop the MBTSA technology for the case of CO₂ capture from a gas-fired power plant. The operating conditions for the flue gas used for the study are shown in Table 2.

The properties of the adsorbent are based on the adsorption properties of the Zeolite 13X adsorbent [11]. For this adsorbent, the equilibrium loading of CO₂ at 303K is 1.83 mol/kg (at the chosen CO₂ partial pressure). Assuming that the system is isothermal, a mass balance can be made in the feed section as a starting point for integration of the equations. Such mass balance assumes isothermal performance and renders that a solid expenditure of 640 kg/s is necessary to capture all the existing CO₂.

The numerical simulations started using this value. However, the heat of adsorption of CO₂ is almost 50 kJ/mol, which is released in an adiabatic system. Although the partial pressure of CO₂ is low, the heat released is enough to

heat the adsorbent and thus reduce its adsorption loading. The flow of cold gas entering counter-currently to the adsorbent is not enough to cool down the adsorbent in a significant proportion. The higher temperature of the adsorbent significantly reduce the CO₂ loading to 0.68 mol/kg. Consequently, the necessary amount of adsorbent required to strip the CO₂ is much higher, around 1705 kg/s.

Table 2. Flue gas conditions used to model the MBTSA process

Feed flowrate	2431 Nm ³ /h (675, 2 m ³ /s)
CO ₂ molar fraction	0,043 (equivalent to 0.04% humid basis)
Temperature	303 K
Other gases	No water, other gases do not adsorb significantly.

The initial observation of the dynamic results is that the adsorption proceed very fast (no kinetic limitations within the Zeolite 13X pellets). Mass and heat profiles of the feed section are shown in Figure 2. The initial steepness in the CO₂ concentration is due to the fast cool-down of the solid produced by the cold flue gas, which is however not enough to cool down the solid to less than 330K. This initial heating of the adsorbent results in a reduced loading towards CO₂. However, the temperature of the adsorbent has increased over 30K without any energy used as input.

Several parameters were changed for the modeling. It was observed that the system is very sensitive to the total flow of adsorbent and in order to operate without CO₂ slip, the amount of adsorbent used has to be slightly higher than the minimum amount. However, if a large amount of adsorbent is used, the CO₂ loading per mass of adsorbent is smaller and thus this has a strong effect in the final CO₂ purity obtained (and of course in the energy spent).

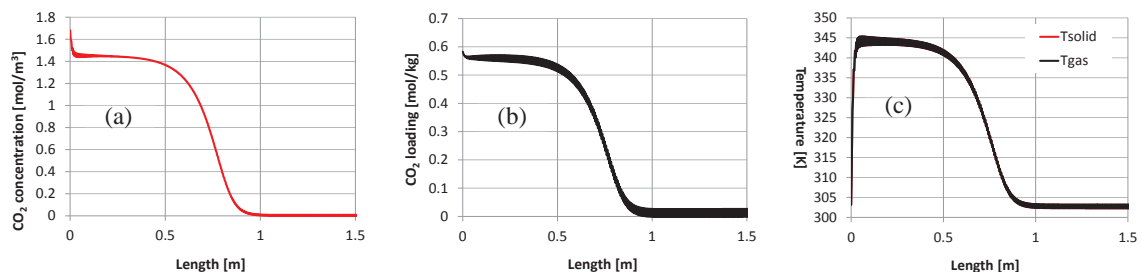


Figure 2. CO₂ concentration (a) and loading (b) in the feed section of the MBTSA unit for CO₂ capture. The temperature profile (c) is also shown.

The initial results have also confirmed that when the adsorbent is not diffusion limited, the adsorption bed length can be quite short.

3.2. Results from the regeneration sections

The performance of the heater is the most important one in the MBTSA unit, and is however the unit with less reported results. The design, heat transfer properties and final performance of the unit is not defined in previous publications and had to be assessed without any previous indicators of performance. We have chosen to use a heat exchanger composed by several parallel plates where steam is used to heat the solid. This was also chosen by Kim et al in their recent modelling work on the effect of integrated heat exchange in moving-bed adsorption process [12].

One important feature in the MBTSA concept is to exchange heat between the hot powder leaving the regenerator with the cold powder entering the regenerator. Kim et al showed that up to 54% of the heat needed for the regeneration can be provided by such heat exchange [12]. The modeling results from the pre-heater section show very interesting results: The solid that is entering at 338K suffers a nearly linear heating. The global heat exchange

is dominated by a relatively high heat transfer ($UA = 5000 \text{ W/K}$) idealized by a large heat area available from putting 1 inch diameter tubes for homogeneous heat transfer. At the very beginning of the pre-cooler section, a stream with a higher concentration of CO_2 comes back from the heat exchanger (gas with slightly gas density). Initially it was expected that such "heavy reflux" was a slip of CO_2 and will reduce the performance of the MBTSA. The observed results indicate exactly the opposite: A stream with some CO_2 (around 57%) results in extra adsorption of CO_2 in the adsorbent, further increasing the temperature of the solid. Since this adsorbent does not present kinetic limitations to diffusion, the adsorption is very fast and contributes to an additional increase of temperature of 25K, reducing further energy consumption. The modeling results of the pre-heater section are detailed in Figure 3.

The results from the pre-heater are linked to the temperature of the hot fluid coming from the pre-cooler. The pre-cooler step is also having similar performance of the pre-heater (almost linear heat transfer) without the effect of enhanced temperature changes due to adsorption/desorption.

The main uncertainty in the initial design of the MBTSA concept relies in the heat transfer coefficients to be used in the heat-exchanger in the regeneration section. From initial simulations, it was clear that if the flue gas was going to be used to heat the solid in a parallel plate heat exchanger, the heat transfer coefficient has to be increased: the heat capacity of hot gas is around 4 times smaller than the heat capacity obtained using steam. In order to assess the heat transfer parameters, 2D simulations were carried out using COMSOL Multiphysics. The simulations involve the utilization of flaps in the parallel plates in order to increase the heat transfer, without imposing severe pressure drop in the flue gas. The results indicate that a $U = 80 \text{ W/m}^2\text{K}$ can be used for the design. The expected pressure drop in the gas phase that is quite small (less than 70 Pa/m). Using the determined heat transfer coefficient, it was estimated that the size of the heat exchanger should be around 20 meters.

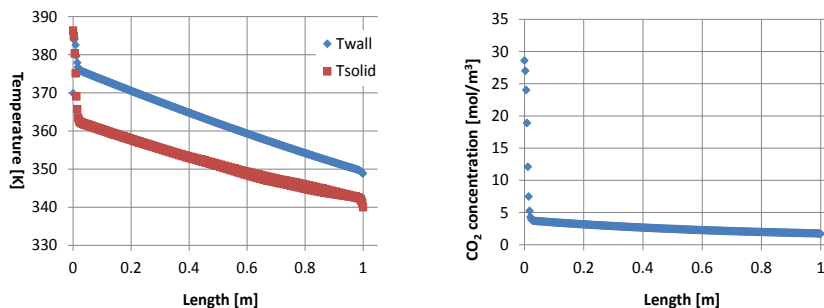


Figure 3. Temperature and CO_2 concentration in the pre-heater zone of the MBTSA unit. Note that the solid adsorbent flows from right to left in the figure.

After the pre-cooler section, the solid is at a temperature of 365K and should be further cooled down to 303K before re-entering the adsorption section. No transient simulations were done in the cooler section since several configurations can be used, but assuming that cold water at 293K is available and that $UA = 10000 \text{ W/K}$ can be used, a length of 2 meters is expected for a cooler section. The overall picture of the MBTSA for CO_2 capture from gas-fired power plants obtained from these simulations is shown in Figure 4. Although 1D simulations were carried out, it should be advisable to divide the unit into five or six towers instead of a large "thick" tower.

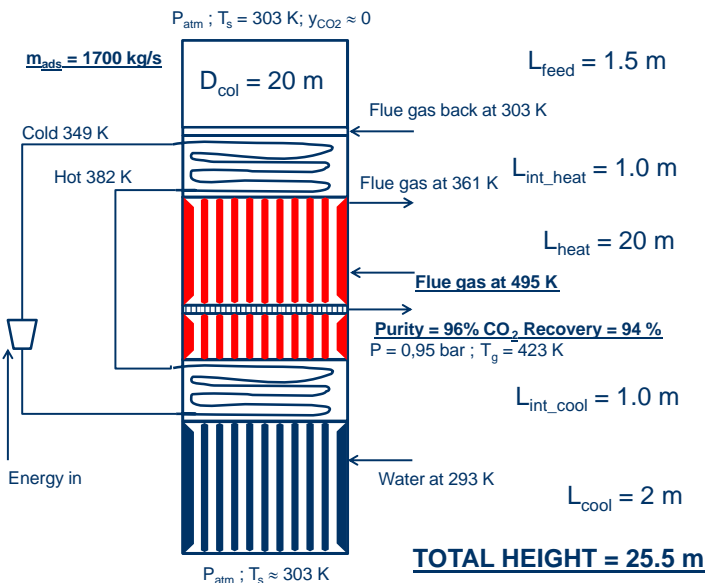


Figure 4. Estimated dimensions of the MBTSA process for CO₂ capture from gas-fired power plants.

The major source of energy consumption of the unit comes from utilization of hot flue gas to make the desorption. This was estimated as:

$$Q_h = \dot{m} \cdot C_p \cdot (T_{in} - T_{out})$$

Here, \dot{m} is the flue gas flow-rate and C_p is the average heat capacity. By an average C_p value of 1.08 kJ/kg C (obtained from Hysys). The estimated losses here were estimated to be 114 MW_{th}.

Assuming a pressure drop of 150 Pa/m of pressure drop, the blower consumption was estimated to be 2.5 MW_{el}.

With a CO₂ is extracted pressure of 0.95 bar, the compression energy is estimated to 16,4 MW_{el}.

The energy expected to be used in the conveyor belt is: 0.8 MW_{el} (estimated using the potential energy change with 50% efficiency).

4. MBTSA benchmarking against reference case

In Table 3 the energy requirement for the MBTSA and the reference case is summarized. The data for the reference case is taken from the European Benchmark Task Force work carried out through four different EU FP6 projects to make it consistent [9]. The main gain for the MBTSA process is in the heat requirement for regeneration which is around 76% of the reference case at the chosen conditions, while the resulting total electricity requirement is similar for the two cases.

In the present study 222°C flue gas from the power plant is used to heat the regenerator. In state-of-the-art power plants, flue gas is available at lower temperatures meaning that some electricity will not be produced (negative penalty). If steam should be used to produce this heat, the steam quality must be higher: Saturated steam, which condenses at 230 °C has a pressure of around 30 bar. According to Bolland and Undrum [13] the ratio of incremental power reduction to incremental heat output is approximately 0.32. This means that in order to provide 114 MW_{th} energy, this requires an electric power duty of 36.5 MW_{el}. For the reference plant, which is totally integrated with the power plant, low pressure steam is available at the LP/IP crossover valve at around 4 bar, which makes it suitable for the reboiler conditions (saturated steam at 4 bar condenses slightly below 140°C) The corresponding ratio of incremental power reduction to incremental heat output is approximately 0.22 for this steam quality and thus the heat requirement of 149 MW_{th} implies a loss in electric power production of 31.5 MW_{el}.

However, it should also be noticed that in any future applications of MBTSA the process would be more integrated with the power plant which will lower the energy needs even further.

Table 3: Comparison of heat requirement, MBTSA and reference MEA based processes for the 500 MW NGCC case (heat provided by steam from power plant cycle)

	NGCC without capture ^b	NGCC MBTSA	NGCC EBTf 430 MW MEA reference. ^b
Heat requirement (MW _{th})	-	114	149
Specific Heat requirement (GJ _{th} /tonne CO ₂ captured)	-	2.3	4.0
Loss in el. production due to heat (MW _{el})	-	36.5	31.5
Blower (MW _{el})	-	2.5	7.4
CO ₂ compression (MW _{el})	-	16.4	13
Pumps (MW _{el})	-	1.0 ^a	3.6
Total el. Requirement (MW _{el})	-	56.4	55.5
Total efficiency (%)	58.0	51.5	49.3
Net electrical output (MW _{el})	500.0	443.6	388.3

^a Set arbitrary to 1.0, it should be low. ^b Take from ref [9].

5. Conclusions

We have compared MEA solvent based CO₂ capture technology (TRL 7-8) with MBTSA technology which is more on the proof-of-concept level (TRL 3-4). Such a comparison is difficult since many assumptions have to be done concerning the most immature technology. For the MBTSA case, the largest uncertainties are connected to the heat transfer sections for adsorbent regeneration and CO₂ withdrawal. This is the part that has to be studied (experimentally) in order to come up with more accurate numbers.

The specific heat requirements for the MBTSA process and the MEA reference process are estimated to 2.3 and 4.0 GJ_{th}/ton CO₂ captured (see Table 3). Even when knowing that MEA processes further have developed during the last years now reaching specific energy requirements down to around 3.0 GJ_{th}/ton CO₂ captured [14], this study clearly indicates that the MBTSA might have a potential for significant improvements as a post combustion CO₂ capture process from NG fired power plants.

For the MBTSA the heat required for regeneration generated by steam is more realistic than using hot flue gas. Using steam would make the MBTSA process a real retrofit post-combustion process. To get down the energy penalty further would need a reduction in regeneration temperature needed and/or an increase in the working capacity leading to a lowering of the sensible heat needed. Thus, adsorbents having lower adsorption enthalpy and higher working capacity coupled with improved design and efficiency of the heat exchange unit would further bring down the energy penalty of the process.

SRI claim an energy penalty of only 3.8 %-points for their process based on the use of activated carbon adsorbent and flue gas from coal fired power plant [7]. We believe the main reason for this low penalty compared to our value of 6.5 %-points partly is a consequence of lower adsorption enthalpy of CO₂ on activated carbon as compared to Zeolite 13X (around 27 vs. 45 kJ/mole, respectively) and much lower temperatures are needed for regeneration (no information on regeneration temperature has been given). For the NG case, due to the low adsorption energy with activated carbons, very low working capacities will be obtained, giving huge reactor systems if not rapid cycles can be used (< 2-3 minutes). But, certainly, the most positive by using activated carbon adsorbents is that direct heating with steam might be possible avoiding inefficient indirect heating which is necessary when using Zeolite base adsorbents as in the Knaebel MBTSA concept.

When it comes to process footprint, the diameter of a "single unit" of MBTSA is estimated to 20 meters. The unit

has to be equipped with a conveyor bucket (or another device) to transport the powder from the exit back up to the entrance of the adsorption section. However, it would be advisable to use more than one MBTSA unit in the plant. Assuming that the MBTSA unit is split into 5 smaller units, they should have a diameter of 9 meters. If all these units are close to each other (which should be desirable), the approximate area occupied by the MBTSA capture plant is approximately 600 m² (20m x 30m) thinking that some space will be required to make slight vacuum but without taking into account the CO₂ compression for storage.

The present study has shown that there are strong dependencies of the adsorbent properties on the process performance, especially on the potential CO₂ purity and capture rate. There is an integrated relationship between parameters such as heat of adsorption, cyclic capacity and gas diffusion kinetics on the MBTSA performance, and the intuitively good adsorbents might not always give the best process! Finding the optimal adsorbent should also be a task for the future. The effect of impurities should then also be looked into from an experimental side.

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