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Experimental Results of Pressure Swing Adsorption (PSA) for Pre-combustion CO_2 Capture with Metal Organic Frameworks

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Abstract

Vacuum Pressure Swing Adsorption (VPSA) has already proved that it can be used for capture of CO_2 from the tail gas of the PSA process for hydrogen purification. The demo operated in Port Arthur by Air Products has already captured more than 1 million metric tons of CO_2.

In this work we are evaluating the utilization of a formulated metal-organic framework (UTSA-16) for capture of CO_2 from steam-methane reforming off-gases with the aim of selectively capture CO_2, while allowing hydrogen and other components to pass through it, aiming to remove the requirement of vacuum for CO_2 capture in this application. We have measured quaternary breakthrough curves with 76% H_2, 17% CO_2, 3% CH_4 and 4% CO simulating the off-gas of a typical steam-methane reformer. We have also simulated the results using a mathematical model that constitutes the basis for design and improvement of the PSA unit.

1. Introduction

One of the largest demo plants for CO_2 capture is installed in Port Arthur, United States and uses an adsorption process as a selective method to capture bulk CO_2 from a steam-methane reforming (SMR) off-gas [1]. This demo unit has already captured over 1 million tons of CO_2 without reported problems demonstrating that adsorption is a mature technique that should be considered for CO_2 capture technologies.

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Specifically, the technology used is a dual Pressure Swing Adsorption (PSA). The first PSA unit is a state-of-the-art technology for purification of hydrogen allowing hydrogen purity of >99.9% [2]. The tail gas from the first PSA is available at low pressure and is constituted by a mixture of some lost hydrogen and all unconverted methane, carbon oxides (CO and CO_2) and water. This stream is normally burned to recover calorific power to the SMR reactor. In this plant, it is routed to a second PSA unit that operates under vacuum and for this reason is denoted as VPSA. From this unit is possible to recover purified CO_2 on one end and all other gases on the other.

The idea of such dual PSA technology was to retrofit a CO_2 capture unit in an existing refinery. The necessity of using vacuum is due to the availability of the tail gas containing CO_2 at low pressure. However, if the purification section can be designed for a new plant, a different approach can be adopted. Since the SMR off-gas is available at relatively high pressures, it is possible to capture CO_2 first without the need of using vacuum [3]. The gas exiting this unit can be treated by a normal PSA unit for H_2 purification, with a reduced amount of CO_2 to process. The difference between both process schemes is shown in Figure 1.
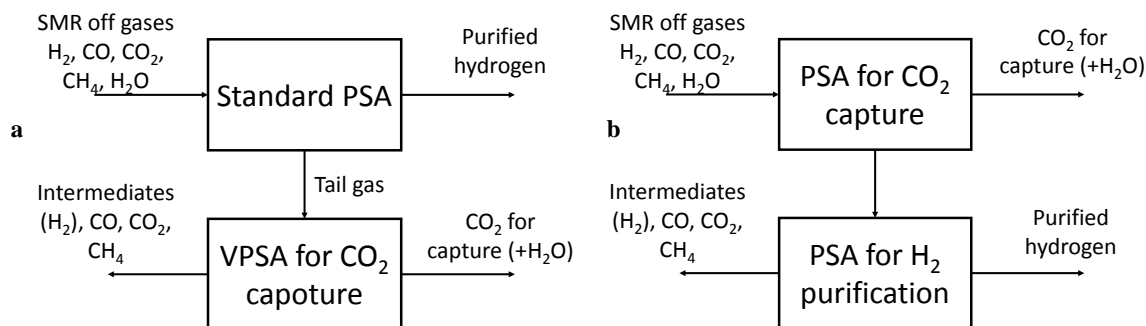

Figure 1. (a) PSA + CO_2 capture VPSA unit retrofitted to Port Arthur; (b) dual PSA scheme for CO_2 capture and hydrogen purification.

For pre-combustion schemes, the amount of intermediates (CO and CH_4) is smaller and then, there is even the possibility of using only one PSA unit, provided that some CO_2 can be allowed to the hydrogen stream for power generation. In any case, the design of the PSA for CO_2 capture is similar in both cases.

The partial pressure of CO_2 in SMR off gases or in pre-combustion schemes is relatively high in the order of several atmospheres. This is a very important specification in order to select the right adsorbent material. For example, zeolites adsorb large quantities of carbon dioxide [4-6] but its desorption requires very low vacuum or temperature. Activated carbons are the adsorbents already used in PSA unit for CO_2 removal in the hydrogen purification PSA and thus are important candidates [7]. Despite its low density and selectivity, the adsorbent cost is a very positive indicator of this material.

On the other hand, novel materials can offer desired properties of selectivity, capacity and cost. Metal-organic frameworks are relatively new materials where combinations of organic linkers and inorganic metals are grouped. Due to this combination, there are basically thousands of possible structures that can be synthesized. Indeed, the number of publications of MOF structures is very high. Unfortunately, many of these materials is not stable in air or water. Additionally, many of them are synthesized with very expensive linkers and thus they should be proper for other applications than CO_2 capture. Finally, the number of MOFs that were formulated without damaging their high surface area and CO_2 selectivity is very reduced.

One MOF material termed UTSA-16 [8] can be a very interesting candidate for this application. It has a relatively high adsorption capacity for CO_2, with not so steep isotherms and a good selectivity towards other gases. The linker of this material is citric acid (not so expensive linker). Moreover, we have already demonstrated that is possible to scale-up this material and also to formulate it with minimal decay in surface area and CO_2 adsorption capacity [9].

Furthermore, and differently from many MOF materials, has a density comparable to zeolites (and higher than activated carbons). This means that when isotherms normally reported in mol/kg are converted to mol/m^3, the value

is still attractive and very competitive. We have already measured fundamental properties of single gas adsorption and diffusion on pellets of this material and used this data to simulate the behavior of a H_2 PSA unit [10].

In this work we have extended our previous study by measuring adsorption breakthrough curves of the quaternary mixture of gases exiting the SMR process (dry stream). The measurements were done using more than 100 grams of formulated adsorbent aiming to understand if the properties measured from single components can be really extended to real systems and also to understand if the UTSA-16 formulation procedure has been homogeneous for larger samples. The results were also used to calibrate heat and mass transfer parameters of a mathematical model that is used to determine proper PSA scheduling for CO_2 capture.

2. Experimental

Adsorption isotherms of the formulated (extrudates) UTSA-16 are shown in Figure 2. The CO_2 adsorption capacity is much larger than the ones of other gases. The steepness of the CO_2 isotherm is intermediate between an activated carbon and a zeolite.
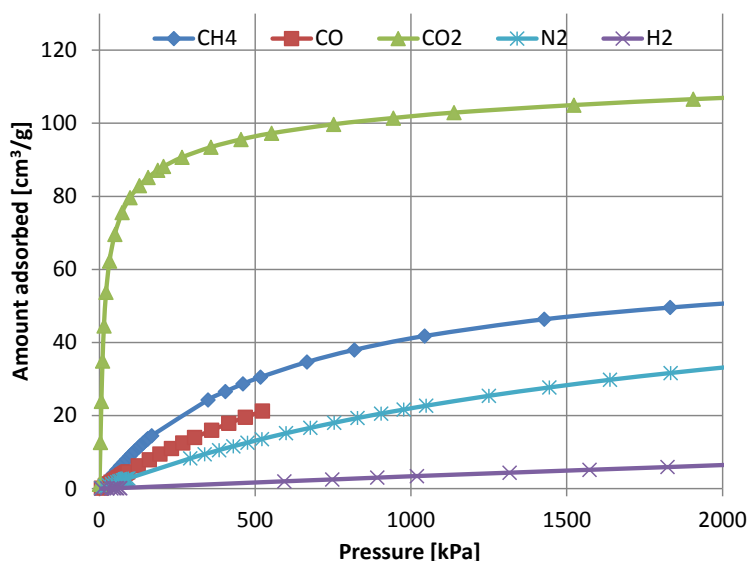

Figure 2. Adsorption equilibrium isotherms of CH_4, CO, CO_2, N_2 and H_2 on UTSA-16 extrudates at 298K.

Quaternary breakthrough curves of a gas mixture of 76% H_2, 17% CO_2, 3% CH_4 and 4% CO were measured in a 4-column PSA unit available in SINTEF. The gas was provided as a ready mixture from Yara, Norway. Experiments were performed at a total pressure of 16 bars and a temperature of 305 K. Variable flowrates were used in order to understand the effect of dispersion and diffusion in the final shape of the breakthrough curves. The operating conditions used for making the experiments are listed in Table 1.

Table 1. Experimental conditions for quaternary breakthrough curves.

Condition	Value
Temperature [K]	305
Pressure [bar]	16
Composition [%]	76% H_2, 17% CO_2, 3% CH_4 and 4% CO
Flowrate [SLPM]	0.5, 1.0, 1.5, 2.0
Column length [m]	0.56
Column diameter [m]	0.0212 m
Adsorbent mass [g]	107.9

3. Theoretical

The isotherms were fitted with the Dual Langmuir model and the parameters are available in literature [10]. The single component isotherms were used in the theoretical expression for prediction of the multicomponent behavior.

The breakthrough curves were modelled with an existing fixed bed model that has been validated for many systems [11,12]. For the sake of brevity, we will not include the model in this publication since is already published in many different publications. This 2D model (time and axial coordinate) consist of seven partial differential equations (PDEs) corresponding to mass balance in the gas, macropores and micropores of the adsorbent, energy balance in the gas, the solid and the column wall and the momentum balance, simplified by the Ergun equation. These PDEs are coupled with the ideal gas and isotherm equations. The mathematical model was solved in gPROMS (PSE, UK) using the centered finite element method with at least 100 elements on the axial axis.

4. Results and Discussion

Breakthrough curves measured at four different flowrates are displayed in Figures 3-6. In the images we show the molar fraction of the different gases exiting the column as well as the temperature in four different places in the column.
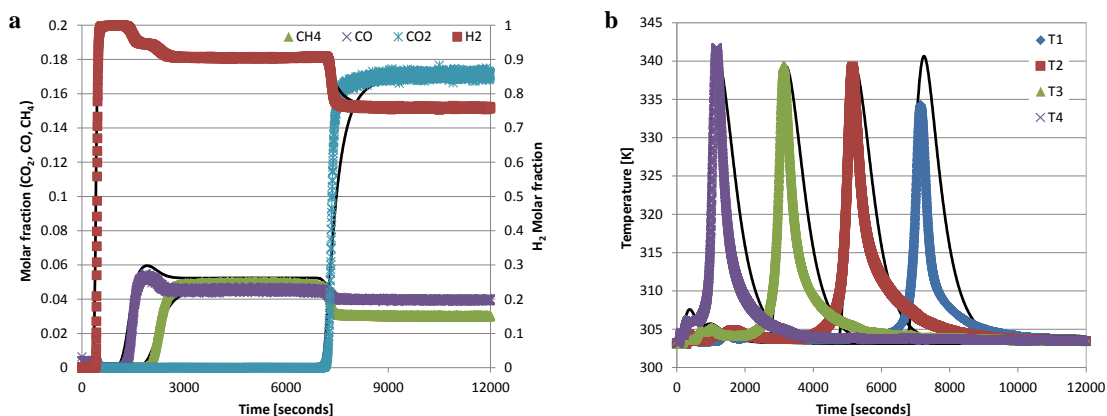

Figure 3. Quaternary breakthrough curve of H_2, CO, CO_2 and CH_4 in UTSA-16 extrudates at 16 bar and 305K with a total flowrate of 0.5 SLPM. (a) molar flowrate of gases exiting the column; (b) temperature in 4 thermocuples in the column. Solid lines are the results obtained from the mathematical model.
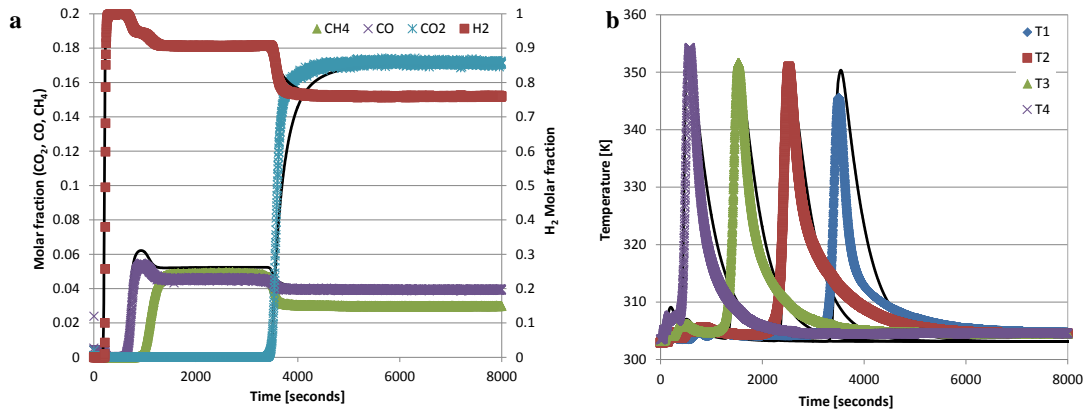
Figure 4. Quaternary breakthrough curve of H_2, CO, CO_2 and CH_4 in UTSA-16 extrudates at 16 bar and 305K with a total flowrate of 1.0 SLPM. (a) molar flowrate of gases exiting the column; (b) temperature in 4 thermocuples in the column.
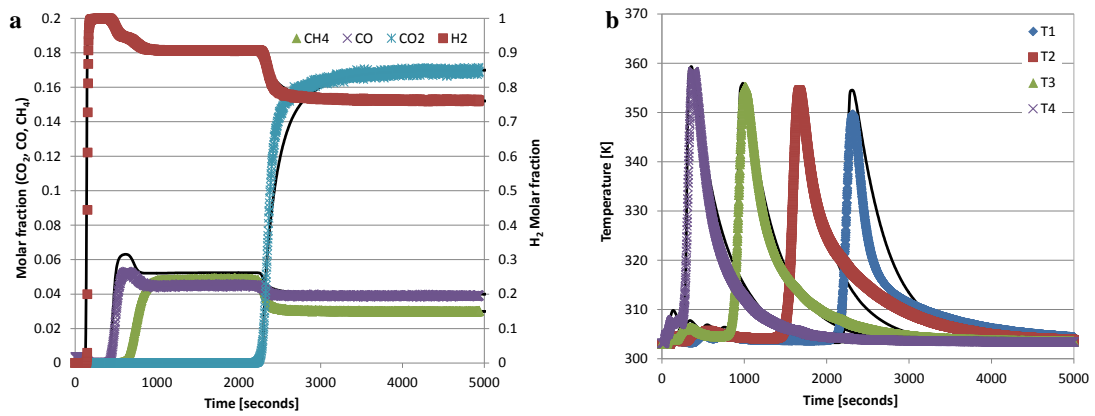

Figure 5. Quaternary breakthrough curve of H_2, CO, CO_2 and CH_4 in UTSA-16 extrudates at 16 bar and 305K with a total flowrate of 1.5 SLPM. (a) molar flowrate of gases exiting the column; (b) temperature in 4 thermocuples in the column.
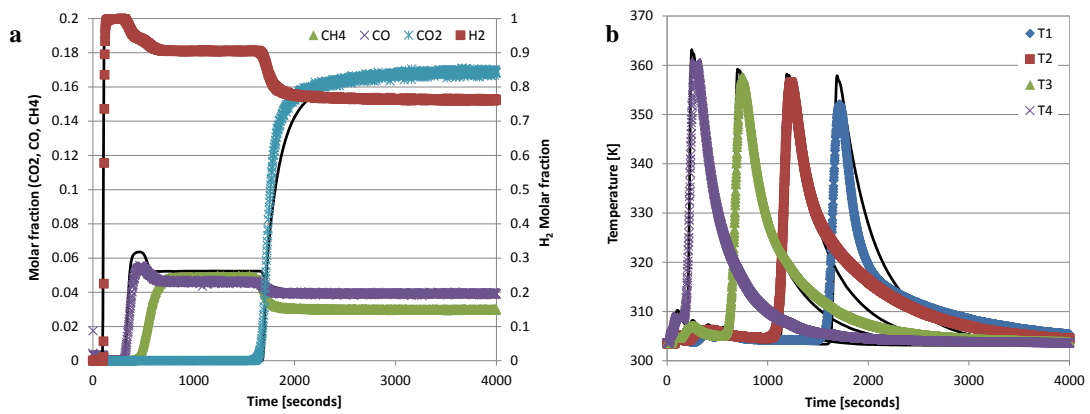

Figure 6. Quaternary breakthrough curve of H_2, CO, CO_2 and CH_4 in UTSA-16 extrudates at 16 bar and 305K with a total flowrate of 2.0 SLPM. (a) molar flowrate of gases exiting the column; (b) temperature in 4 thermocuples in the column.

The results indicate that carbon dioxide is indeed much more adsorbed than the other gases, even in the quaternary mixture. Also it can be observed that the heat generation due to adsorption of carbon dioxide is considerable with temperature increase in the column between 35 K for low flowrate and 55K for higher flowrates. The main reason of the temperature increase when the flowrate increases is due to a faster heat generation while the transfer of heat is mostly limited by natural convection from the column wall to the oven surroundings.

The important result here is that it is possible to describe the system with the mathematical model used that will allow us to design a PSA unit for CO_2 capture, in principle, not requiring vacuum for CO_2 desorption.

4. Conclusions

Adsorption of multicomponent gas mixtures has been studied in formulated metal-organic framework UTSA-16. In this material, CO_2 is much more adsorbed than the other gases, although is possible to remove it just by reducing its partial pressure (not requiring thermal treatments). The capacity of this material towards CO is also high when compared with zeolites. For this reason, this material can be used for simultaneous production of hydrogen and capture of carbon dioxide.

Adsorption processes have the advantage of being able to be retrofitted to hydrogen production plants where there is one existing unit for hydrogen purification. However, in new plants, a more efficient redesign of the separation schemes can result in important savings of energy.

Acknowledgements

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