Cyclic Adsorption Processes

Cryogenic Adsorption

This work focused on cryo-adsorptive processes for purifying hydrogen and natural gas for energy applications by removing impurities like CO_2 at low temperatures. Therefore, the adsorption equilibria of the gases involved in the hydrogen and natural gas purification were measured on UiO66(Zr)_(COOH)2 metal-organic framework (MOF) agglomerates across various temperatures (223 to 273 K) and pressures (up to 60 bar). The adsorption capacity of this MOF material follows the order CO_2, CH_4, N_2, CO, and H_2. On the other hand, a pressure-temperature swing adsorption (PTSA) process, packed with binderless 13X zeolite beads, was designed, simulated, and optimized to produce high-purity methane (> 99.995 %) for liquefied natural gas transport at an extensive range of temperature (206 to 473 K) and pressure (up to 70 bar). The possibility of this separation process to substitute an existing multicolumn cryogenic distillation technology was evaluated. The simulation results revealed that even though a complete replacement of the distillation process, which allows the decrease of the CO_2 concentration from 50.6 % to 50 ppm, might not be feasible, its last two columns can be replaced by a cryo-PTSA technology capable of reducing the CO_2 content from 10.6 % to 46 ppm using a lower power consumption (3.6 MW) despite a minor CH_4 recovery being achieved (33.16 %).

Introduction

Although extensive work on gas adsorption in various porous solids at ambient temperatures or above is available, there is a lack of data in the open literature for extreme conditions (*i.e.*, cryogenic temperatures and high pressures). Hydrogen storage and natural gas upgrade are some industrial applications where cryo-adsorptive methods are being reviewed. The main impurity contained in natural gas and hydrogen to be removed by cryo-adsorptive processes is typically CO_2.

Hydrogen has been studied as a clean energy source for transportation because of its high energy density and carbon-free combustion products. Various studies have been done on hydrogen storage in metal-organic frameworks (MOFs) for further implementation in fuel cell technologies because hydrogen is particularly hard to liquefy or compress, given its low boiling point. Using MOFs makes it possible to retain hydrogen at 77 K and at a pressure of less than 100 bar, which requires much less energy than traditional cryogenic hydrogen tanks. On the other hand, natural gas emerged as a cleaner energy source compared to other petroleum-derivate fuels, capable of fulfilling society's energy demands. Cryogenic distillation is one of the technologies available to reduce the CO_2 content in natural gas streams until the specifications required for its liquefaction and transport (< 50 ppm). Cyclic adsorptive processes, particularly pressure temperature swing adsorption (PTSA), are considered a viable alternative due to lower energy requirements.

One of the main scopes of this work was to assess the adsorption properties of the UiO-66-(COOH)2 MOF concerning the gases involved in the industrial hydrogen/natural gas purification processes over a broad temperature and pressure range. Therefore, single adsorption equilibrium isotherms of O_2, CH_4, CO, N_2, and H_2 on UiO66(Zr)_(COOH)2 agglomerates were measured by the gravimetric method in the temperature range of 223 to 273K and up to 60 bar.

Another important goal of this work was to develop an industrial-scale PTSA technology capable of producing a CH_4

stream with a purity higher than 99.995 %. This process would replace an existing cryogenic distillation process reported by Berstad et al., where a natural gas stream with an initial CO_2 concentration of 50.6 % is treated in three sequential columns at cryogenic conditions. The thermodynamic properties were estimated with the GERG-2008 equation of state (EoS) using the REFPROP software package and then fitted to surface equations (SEs) that were implemented in the mathematical model as a way to reduce the CPU time during the process optimization. The SEs are especially useful in this study since the PTSA simulations are performed using high-temperature changes in the bed and large operating pressures, and, consequently, it can not be assumed that the mixture behaves as an ideal gas.

Current Development

Adsorption properties of the UiO-66-(COOH)2 MOF for H_2/CH_4 purification applications

In this work, the single adsorption equilibria of CO_2, CH_4, CO, N_2, and H_2 were assessed at temperatures between 223 and 373 K and pressures up to 60 bar for the UiO-66(Zr)_(COOH)2 MOF, shaped as small granules. This adsorbent material is selective for CO_2, presenting the highest adsorption capacities among all of the tested gases (see Fig.1). The adsorption capacity then follows the order CH_4, CO, N_2, and H_2. Indeed, the very low capacity toward CO is a remarkable feature of this material. The adsorption equilibrium model that best represented the experimental data is the dual-site Sips (DSS) model. The CO_2/CH_4 ideal selectivity is 44 at 220 K, 40 bar, and feed composition of 99 % of CH_4 and 1 % of CO_2. The isosteric heats of adsorption mirror the adsorption capacity, that is, CO_2 has an adsorption heat between 40 and 20 kJ·mol⁻¹, and CH_4 has a adsorption heat between 25 and 10 kJ·mol⁻¹. N_2 and CO have the lowest adsorption heats of about 20–10 and 15–10 kJ·mol⁻¹, respectively. Thus, the UiO-66(Zr)_(COOH)2 MOF presents a high potential for relevant industrial processes such as the natural gas/biogas upgrade, hydrogen production, and syngas composition tuning.
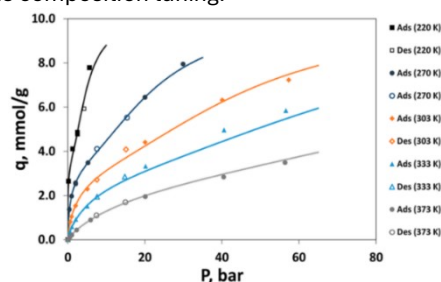

Fig 1. CO2 adsorption equilibrium isotherms on UiO-66(Zr)_(COOH)2.

Optimization of a cryo-PTSA for CH_4 purification

This work presented two case studies for the simulation of a PTSA process at low temperatures that would allow the substitution of the columns of the cryogenic distillation plant described in Berstad *et al*. The intent is to produce a CH_4 product with a CO_2 content lower than 50 ppm using binderless 13X zeolite beads as the adsorbent. For both cases, it was considered that the adsorbent regeneration was done with part of the CH_4 product at 473 K and 5 bar. The single adsorption equilibrium data of CO_2 and CH_4 and corresponding fitting by the Dual Site Langmuir (DSL) model used in this study are reported by Moreira et al. The extended DSL model was used to

predict the multicomponent adsorption equilibria. To obtain accurate simulation results while minimizing computational time, the density, viscosity, and thermal conductivity were calculated by SEs, which were obtained by fitting the values given by GERG-2008 EoS. It was concluded that the SEs values were in good agreement with the GERG-2008 EoS values for mixtures with a CO_2 molar fraction up to 55 %. Besides, the compressibility factor and heat capacities at constant volume and pressure values were obtained using the SEs developed by Moreira *et al*. All process simulations were performed in the gPROMS® ModelBuilder using the orthogonal collocation in finite elements (OCFEM) as the numerical method.

Case study 1 corresponds to two parallel and equal PTSA units fed with a stream of 50.6 % CO_2 at 313 K and 70 bar designed to replace the entire cryogenic distillation process. The breakthrough curve results for the heating step show that the concentration and temperature waves do not behave as expected. That is, instead of observing a continuous decrease in the CO_2 content until 50 ppm with the increase in the bed temperature, a concentration front of 50.6 % of CO_2, at 313 K, should exit first, followed by a higher amount of desorbed CO_2, caused by the increase of the bed temperature, and then by a concentration front of 50 ppm of CO_2, at 473 K, that corresponds to the feed conditions. Therefore, the entire replacement of the cryogenic distillation process by PTSA units might not be feasible and, if possible, will be hard to achieve.

Afterward, a second case study was considered, in which two parallel and equal PTSA units were designed to substitute the last two columns of the cryogenic distillation process, treating a feed stream with 10.6 % CO_2 at 206 K and 40 bar. For this case, the breakthrough curve of the heating step exhibits the behavior expected. Thus, it was possible to proceed with the next step, designing and simulating the PTSA cycle. The proposed PTSA cycle (Fig. 2) comprises the following steps: adsorption (pressurization plus feed), pressure equalization-depressurization, blowdown, heating, and pressure equalization-pressurization. The process simulations were carried out considering the extension of the cycle to a six-column unit to allow continuous feed consumption. The duration of each pressure equalization step was set to be equal to the adsorption step, and the duration of the blowdown plus heating step was considered to be three times the adsorption step. The total cycle time is 31800 s (8.8 h).
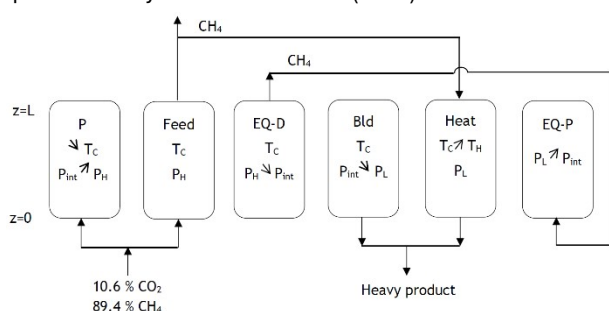
Fig 2. Proposed PTSA cycle to replace the last two distillation columns.

The CO_2 molar fraction and temperature values obtained in this case study at the column outlet in the cyclic steady state are shown in Fig. 3. As can be seen, practically all CO_2 is adsorbed during the adsorption time, resulting in the production of a CH_4 stream with purity of 99.9954 %, which fulfills the required specification for liquified natural gas transport. During the blowdown and heating steps, the adsorbent is regenerated by decreasing the total pressure and

increasing the bed temperature, respectively, which results in the desorption of CO_2, which exits the column. So, the simulation results of the PTSA process revealed that it is possible to obtain a CH_4 product with a CO_2 content lower than 50 ppm but with a lower CH_4 recovery when compared to the distillation process (33.16 % against 96.4 %). Also, a CH_4 productivity of 2.49 $mol^{-1} \cdot kg^{-1} \cdot h^{-1}$ and a power consumption of 3.6 MW were achieved.
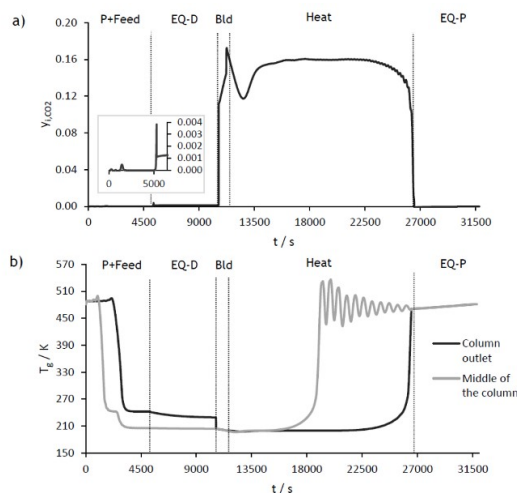
Fig 3. PTSA cycle simulation results for the replacement of the last two distillation columns: a) CO2 molar fraction at the column outlet; b) gas temperature at the outlet and middle of the column.

Future Perspectives

For future work, it was proposed to exploit further the possibility of using the UiO-66-(COOH)₂ MOF in industrial-relevant cryo-adsorptive processes, for example, in future continuing studies of the abovementioned cryo-PTSA process for high-pure CH_4 production to see if its performance can be improved using an adsorbent with a lower CO_2 adsorption heat. The results related to the study of this PTSA also showed that this process is a solid starting point for developing an advanced PTSA cycle that could allow the complete replacement of the cryogenic distillation plant with high efficiency, but further steps must be taken before that can happen, namely, adding other steps to the PTSA cycle besides exchanging the adsorbent.

Related Sustainable Development Goals

Outputs

Master Dissertations
[1] Mariana Carolina Nunes Bessa, Design of Pressure Temperature Swing Adsorption process for methane upgrade, MIEQ, FEUP, 2020

Selected Publications
[1] M.A. Moreira *et al.*, J Chem Eng Data 64, 4724-4732 (2019)

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