Nitrogen rejection by dual reflux pressure swing adsorption using ETS-4

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Abstract

The need for cost-efficient technologies for natural gas processing coupled with low environmental impact is becoming increasingly important due to the growing production of natural gas from subquality gas wells. The removal of nitrogen from such gas sources is especially challenging because of the similar properties of nitrogen and methane. This work studies the separation of an 85 mol% CH₄ + 15 mol% N₂ gas mixture by dual reflux pressure swing adsorption (DR PSA) using a N₂-selective Engelhard titanosilicate type 4, ETS-4, as adsorbent via numerical simulations. Key DR PSA process parameters, such as the heavy product to feed flow ratio, the light reflux flow rate, and the feed step duration, were investigated to maximize the separation performance. In addition, productivity and energy requirements of the four DR PSA cycle configurations, namely PL-A, PH-A, PL-B and PH-B, were determined. The goal was to evaluate the capabilities of the nitrogen-selective ETS-4 in conjunction with the DR PSA process aiming to produce two useful product streams meeting pipeline specifications (> 93 mol% CH₄) and environmental regulations (> 99 % N₂). It was found that ETS-4 can easily upgrade the CH₄ content of the gas mixture to pipeline specifications at high recovery but cannot meet the environmental regulations. The gas enriched in N₂ needs to be further processed or can be used for electricity production via post-combustion.

Keywords: DR PSA; Methane Emission; Methane Upgrading; Nitrogen Rejection; ETS-4

1. Introduction

The role of natural gas in the global energy mix has been becoming increasingly important: its share was 23 %, close to coal's share of 26 % in 2019.¹ The constantly growing need of natural gas has incentivised the exploitation of small-scale and sub-quality reservoirs once deemed as economically unattractive.² The high nitrogen content in these gas resources is problematic because it decreases sales gas heating value, increases transportation cost and poses a risk when transported as liquefied natural gas (LNG), due to stratification and rollover issues.^{2,3} The most common separation methodology for methane and nitrogen mixtures is cryogenic distillation, which is economically viable only for large-scale production (> 25 MMscfd), due to high investment and operational costs.⁴ For smaller scales (< 15 MMscfd), pressure swing adsorption (PSA) has been studied as a low-cost alternative along with other technologies^{4,5}, such as membranes.^{6,7} The selection of a suitable adsorbent material with the required capacity and selectivity is crucial for the efficiency of any process based on adsorption and its economic feasibility.⁸

In general, the removal of the minor component (N_2 in this case) of a gas mixture is considered to be more energy efficient. Most commercially available materials with high adsorption equilibrium capacities are CH_4 -selective as outlined in the screening for N_2 rejection materials by Rufford et al.⁴ Equilibrium N_2 -selective materials are not available at industrial scale although there are reports about MOFs showing such properties at a lab scale.^{9,10} Kinetic/size selective N_2 materials are available at industrial scales and have been used for some N_2/CH_4 separation applications.^{7,11-14} Molecular carbon sieves (MSC) are kinetically N_2 selective adsorbents, because they show much faster N_2 rates of adsorption compared to CH_4 .^{4,12} Fatehi et al.¹⁵ performed experimental two-column PSA experiments using MSC enriching a 60 mol% and 92 mol% CH_4 feed gas up to 75 mol% and 96 mol%, respectively. The separation performance suffered from low CH_4 recovery. Effendy et al.¹⁶ numerically studied the N_2 rejection from natural gas by pressure vacuum swing adsorption (PVSA) using a Takeda molecular sieve. A 9-step PVSA process could enrich an 80 mol% CH_4 + 20 mol% N_2 mixture to pipeline specifications with 99 % CH_4 recovery. Xiao et al.¹⁷ first reported the use of a kinetically selective adsorbent in combination with a 4-step dual reflux pressure swing adsorption (DR PSA) process. A feed containing 75 mol% CH_4 + 25 mol% N_2 was separated using N_2 -selective molecular sieve MSC-3K 172. Both experiments and numerical simulations were conducted and 90 mol% CH_4 purity and 90 % CH_4 recovery were achieved.

Engelhard titanium silicate (ETS-4), which was patented by Kuznicki et al. in 1990¹⁸, is a size selective N_2 adsorbent. ETS-4 has been used in commercial PSA process for natural gas purification¹⁹⁻²¹, and its ion-exchanged derivatives have been widely studied to improve thermal stability and process performance.^{11,13,20,22,23} Jayaraman et al.²⁴ tested different cation exchanged clinoptilolites (N_2 -

selective), and compared their performance to that of Sr-ETS-4 by simulating a 5-step PSA process using a bed with 2 m length and 0.2 m diameter. The feed mixture contained 85 mol% CH₄ and 15 mol% N₂. Up to 97 mol% CH₄ product purity were achieved with a CH₄ recovery of 53 % for the Sr-ETS-4. Higher recoveries up to 80 % were possible by sacrificing CH₄ purity, which was reduced to 93 mol% CH₄. Bhadra et al.²⁵ compared carbon molecular sieves with barium and strontium exchanged ETS-4 at different dehydration temperatures to separate a 90 mol% CH₄ +10 mol% N₂ mixture using a kinetic model. Different parameters such as the pressurization time or the low and high pressure were investigated using a bed with 0.5 m in length and 0.038 m in diameter. The PSA simulations revealed that the ion-exchanged ETS-4 adsorbents were superior to carbon molecular sieves that barium exchanged ETS-4 achieved the highest separation performance with > 96 mol% CH₄ purity and approximately 75 % CH₄ recovery.

Figure 1: Half-cycle of the DR PSA process showing the feed/purge and pressurization/blowdown step. The combination of feed to low (PL) or high pressure bed (PH) as well as pressure swing with either heavy (A) or light gas (B) leads to the four cycle configurations PL-A, PH-A, PL-B and PH-B.

In this work, we propose to use ETS-4 in a dual-reflux pressure swing adsorption process (DR PSA) for the separation of N₂ and CH₄ to explore its feasibility in upgrading sub-quality natural gas. The DR PSA process has been investigated by several research groups due to its advantage of being theoretically capable of producing two pure product streams, which is a limitation of conventional PSA systems.²⁶⁻
²⁸ Figure 1 schematically depicts a half-cycle of the DR PSA process and its four basic cycle configurations (identified by Kearns et al.²⁸). The DR PSA configurations are combinations of the feed inlet column, which is either the high-pressure (PH) or low-pressure (PL) bed, and using either heavy (A) or light (B) gas for pressure swing leading to PH-A, PH-B, PL-A and PL-B. Both numerical models and experimental data have been reported in the open literature for different gas mixtures, such as CH₄ + N₂, CO₂ + N₂ and N₂ + O₂.^{17,26-40} Our group reported both numerical simulations and experimental results of different CH₄ + N₂ mixture separations by DR PSA.^{17,33,35,38-41} Most recently, we investigated

N₂ rejection from sub-quality natural gas (85 mol% CH₄ + 15 mol% N₂) by DR PSA using a novel CH₄-selective adsorbent and achieved 93 mol% CH₄ purity and 99 % CH₄ recovery. In addition, the purity of the N₂ rich product was > 99 mol% N₂ allowing to vent it to the atmosphere, which is beneficial in cases where combustion is impractical.³⁸ The combination of DR PSA process with ETS-4 as an adsorbent has never been reported before.

2. Simulation Details

2.1 Model description and parameters

The numerical DR PSA model was developed using Aspen Adsorption with the multi-bed approach to simulate the experimental set-up in our lab. The agreement between the model and experimental data was within the uncertainties of the measured quantities.^{17,39} Details of the model can be found in previous publications.^{17,33,38,39}

Figure 2 depicts the schematic structure of the model. Two adsorption blocks were used to represent each of the two adsorption beds to allow intermediate feed to the columns and change of feed locations. “Comp_bot” was used to model the compressor for heavy reflux in both A- and B-configurations and for pressure swing in A-configurations. “Comp_top” was only used for pressure swing in B-configurations. Heavy (T_H) and light (T_L) products holdup vessels were employed to dampen oscillations of the product compositions and to provide sufficient gas for refluxes. “MFC_LR” was used to specify the light reflux flow rate, and “MFC_HP” was operated as a heavy product flow controller which in turn allows the control of the heavy product to feed ratio. The specifications of the boundary streams “Feed”, “Light Product” and “Heavy Product” are summarized in Table 1.

Table 1: Details on the boundary conditions of the process.

Boundary stream	T [K]	p [bar]	Flow
Feed	293.15	20.1	Specified via MFC (1.25 SLPM during FE/PU)
Light Product	293.15	1.0	Specified via valve coefficient (4.5×10^{-9} kmol/s/bar)
Heavy Product	293.15	1.0	Specified via MFC (depending on H/F ratio)

The model used finite difference method to solve partial differential equations (PDEs) governing the adsorption beds. Each of the half-beds (i.e. Bed1_top, Bed1_bot, Bed2_top, and Bed2_bot) was discretized by the first order upwind differencing scheme 1 (UDS1) with 40 nodes, which is an appropriate node number that provided a good balance between simulation accuracy and computational time, as can be inferred from Figure S1. Other key numerical settings are the same as those used by Zhang et al.³⁹ and are also provided in Table S1. The relative change in solid temperature and loading between two consecutive cycles was used as cyclic steady state (CSS) criterion and

specified to be $< 10^{-5}$. The computational time to reach CSS ranged from 5 h to 10 h using a multi-core machine with an Intel i7 chip (2.7 GHz) and with 8 GB RAM.

Figure 2: Simplified process flow diagram of the DR PSA process, shading of valves indicates the feed/purge step of the PL-A cycle (white: open, black: closed).

The column and process parameters that were held constant in this work are summarized in Table 2. The feed position was fixed at the exact middle of the adsorption bed in this work because preliminary simulations (Figure S2) showed that the feed location had limited impact on the separation performance within the tested range, which was reflected by a previous study⁴² for a system with a different adsorbent. The low-pressure was chosen to account for safety concerns (approximately atmospheric to reduce the possibility of oxygen entering the system) and the high-pressure was set comparatively high to 20 bar due to the low N_2 capacity of ETS-4, with the goal of increasing the cycle's productivity. Note that in this work, axial dispersion was neglected and plug flow was assumed due to numerical issues as discussed in the next section. A polytropic compressor model was employed, which includes temperature dependent heat capacities for both CH_4 and N_2 . The polytropic model is the same as previously reported³⁸ and the governing equations and constants for heat capacity calculations can be found in the supplementary Table S2 and Table S3, respectively.

Only one compression stage was assumed for compression, which may lead to elevated outlet temperatures at high pressure ratios. For an industrial application, several compression stages with intercooling are possibly required. In this model, the high outlet temperatures did not influence the adsorption process because the tanks (downstream the compressors) providing refluxes or being used during pressure swing were modelled to have the same temperature as the environment due to their large size and the high heat transfer coefficient between the vessel and the environment.

Table 2: Parameters of the adsorption bed for the DR PSA model³⁹ and operational parameters held constant in this work.

Bed parameters	Value	Operational parameters	Value
Total length [m]	0.98	Low pressure [bar]	1.0
Internal diameter [m]	0.035	High pressure [bar]	20.0
Wall thickness [m]	0.0016	Feed flow rate [SLPM]	1.25
Heat transfer coefficient [$\text{W m}^{-2} \text{K}^{-1}$]	10.0	Feed location [-]	0.5
Wall thermal conductivity [$\text{W m}^{-1} \text{K}^{-1}$]	16.0		
Wall specific heat capacity [$\text{J kg}^{-1} \text{K}^{-1}$]	500.0		
Adsorbent Details			
Inter-particle voidage	0.39		
Intra-particle voidage	0.31		
Bulk solid density [kg m^{-3}]	983		
Particle radius [m]	0.0015		

2.2 Material balance

Previous publications using the Aspen Adsorption software platform for DR PSA simulations reported material balance errors^{30,33,38-40} of up to several percent, which seems unusually high for numerical simulations. Zhang et al.³⁹ suggested a correction method to offset the error by reconciling the erroneous material balance until certain time during the simulation that the error was negligibly small. Enforcing the closure of the material balances by reconciliation may not reflect the actual separation performance well. In this work, we found that the component balance errors were extremely high when using adsorbent ETS-4 (up to 50 % for the CH_4 balance), which cannot be tolerated or corrected reliably. It was found that the error was caused by axial dispersion during the pressure transfer step, which becomes infinitively high when the pressure stabilizes, and the gas velocity approaches zero. It is unclear whether this is a mathematical artifact or a bug in the program. Therefore, plug flow was assumed in this work, which is a valid assumption due to the typically high values of the axial Peclet number of these systems.⁴³ In addition, the impact of the axial dispersion on the separation performance is expected to be minor due to the high aspect ratio of the column (length/diameter = 28). The average mass balance errors were $[100 \% * (\text{out-in})/\text{out}]$: -0.005 % overall, -0.02 % for CH_4 and 0.1 % for N_2 for all simulations.

3. Results and Discussion

3.1 Adsorbent details

The measurement of N_2 and CH_4 adsorption on ETS-4 adsorbent pellets (2 mm) was performed by Saudi Aramco's Research & Development Center. The measured amount of CH_4 was within the

experimental uncertainty due to the limited access for CH₄ into the purposely sized pores of ETS-4^{18,23}, therefore the CH₄ adsorption was assumed to be zero in this work. To justify this assumption, the CH₄ uptake data is presented in the Supplementary Information (Figure S1) showing that the CH₄ adsorption is both very low and extremely slow and therefore insignificant for this process. The N₂ adsorption amount at different pressure and temperature was obtained and the data were fitted with the Dual-Site Langmuir (DSL) isotherm equation, as shown by Equation 1.⁴⁴

$$w_{eq} = \frac{m_{0,1} \cdot b_{0,1} \cdot \exp\left(\frac{-\Delta H_1}{R \cdot T}\right) \cdot p}{1 + b_{0,1} \cdot \exp\left(\frac{-\Delta H_1}{R \cdot T}\right) \cdot p} + \frac{m_{0,2} \cdot b_{0,2} \cdot \exp\left(\frac{-\Delta H_2}{R \cdot T}\right) \cdot p}{1 + b_{0,2} \cdot \exp\left(\frac{-\Delta H_2}{R \cdot T}\right) \cdot p} \quad (1)$$

Here w_{eq} is the equilibrium adsorption capacity, $m_{0,i}$ is the saturation capacity parameter, $b_{0,i}$ is the pre-exponential factor, ΔH_i is the adsorption energy, i denotes adsorption sites 1 and 2, T is the temperature of the adsorbent, R is the ideal gas constant and p is the pressure of N₂. The regression parameters $m_{0,i}$, $b_{0,i}$ and ΔH_i are shown in Table 3.

Table 3: Dual-Site Langmuir isotherm parameters for ETS-4.

Parameter	Value	Parameter	Value
$m_{0,1}$ [mol kg ⁻¹]	3.74×10^{-1}	$m_{0,2}$ [mol kg ⁻¹]	2.08×10^{-1}
$b_{0,1}$ [bar ⁻¹]	1.80×10^{-7}	$b_{0,2}$ [bar ⁻¹]	2.02×10^{-6}
ΔH_1 [J mol ⁻¹]	3.24×10^4	ΔH_2 [J mol ⁻¹]	3.31×10^4

Kinetic data were not experimentally determined but sourced from literature. Delgado et al.²² measured the diffusion time constant (D_c/r_c^2) of ETS-4 by breakthrough experiments. The values for the diffusion time constant were used to calculate the mass transfer coefficient k_s for the linear driving force (LDF) model used in this work, as shown in Equation 2. The corresponding numerical values for k_s were 0.75 and 0.06 for N₂ and CH₄, respectively.

$$k_s = \frac{\Omega \cdot D_c}{r_c^2} \quad (2)$$

With $\Omega = 15$ for spherical particles.⁸

3.2 Separation & process performance

3.2.1 Separation boundary as a function of heavy product to feed ratio

The main advantage of the DR PSA process over conventional PSA is that its performance is not restricted by the nominal pressure ratio in the adsorbent beds because the theoretically achievable product purity limits in DR PSA are only determined by the system material balance.^{27,45,46} The heavy and light product purities (y_H and y_L , respectively) boundary curves as a function of the heavy product to feed ratio (H/F) are shown in Figure 3a. For the composition (15 mol% N₂ + 85 mol% CH₄) of feed gas in this work, the separation boundary for the heavy product was determined by assuming $y_L = 0$

(when $H/F > 0.15$) and that for the light product was obtained by setting $y_H = 1$ (when $H/F < 0.15$). Complete separation of N_2 and CH_4 is only possible at $H/F = 0.15$, however, the separation can be shifted either towards increased heavy product N_2 mole fraction (y_H) by decreasing H/F or towards increased light product CH_4 mole fraction ($1 - y_L$) by increasing H/F .

The effect of H/F on the product compositions of the four DR PSA configurations is shown in Figure 3a. It is clear from the figure that the performance trends of the DR PSA configurations follow that of the separation boundary, both y_H and y_L decrease with the increase of H/F . The y_L traces the separation boundary for light product more closely than y_H does for heavy product, which indicates that nitrogen could be easily removed from the mixture, thanks to the N_2 selective feature of the adsorbent. Stripping N_2 from the gas mixture is best achieved by PL-A cycle reaching 4.3 mol% N_2 in the light product at $H/F = 0.15$, which is equivalent to 95.7 mol% CH_4 in the stream, satisfying regional pipeline CH_4 specifications (> 93 mol% CH_4). The enrichment of N_2 to a required high concentration (> 99 mol% N_2) is challenging. The maximum N_2 mole fraction achieved at the simulation conditions for the heavy product was 0.773, by the PL-A cycle at low H/F values. The reason for the lower than desired N_2 concentration in the heavy product is due to the low N_2 adsorption capacity of the adsorbent that the desorbed N_2 in the low pressure purge step is diluted by the non-adsorbing CH_4 in the bed void spaces. In addition, it has to be noted that this heavy product stream can neither be directly emitted to the environment since it still contains 0.227 mole fraction of CH_4 nor be burned for power production because the insufficient content of CH_4 for combustion. Further optimization of operating conditions is required to either emit the stream directly or make this stream combustible.

Figure 3b shows the relationship between CH_4 recovery and CH_4 purity. Both A-cycles show linear trends achieving approximately 95 mol% CH_4 purity and 95 % CH_4 recovery with PL-A cycle being slightly superior. This result is comparable with the separation performance reported by Jayaraman et al.⁴⁷ using ETS-4, but they used more adsorption beds. In their PSA configuration, they employed a 4-bed 5-step high-pressure PSA cycle, which achieved approximately 96 mol% CH_4 purity and 96 % recovery operating at 7 atm high and 1 atm low pressure. Both B-cycles perform comparatively poorly, which is in agreement with results reported recently³⁸ for a similar separation using CH_4 -selective adsorbents. Although both CH_4 purity and CH_4 recovery of A-cycles are satisfying industrial needs, the purity of the N_2 -rich stream still needs to be improved to meet the desired environmental specification.

The effect of H/F was studied with feed step duration $t_F = 60$ s and the light reflux flow rate $R_L = 0.5$ SLPM, which were estimated according to previously published results³⁸ aiming to avoid breakthrough or exceeding bed's adsorption capacity. Therefore, these operating conditions may not have produced the optimal separations and improvement on separation performance may be possible. Thus, the

variation of t_F and R_L , both significant parameters in DR PSA cycles, will be discussed in the following section.

Figure 3: (a) Heavy (y_H : hollow symbols) and light (y_L : filled symbols) product N_2 mole fraction at varying H/F with material balance constraints (dashed lines) and (b) CH_4 recovery versus CH_4 purity at constant $t_F = 60$ s and $R_L = 0.5$ SLPM.

3.2.2 Effect of t_F and R_L

The feed step time t_F and the light reflux flow rate R_L are important operational parameters in DR PSA systems. Longer t_F can lead to breakthrough of the heavy component N_2 into the light product compromising the purity, whereas shorter t_F reduces the productivity of the process. Similarly, a higher than proper R_L would lower the heavy product purity while a lower R_L would reduce the recovery of the heavy component. Therefore, the effect of the feed step time t_F and the light reflux to feed ratio R_L/F on N_2 and CH_4 product purities y_H and $(1 - y_L)$ were studied. An H/F ratio of 0.10 rather than $H/F = 0.15$ was selected to shift the separation towards the enriched heavy product end, aiming to produce a N_2 stream that meets specification. The results of t_F and R_L studies are shown in Figure 4 and Figure 5 for A- and B-cycles, respectively.

Figure 4a and Figure 4b show that a maximum separation performance can be observed for both PH-A and PL-A cycle, which indicates that an optimal R_L/F can be determined to deliver maximum product purities $(1 - y_L)$ and y_H . PL-A achieves the highest performance of 92.1 mol% CH_4 and 78.4 mol% N_2 at $R_L/F = 1.2$ and $t_F = 30$ s. In this case, the increase of R_L/F leads to improved separation performance until a maximum is reached, indicating that the bed had been used to full capacity. This maximum was shifted towards lower R_L/F with increasing t_F because the higher amount of gas entering the bed at prolonged t_F made higher usage of the bed's capacity and therefore leaving less capacity for the internal reflux flows. Consequently, the separation performance is decreasing with increasing t_F .

Figure 4: Effect of light reflux flow rate to feed ratio (R_L/F) and feed step time (t_F) on the separation performance of (a) the light product CH_4 mole fraction $(1 - y_L)$ and (b) the heavy product N_2 mole fraction y_H for both A-configurations at constant $H/F = 0.10$.

The separation performance of B-cycles in terms of CH_4 and N_2 product purities is shown in Figure 5a and Figure 5b, respectively. The trends for the light product $(1 - y_L)$ are very similar to the ones observed for the heavy product y_H . The maximum achievable separation performance is achieved by the PH-B cycle at $R_L/F = 0.8$ and $t_F = 60$ s, which reaches 90.1 % CH_4 and 60.7 % N_2 in the light and heavy product, respectively. The performance is lower compared to A-cycles, especially the enrichment of N_2 due to the use of light gas for pressure swing. The trends for PL-B are similar to the

ones of the A-cycles, although a clear maximum is not detectable. It is straightforward to understand the decreasing trend of y_H with t_F for PL-B configurations that the N_2 purity in the heavy product is more diluted by the dominant non-adsorbing CH_4 in the feed and in the light reflux with longer t_F , considering the heavy product is drawn directly from the low-pressure column (flow directions according to Figure 1). Therefore, from the mass balance point of view, the N_2 purity (y_L) in the light product increases and that in turn results in a decreasing trend for $(1 - y_L)$. Meanwhile, from the mechanistic perspective, the decreasing of $(1 - y_L)$ with t_F is due to the outweighing of N_2 desorption over N_2 adsorption in the high-pressure column caused by the increased CH_4 purity in the heavy reflux stream. A contrary $(1 - y_L)$ trend of the PH-B configuration to the other configurations is observed, where the product purities increase with increasing t_F . This is because CH_4 in the pressure reversal step (by light component) penetrates to the lower part of the high pressure column that higher t_F initially compresses the CH_4 concentration front towards the top of the column before the N_2 in the heavy reflux eventually breaks through the top. The composition of the heavy product y_H is also positively affected due to improved purge effect of the light reflux during the desorption step.

Figure 5: Effect of light reflux flow rate to feed ratio (R_L/F) and feed step time t_F on the separation performance of (a) the light product CH_4 mole fraction $(1 - y_L)$ and (b) the heavy product N_2 mole fraction y_H for both B-configurations at constant $H/F = 0.10$.

3.2.3 Productivity and cycle work

Next to product purities and recovery, the productivity in terms of CH₄ produced is an important parameter to evaluate the process performance. It describes the amount of product produced per time and per unit mass of adsorbent. The productivity Z_P is defined as:

$$Z_P = \frac{(1-y_L) \cdot L \cdot t_F}{(t_F + t_P) \cdot m_{ads}} \quad (3)$$

Here L is the light product flow rate, t_P is the duration of the pressurization/blowdown step and m_{ads} is the mass of the adsorbent in the adsorption column.

Figure 6 shows the productivity Z_P as a function of the required cycle power per mole feed gas. The power per mole of feed gas was calculated as follows: the power used during the Pressurisation/Blowdown and Feed/Purge steps in the cycle was divided by the overall amount of feed gas processed in one cycle. In the Pressurisation/Blowdown step, the inlet pressure to the polytropic compressor model varied (from 20 bar to 1 bar), but the outlet pressure was constant at 20 bar. In the Feed/Purge step, the compressor inlet pressure was 1 bar and outlet pressure was 20 bar. Each point corresponds to the optimum separation performance determined in Figure 4 and Figure 5 for each cycle configuration at the three different feed step times. The trends are similar for all configurations and show that the productivity increases with decreasing power. This positive trend comes at the cost of reduced product purities attributed to the high t_F to achieve high Z_P and the low R_L to achieve low energy requirements. For instance, the highest product purities of 92.1 mol% CH₄ in the light and 78.4 mol% N₂ in the heavy product achieved by the PL-A cycle comes at the price of high energy requirements of 65.5 kJ/mol at a comparatively low productivity of 0.91 mol/h/kg. The PH-B cycle only requiring 9.1 kJ/mol compression energy at a productivity of 1.79 mol/h/kg is able to separate the feed mixture into a 90.0 mol% CH₄ light and 60.4 mol% N₂ heavy product stream. As a result, there is a strong trade-off between product purities and bed productivity as well as cycle power that needs to be considered in the process design.

Figure 6: Bed productivity as function of the compression power required per cycle and per mole processed feed gas with varying t_F and R_L/F at maximum product purities and at constant $H/F = 0.10$ for each cycle.

3.3 Solid loading on the adsorbent

Numerical simulations allow to access parameters that are difficult to determine experimentally, such as the loading of the adsorbed gas on the adsorbent. Figure 7 shows the evolution of the adsorbed amount of N_2 (w) as a ratio to the equilibrium capacity of N_2 (w_{eq}) over the time of a cycle at CSS. Trends for the PH-A and PL-A cycles are similar as shown in Figure 7a and Figure 7b. The N_2 loading in the lower parts of the low-pressure column decreases during the initial desorption step, but still remains high (> 0.6). At the top end of the low-pressure column ($z = 1$), the N_2 loading decreases significantly due to the purging effect of the light reflux pushing the N_2 towards the bottom end ($z = 0$). The slightly lower loading ratio of PL-A cycle compared to PH-A is caused by the feed gas, rich in CH_4 , entering at $z = 0.5$ that leads to additional purging of N_2 . In the pressure reversal step, the low-pressure bed experiences pressurization from the bottom end. The loading of N_2 on the adsorbent in the lower part of the bed increases progressively; however, the adsorption front does not reach the top end, which therefore remains at low N_2 loading, which is essential for the stripping performance of the process. Then in the now pressurized column, the N_2 loading ratio at $z = 1$ increases from 0.10 to 0.80 indicating partial breakthrough of the heavy component with the lower part of the bed being close to saturation leading to a decrease of the product purity. Finally, the high-pressure column is depressurized, and the pressure decrease causes desorption of N_2 and a decrease of the loading ratio, which stabilizes after the initial steep pressure drop.

The PL-B and PH-B cycles are shown in Figure 7c and Figure 7d, respectively. During the FE/PU step of both cycles, the N_2 loading decreases significantly due to the low pressure and therefore desorption especially at the top end ($z = 1$), which is in contact with the purge flow. The N_2 loading ratio does not drop below 0.2, indicating that the light reflux flow does not provide a strong purging effect. The B-cycles show an unexpected increase of the N_2 loading ratio at the bottom end of the bed at the beginning of the FE/PU step, which is caused by the light reflux pushing N_2 , which accumulated in the middle section of the bed during the previous blowdown step, towards $z = 0$. The N_2 loading decreases after the accumulated gas exits the bed, with the decrease of the PL-B cycle being steeper due to the higher reflux flow rate at maximized conditions as well as the purging effect of the feed gas entering the low pressure column. During the pressurization of both B-cycles, the N_2 loading at $z = 1$ increases, whereas it decreases in the lower sections of the column reaching an equilibrium. This means that the top end of the bed is contaminated with heavy component leading to a poor separation performance. The reason behind this is that heavy component N_2 is entrained from the column undergoing blowdown and is transferred during the pressurization step. As a result, the top end of the bed is spilled with N_2 leading to a lower CH_4 purity of the light product. In the following adsorption step, the N_2 loading increases at $z = 0$, where the heavy reflux enters the bed and is stripped from its N_2 content

when propagating through the column. For PH-B cycle, the increase of N_2 loading is slightly lower compared to PL-B cycle because of the feed gas entering the high-pressure bed at $z = 0.5$ containing 85 mol% light component. This will cause a purge effect when propagating from $z = 0.5$ to $z = 1$. The gas enriched in CH_4 appears to have a similar composition as the middle sections of the bed due to the constant loading profiles at $z = 0.35$ to $z = 0.65$. At the top end of the bed, this gas is exposed to the adsorbent that was spilled with N_2 in the previous pressurization step. This leads to a decrease of the N_2 loading at $z = 1$ but also to increased N_2 content in the light product that is not desirable. In the blowdown step, the N_2 loading is expected to decrease due to the pressure drop and therefore affinity to desorb. The B-cycles exhibit an increase of N_2 in the upper part of the column from $z = 0.35$ to $z = 1$. The reason behind this is that the pressure decrease causes N_2 desorption, which is mainly accumulated at $z = 0$, and the desorbed N_2 propagates from the bottom to the top of the bed due to the flow direction of B-cycles transferring gas through the top end during pressure swing steps. Therefore, the desorbed N_2 spreads over the whole bed during the blowdown step not leading to a clearly defined adsorption front. Overall, the N_2 loading profiles help to understand why A-cycles achieve a superior separation performance compared to B-cycles.

Figure 7: N_2 loading on the adsorbent during the different steps of a DR PSA cycle (FE/PU, PR and BD step) at four different locations throughout the adsorption column for (a) PL-A, (b) PH-A, (c) PL-B and (d) PH-B cycle at maximum separation performance conditions.

4. Conclusions

The potential of using N_2 -selective titanosilicate ETS-4 in DR PSA processes for N_2 rejection was investigated with an 85 mol% CH_4 + 15 mol% N_2 gas mixture. The influence of key DR PSA parameters, H/F ratio, feed step time and light reflux flow rate, was studied for PL-A, PH-A, PL-B and PH-B configurations. The H/F ratio allows shifting the separation performance towards N_2 stripping or enrichment, while the optimum feed step time is a compromise between productivity and separation performance, and the light reflux flowrate is used to identify the optimum product purities. The different separation performances of each configuration, especially between A- and B-cycles, were explained by analysing the solid loading on the adsorbent at different locations in the bed over time. The PL-A cycle was identified to perform best under the tested conditions, achieving 95 mol% CH_4 purity and 95 % CH_4 recovery at $H/F = 0.15$. The N_2 -enriched product stream still contained 23 mol% CH_4 , which does not meet environmental regulations. Even shifting H/F towards increased enrichment, approaching the theoretical mass balance boundary, is not sufficient to meet environmental regulations (< 1 mol% CH_4). The reason behind the difficulty to enrich N_2 to a very high purity is that the light component CH_4 is not adsorbed and accumulates in the voids, which dilutes the N_2 product when pushed out. Decreasing the void fractions by means of higher packing densities may improve the N_2 enrichment. Similar PSA processes using other versions of ETS-4 found in literature achieved similar separation performances. To achieve the desired product specifications in this work, N_2 -selective ETS-4 appears to be not suitable due to the requirement of high enrichment of the heavy component. However, the process is useful for CH_4 upgrading if the N_2 -rich product is combusted for energy regeneration instead of simply being considered as waste. Our group³⁸ previously showed that

the separation task of this work can be achieved by using a novel CH₄-selective material, namely ionic liquid zeolite ILZ, exhibiting a CH₄/N₂ selectivity of 4.8, which is twice of that what a commercial activated carbon has. In addition, the power consumption is significantly lower compared to this work due to the lower pressure ratio. This is attributed to the higher adsorption capacity of the material and therefore, the high pressure was only 5.0 bar to provide sufficient adsorption capacity, which is also the reason for the productivity of that material being twice than that of ETS-4.

Acknowledgements

This research was supported by the ARC Training Centre for LNG Futures (IC150100019). RW was in receipt of an Australian Government Research Training Program Scholarship at The University of Western Australia during this research.

Supporting Information

The following are included in the supporting information: numerical solver details, compressor model equations, experimental data, and additional numerical results.

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Abstract Graphic