Accepted Manuscript

Nitrogen rejection from methane using dual-reflux pressure swing adsorption with a kinetically-selective adsorbent

Gongkui Xiao, Thomas L. Saleman, Yuan Zou, Gang Li, Eric F. May

PII: S1385-8947(19)30951-9
DOI: <https://doi.org/10.1016/j.cej.2019.04.166>
Reference: CEJ 21586

To appear in: *Chemical Engineering Journal*

Received Date: 8 February 2019
Revised Date: 23 April 2019
Accepted Date: 24 April 2019

Please cite this article as: G. Xiao, T.L. Saleman, Y. Zou, G. Li, E.F. May, Nitrogen rejection from methane using dual-reflux pressure swing adsorption with a kinetically-selective adsorbent, *Chemical Engineering Journal* (2019), doi: <https://doi.org/10.1016/j.cej.2019.04.166>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Nitrogen rejection from methane using dual-reflux pressure swing adsorption with a kinetically-selective adsorbent

Gongkui Xiao, Thomas L. Saleman, Yuan Zou, Gang Li, Eric F. May*

ARC Training Centre for LNG Futures, Fluid Science & Resources Division, The University of Western Australia, 35 Stirling Highway, Perth WA 6009, Australia

*Corresponding author: eric.may@uwa.edu.au

Abstract

A dual-reflux pressure swing adsorption (DR PSA) processes using a kinetically nitrogen selective molecular sieve carbon, MSC-3K 172, were investigated for the removal of nitrogen from a gas mixture consisting of 75 mol% CH₄ + 25 mol% N₂. The four DR PSA configurations (PL-A, PH-A, PL-B and PH-B) were experimentally demonstrated and compared in terms of their nitrogen rejection and methane recovery performance. The experiment results indicated the PH-B configuration in general performed the best in terms of the methane product purity and recovery using the kinetic MSC-3K 172 adsorbent. A non-isothermal numerical model was constructed for the kinetic DR PSA process to simulate and optimise the performance of the PH-B configuration. Model predicted gas loadings on the adsorbent indicated that selectively removing nitrogen from methane was feasible when a feed step time close to the characteristic adsorption time of nitrogen was selected. The effective usage of the adsorption bed in PH-B configuration was also numerically studied via the capacity ratio $\mathbb{C}$, with the feed step time and light reflux flow as key operational parameters, at fixed heavy product-to-feed ratio, bed pressure ratio and feed location. The numerical model for the PH-B configuration was also employed to study the effect of pressure in the purge step beyond those conditions accessible in the experiment. The simulation results revealed that the PH-B configuration could achieve a separation performance of 90 mol% CH₄ in the light product with 90% CH₄ recovery when the pressure in the light purge column was lower than 40 kPa while the adsorption pressure was maintained at 500 kPa. This result opens new opportunities for efficiently upgrading sub-quality natural gas reserves.

Keywords: Nitrogen Rejection; Sub-quality Natural Gas; DR PSA; Carbon Molecular Sieve; Methane Upgrading

1. Introduction

Natural gas is expected to become the largest single fuel in the global energy mix and play an important role in the transition to renewable energy sources in the next several decades [1]. The increasing demand for natural gas has encouraged its production from reserves that were previously considered sub-quality due to the high concentration of minor components. Nitrogen is one of the most challenging undesirable components to be removed because of its inert nature and similar physical properties to methane [2, 3]. Currently, cryogenic distillation is the most widely used commercial process to separate excess nitrogen from natural gas. However, the economics of this technology favours its application in very-large scale facilities because the cost of removing nitrogen per unit volume of natural gas processed increases rapidly with decreasing feed gas flow rate [4]. Therefore, cryogenic distillation might not be a viable choice when it comes to the treatment of natural gas from sub-quality gas wells with small gas flow rates (below 10 MMscfd) [4]. Several alternative technologies [4, 5] have been proposed to remove nitrogen from such gas wells, and among them, pressure swing adsorption (PSA) is one technology with the potential to efficiently reject nitrogen across various scales of flow rate.

In adsorption processes it is more energy efficient to remove the minor component than to take out the dominant component in a feed mixture; thus using a nitrogen selective adsorbent for low quality natural gas upgrading favors the process economics of PSA units. Currently, there is no adsorbent available on an industrial scale which exhibits equilibrium selectivity for nitrogen over methane, although certain lab scale metal organic frameworks (MOFs) have been reported to be nitrogen selective [6] at equilibrium. However, there are commercially available adsorbents which exhibit nitrogen selectivity based on molecular sieving effects and/or differences between the diffusivities of N_2 and CH_4 [7-13]. Engelhard Titanosilicate-4 (ETS-4) and its ion-exchanged derivatives are the most industrially significant molecular sieving adsorbents for nitrogen and methane separation, and have been used in commercial natural gas purification applications [14, 15]. However, because of the damage to ETS-4 framework caused by structural contraction upon dehydration, both the equilibrium capacity and the uptake rates of nitrogen on these adsorbents will be reduced under thermal activation [16], which potentially limits the wider adoption of this technology for N_2 and CH_4 separation. Molecular sieve carbon (MSC), on the other hand, is a robust adsorbent that has been widely used in various industrial applications and has been shown previously to separate nitrogen from binary mixtures by kinetic means [17, 18]. This kind of adsorbent does not have as high an equilibrium capacity as that of activated carbon or zeolites for nitrogen or methane [19, 20], but is known to offer significant kinetic selectivity for nitrogen over methane. Fatehi et al. have shown via physical experiments that MSC is capable of processing feed streams containing 60 and 92 mol% methane into products with purities of 75 and 96 mol% methane respectively, although the methane recovery was prohibitively low [21]. Recently, Effendy et al. [22] reported the numerical optimisation of a pressure swing adsorption process for

nitrogen rejection from natural gas using a Takeda molecular sieve carbon, and showed that a 9-step PVSA cycle could enrich CH_4 to pipeline gas requirement from a 20 mol% N_2 + 80 mol% CH_4 feed mixture with a maximum CH_4 recovery of 99%. However, the separation performance of this process was only obtained with a high adsorption pressure coupled with a stringent desorption pressure that required to be as low as 10 kPa, which is practically difficult to achieve in large scale PSA systems [23].

To understand and improve the performance of nitrogen rejection processes using kinetically nitrogen selective adsorbents, here we investigate the use of a particular molecular sieve carbon, MSC-3K 172 (also known as Shirasagi 3K-172), with dual-reflux pressure swing adsorption (DR PSA) cycles to remove nitrogen from a 75 mol% CH_4 + 25 mol% N_2 feed gas mixture. MSC-3K 172 is a kinetically selective adsorbent for nitrogen over methane, and the mass transfer coefficient for N_2 in this MSC can be as high as 100 times that for CH_4 [20, 24]. DR PSA processes are a special class of adsorption separation where the use of simultaneous heavy and light reflux streams significantly increases the achievable separation power for a given adsorbent [25-33]. DR PSA cycles have been effectively applied to the capture of methane from a nitrogen rich N_2 + CH_4 mixture using adsorbents with an equilibrium selectivity for CH_4 [34-37]. However, the performance and potential of DR PSA cycles using adsorbents that are kinetically selective has never been reported previously.

In this work, we begin by presenting experimental results for the separation of a feed mixture containing 75 mol% CH_4 + 25 mol % N_2 with MSC-3K 172 using each of the four DR PSA configurations identified previously [29, 30, 35]. The experimental results are compared to identify the best performing DR PSA configuration for this separation application, and the results of the optimal configuration are used to validate a numerical simulation of the specific DR PSA cycle. The simulation is then employed to analyse the impact of different variables on the process performance, extend the range of parameter values studied, and to understand the adsorption dynamics of kinetically nitrogen selective adsorbents within columns that could not be directly studied by the laboratory experiments.

2. Experiment and Simulation

2.1 Adsorbent Characterization and Isotherm Measurement

The molecular sieve carbon adsorbent used in this work, MSC-3K 172, was the same adsorbent as that reported previously [20, 24]. The adsorbent was in cylindrical granule form with average particle diameter of 1.0 mm and particle length of 2.0 mm. Adsorption isotherms for N_2 and CH_4 on MSC-3K 172 were measured using a volumetric method with a Micromeritics ASAP 2020 in the pressure range of 0.05 - 120 kPa at three temperatures (303 K, 333 K and 363 K) after the adsorbent was degassed at 473 K and 0.2 Pa for 12 hours. All the gases used for the measurement of adsorption isotherms were supplied by Coregas Australia with the following stated molar purity: CH_4 : 99.995%; N_2 : 99.999% and He: 99.995%.

2.2 DR PSA Experiments

Nitrogen rejection experiments using MSC-3K 172 adsorbent were performed on the same laboratory scale DR PSA apparatus (schematic shown in Figure 1) as reported in our previous studies [34, 35]. The binary feed gas mixture composed of nitrogen and methane was prepared by flow from source gases with the same purities as those used for isotherms measurement. The mixture gas had a methane fraction of (75 ± 2) mol% where the variation reflects minor differences in the source gas flow rates achieved over the course of different experiments. Experiments in this work only examined the scenario where the gas mixture was fed to the exact middle of a column, each of which contained 614 g of the degassed adsorbent. The temperature of the adsorption column was not actively controlled and fluctuated slowly in line with the room temperature variation over the range of 293 K to 298 K. The four DR PSA cycle configurations (PL-A, PH-A, PL-B and PH-B) in Figure 2 as demonstrated by May et al. [35] in the context of CH_4 capture were experimentally examined here to study their performance for N_2 rejection in methane-dominant feeds. A description of the four DR PSA cycle configurations is given in the supporting information. Details of the duration of the feed/purge (FE/PU) and pressurization/blowdown (PR/BD) steps and other operational parameters are listed in Table 1.

Figure 1 Simplified process flow diagram of the DR PSA apparatus with valve positions (white=open, black=closed) showing a typical step of feed/light purge for Bed 2 and simultaneous heavy purge for Bed 1.

The feed step time and the light reflux flow rate were varied to study their impact on each cycle configuration. Each experiment was run for over 12 hours to ensure the system reached cyclic steady state (CSS), when the absolute change in *nitrogen* mole fraction in the light (y_L) and heavy (y_H) product streams over five consecutive adsorption cycles was less than 0.01. The CSS product compositions, y_L and y_H , reported here correspond to the average values measured over a cycle for N_2 in the 'Light Gas Product' and 'Heavy Gas Product' streams as indicated in Figure 1, respectively. Note that this is contrary to the notation used in our previous work with these compounds where the 'heavy' gas was CH_4 reflecting the methane selective feature of the adsorbent materials used.

Figure 2 Four-step DR PSA cycle sequencing: feed to the low (PL) or high (PH) pressure bed, and pressurization with the heavy (A) or light (B) adsorbate. The combination of these gives the four base configurations of DR PSA: PL-A, PH-A, PL-B and PH-B.

2.3 DR PSA Simulation

The non-isothermal numerical model constructed with Aspen Adsorption software as described previously [35-37] was used in this work. The model assumptions are supplied in the supporting information. Constituent equations and numerical solver parameters for the model can be found in references [35-37], with the specific parameters used in this work being listed in Table 1. Simulations using the model were performed on a multi-core computer with an Intel i7 M chip running at 2.20 GHz with 4 GB RAM, and the computational time to reach cyclic steady state (CSS) varied between (5 to 8) hours depending on conditions of each case. The criteria for reaching CSS were that the relative changes in solid loading and temperature for each spatial node in the adsorption columns were less than 10^{-5} . As pointed out previously [35, 36], the solution of the governing partial differential equations by the finite difference method introduced mass balance errors into the simulations. The calculated overall and methane material balance errors were lower

than 5% and 2%, respectively, comparable to or lower than the literature mass balance errors as summarized by Zhang et al [36]. The mass balance errors in this work were corrected using the method described by Zhang et al [36], which also demonstrated that such corrections have a negligible effect on the key results obtained.

Table 1 Operational and adsorbent parameters used in experiments and simulations

Column Parameters		Operational Parameters	
Parameter	Value	Parameter	Value
Total length (L)	0.98 m	Feed flow rate, F	0.4 SLPM
Axial feed position (z_f)	0.5	heavy product flow rate, H	0.1-0.35 SLPM
Column internal diameter (D_b)	0.035 m	light reflux flow rate, R_L	0.1-2 SLPM
Column thickness	0.0016 m	Column high pressure (P_H)	500 kPa
Column heat transfer coefficient	$10 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$	Column low pressure (P_L)	100 kPa
Void tank heat transfer coefficient	$1000 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$	Ambient temperature (T_{amb})	(293 to 298) K
Wall thermal conductivity (k_w)	$16 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	FE/PU step time (t_F)	60 to 300 s
Wall specific heat capacity	$0.5 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	PR/BD step time	20 s
Axial dispersion coefficient (D_L)	$3.8 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1}$		
Adsorbent Parameters			
Bulk density (ρ_b)	657.9 kg/m^3	Inter-particle porosity (ϵ_i) (-)	0.33
Adsorbent particle radius (r_p)	0.0175 m	Intra-particle porosity (ϵ_p) (-)	0.46
Adsorbent specific heat capacity (C_{ps})	0.0011 MJ/kg/K		
	N₂	CH₄	
* Mass transfer coefficient (k_f)	0.015 s^{-1}	$1.26 \times 10^{-4} \text{ s}^{-1}$	

* Refer to Equation 7 in Ref. [36].

3. Results and Discussion

3.1 Adsorption Equilibria and Kinetics

Single component N₂ and CH₄ adsorption isotherms measured on MSC-3K 172 at (302, 332, and 365) K in the pressure range of 0.05 - 120 kPa are displayed in Figure 3, and the corresponding equilibrium adsorption amounts are tabulated in SI.Table 1 and SI.Table 2 of the Supplementary Information. It is worth noting that the measured isotherms do not cover the full pressure range of this work due to experimental limitations caused by the extremely slow kinetics of CH₄ adsorption as reported previously [20]. However, the comparison (SI.Figure 1) of the N₂ isotherms measured in this work with those measured previously [20] shows a reasonable consistency between the two data sets that is within the combined experimental uncertainties. This affords confidence in the extension of the isotherm model to the operating conditions covered in this work. The measured data were regressed using the Langmuir Adsorption equation (Eqn. 1) to extract isotherm parameters that were used in the DR PSA simulations, and the optimal regression parameters are listed in Table 2. The Langmuir regression curves are plotted alongside the data points in Figure 3 for a comparison of the two.

$$Q = Q_{max} \frac{bP}{1+bP} \quad b = b_0 \exp\left(\frac{-\Delta H}{RT}\right) \quad \text{Eqn. 1}$$

$$\alpha_{CH_4/N_2} = K_{CH_4}/K_{N_2} \quad K = Q_{max}b \quad \text{Eqn. 2}$$

$$\beta_{N_2/CH_4} = \frac{K_{N_2}}{K_{CH_4}} \sqrt{\frac{k_{N_2}}{k_{CH_4}}} \quad \text{Eqn. 3}$$

Here Q is the adsorption capacity, Q_{max} is the adsorption amount at infinite pressure, b is the adsorption Henry constant at certain temperature, b_0 is the adsorption Henry constant at infinite temperature, ΔH is the differential enthalpies of adsorption, R is the universal gas constant, α_{CH_4/N_2} is the equilibrium selectivity, K is the Henry's law adsorption parameter, and β_{N_2/CH_4} is the kinetic selectivity of the adsorbent [38].

Figure 3 Measured and correlated adsorption isotherms of a) pure N_2 and b) pure CH_4 on molecular sieving carbon MSC-3K 172

Figure 4 Experimental adsorption uptake of CH₄ and N₂ on MSC-3K 172 at 303 K and about 100 kPa. Q_t represents the transient uptake amount of gases on the adsorbent, t is the adsorption time

Table 2 Regressed Langmuir isotherm parameters and their respective statistical uncertainties. RMSD represents the root-mean-square-deviation between the regression and measured adsorption capacities

		Q_{max} (mmol/g)	$b_0 \times 10^6$ (kPa ⁻¹)	ΔH (kJ/mol)	RMSD (mmol/g)
MSC-3K 172	CH ₄	1.60 ± 0.02	6.15 ± 0.23	18.57 ± 0.11	0.0032
	N ₂	1.34 ± 0.02	1.76 ± 0.03	18.89 ± 0.06	0.0002

Figure 3 shows that the equilibrium adsorption capacities of CH₄ are higher than those of N₂ at the same temperature and pressure, which means the MSC-3K 172 would be CH₄ selective if only the equilibrium capacities were considered. However, the adsorption rate of CH₄ is much slower than that of N₂ on this adsorbent as can be seen from Figure 4 which shows an example of pure CH₄ and N₂ uptake at 303 K and about 100 kPa as a function of time. The adsorption uptake of N₂ was higher than that of CH₄ in the 400 seconds period of measurement and much higher in the initial 100 seconds although the equilibrium CH₄ adsorption amount was about 2.5 times that of N₂ at this condition. Our previous studies [20, 24] have shown that the mass transfer coefficients of N₂ adsorption on MSC-3K 172 could be about 30 - 100 times that of CH₄ depending on the adsorption conditions, and using Eq (3) this translates to the kinetic selectivity of N₂/CH₄ (β_{N_2/CH_4}) in the range of 1.4 - 2.3, making MSC-3K 172 a kinetically N₂ selective adsorbent. For the conditions in this work, the kinetic selectivity of N₂/CH₄ was around 2.2 depending on the temperature of each simulation run.

3.2 DR PSA Experiment Results

Thirty four nitrogen rejection DR PSA experiments were performed on MSC-3K 172 with PL-A, PH-A, PL-B and PH-B configurations using the DR PSA apparatus. Each of the experiments is indexed with a run number for the convenience of referencing them in the following sections. The experimentally specified values of feed step time (t_F), feed flow rate (F), methane mole fraction in feed ($1-y_F$), heavy product (H) and light reflux (R_L)

flow rates, as well as the measured values of the methane mole fractions in the light ($1-y_L$) and heavy ($1-y_H$) product streams at cyclic steady state (CSS) are all listed in Table 3. Using the same method reported by May et al. [35], the average values of the overall and methane material balance errors for the 34 experiments were calculated to be 2.55 % and 3.20 %, respectively. These errors arose primarily from the uncertainties of the measured light and heavy product flow rates and the measurements of corresponding compositions of these product streams.

Table 3 Experimental results obtained using MSC-3K 172 to separate 75 mol% CH₄+ 25 mol% N₂ mixture with the four different DR PSA cycle configurations

Runs	t_F s	F SLPM	$1-y_F$ (CH ₄)	H SLPM	R_L SLPM	$1-y_H$ (CH ₄)	$1-y_L$ (CH ₄)
PL-A							
1	60	0.989	0.760	0.323	1.075	0.60	0.83
2	60	0.787	0.763	0.256	1.059	0.60	0.84
3	60	0.387	0.778	0.114	0.356	0.63	0.83
4	60	0.386	0.778	0.110	0.713	0.61	0.84
5	30	0.973	0.768	0.302	2.731	0.67	0.81
6	240	0.400	0.750	0.119	0.365	0.51	0.85
7	300	0.397	0.757	0.123	0.365	0.55	0.84
8	180	0.394	0.762	0.119	0.364	0.53	0.85
9	120	0.391	0.767	0.116	0.365	0.54	0.86
10	120	0.391	0.767	0.117	0.729	0.57	0.84
PH-A							
11	240	0.398	0.754	0.122	0.726	0.56	0.83
12	240	0.398	0.754	0.123	0.366	0.52	0.85
13	300	0.398	0.753	0.122	0.365	0.52	0.85
14	420	0.399	0.752	0.122	0.364	0.55	0.84
15	180	0.398	0.755	0.118	0.366	0.51	0.85
16	120	0.396	0.759	0.117	0.360	0.54	0.84
17	60	0.391	0.766	0.115	0.352	0.63	0.82
PL-B							
18	180	0.394	0.762	0.125	0.335	0.64	0.81
19	120	0.391	0.768	0.121	0.355	0.63	0.82
20	240	0.395	0.759	0.129	0.355	0.65	0.81
21	300	0.396	0.757	0.132	0.350	0.66	0.80
22	60	0.382	0.785	0.114	0.347	0.68	0.83
PH-B							
23	300	0.398	0.753	0.121	0.346	0.52	0.85
24	240	0.398	0.754	0.118	0.358	0.50	0.85
25	180	0.397	0.755	0.116	0.354	0.48	0.86
26	120	0.395	0.758	0.114	0.361	0.47	0.87
27	60	0.392	0.765	0.105	0.322	0.47	0.87
28	60	0.391	0.767	0.103	0.644	0.50	0.86
29	60	0.390	0.768	0.103	0.461	0.48	0.87
30	60	0.392	0.766	0.103	0.212	0.46	0.87
31	60	0.391	0.768	0.103	0.140	0.47	0.87
32	120	0.395	0.759	0.111	0.218	0.44	0.88
33	120	0.396	0.758	0.115	0.508	0.50	0.86
34	180	0.397	0.756	0.112	0.136	0.41	0.88

The experiment results are also displayed as a function of the H/F ratio in Figure 5.a along with the theoretical separation limit based on the overall and component material balances. The material balance constrains the allowable CH₄ mole fractions in the 'heavy product' given a pure 'light product' (N₂ mole fraction $y_L=0$, thus CH₄ mole fraction $(1-y_L)=1$), which in turn determines the limit of CH₄ recovery in the process.

All the PL-A, PH-A and PL-B experiments were conducted with an H/F ratio in the range of 0.26 – 0.33, shifted away from $H/F = y_F$ for a purer light CH₄ product. The PH-B experiments were performed in the range

of $0.26 \leq H/F \leq 0.30$ to study the effect of heavy product flow rates on the process performance. With these H/F ratios, the four DR PSA cycle configurations achieved a CH_4 mole fraction of 0.8 - 0.9 in the light (methane rich) product and 0.4 – 0.7 in the heavy product. It should be noted that the feed step time and the amount of refluxes were varied among these experimental trials with the purpose of optimizing these process parameters, and this accounts for the small variations in the separation performance achieved at similar H/F ratios. The best separation performance was achieved for the PH-B cycles at $H/F \approx 0.28$.

Figure 5 a) The experimental product compositions for all four configurations plotted as a function of H/F , where $(1-y_L)$ is the purity of the light, methane-rich product, and $(1-y_H)$ is the methane fraction lost to the heavy N_2 -rich product; b) plot of CH_4 recovery and N_2 mole fraction in the light, methane rich product, y_L , for experiments performed with the four DR PSA cycle configurations.

Figure 5.b shows the correlation between CH_4 recovery (which was calculated from the ratio of CH_4 amount in the light product to that in the feed) and the heavy product CH_4 mole fraction for all the experiments with the four DR PSA configurations. It can be observed from Figure 5.b that in general the higher CH_4 mole fraction in the heavy product the lower CH_4 recovery of the process because CH_4 in the heavy product was

not recovered. PH-B experiments in general performed the best in terms of the CH_4 recovery, which also implicitly indicated its CH_4 mole fraction in the light product was higher than other configurations because the feed and light product flow rates were relatively constant. Also for PH-B, it can be seen from Runs 27-31 in Table 3 that increasing the light reflux flow rate (R_L) slightly increased the CH_4 mole fraction in the heavy product, which means the light reflux had exceeded the optimal R_L and entered the heavy product. Therefore, the amount of light reflux (R_L) needs to be reduced to maximize the recovery of methane. However, the R_L in experiments could not be further decreased because of the limitation of the accuracy range of the mass flow controllers in the DR PSA apparatus. The effect of feed step time (t_F) was also examined in the experiments (Run 23 to Run 27), and the results indicate that with the increase of t_F the CH_4 mole fraction in the light product decreased slightly from 0.87 to 0.85 while CH_4 mole fraction in the heavy product increased from 0.47 to 0.52, indicating CH_4 recovery reduces with increased t_F . A DR PSA numerical model was used to further study the effect of R_L and understand the effect of time t_F on the PH-B process performance.

3.3 Comparison with Simulation

All the PH-B experiments performed on MSC-3K 172 were simulated using the DR PSA numerical model. Figure 6.a shows the product purities obtained from experiments and simulations for runs 23-34, and Figure 6.b shows the deviation between each experiment and simulation for all the runs. It can be concluded from these two figures that the simulation results match the experimental values well, with deviations randomly scattered around zero and the root-mean-squared deviations being 0.008 for $(1-y_H)$ and 0.003 for $(1-y_L)$. Given the good agreement between experiment and simulation demonstrated in Figure 6, the numerical model was used to efficiently explore the effects of varying feed step time (t_F), light reflux flow rate (R_L) and purge step pressure (P_L) on the process performance.

Figure 6 Comparison of simulated separation performance for the PH-B configuration with corresponding data measured in experiments for Runs 23-34: a) absolute values of $(1-y_H)$ and $(1-y_L)$; b) deviations of $(1-y_H)$ and $(1-y_L)$

The experimentally measured and numerically simulated pressure and temperature profiles for Run 32 are displayed in Figure 7 to further elucidate the dynamics of the PH-B experiments. As shown in Figure 7.a, the simulation matches the measured pressure history across a complete cycle well with an overall deviation at about 3% of the high pressure. The small fluctuations in the ‘high pressure’ steps in experiments were not reflected by the simulation because the PID controller in the simulation could more quickly respond to any pressure fluctuations about the set point, while the back pressure regulators used in the experiments had response delays which led to an under-damping of pressure disturbances.

Figure 7 Comparison of simulated bed pressures and temperatures with corresponding experimental results at CSS for PH-B cycles with 120 s feed time and 0.1 SLPM light reflux flow rate. a) Pressure as measured by the sensor at the top of the column; pressure drop across the bed was negligible. b) Temperature: T1-top of the column, T6-middle of the column, T11-bottom of the column

Figure 7.b shows the comparison of bed temperatures at CSS calculated at nodes corresponding to the measurements made using sensor T1 located at the light reflux end of the column, sensor T11 located at the heavy reflux end of the column, and sensor T6 in the middle of the column. Overall, the simulated temperatures are in reasonable agreement with the measured ones, particularly given the idealizations required in the simulation regarding heat loss to the environment from the entire column being spatially uniform and represented by a single heat transfer coefficient. In particular, the root-mean-square-deviation between the measured and calculated temperatures ranges from 0.05 K for T6, to 0.11 K for T11, with the largest difference during the cycle being about 0.17 K for T11 at the middle of the FE step. The largest temperature swing (1.7 K) observed here is much smaller than that (8 K) reported in our previous work [34] using activated carbon in the same adsorption column, indicating that the extent of adsorption taking place on the molecular sieve carbon used in this work was comparatively limited. The relatively small uptake of gases in this process was expected because the feed step time was much shorter than the characteristic adsorption time of the gases on the MSC-3K 172 as indicated in Figure 4 and in our previous work [24]: there would be only about 0.08 mmol/g CH_4 and 0.23 mmol/g N_2 adsorbed on MSC-3K 172 in the feed step time due to the slow mass transfer between the gases and the adsorbent. While for Norit RB 3 [34], both CH_4 and N_2 approached their saturation adsorption capacity with CH_4 reaching 0.75 mmol/g and N_2 reaching 0.20 mmol/g in the feed step time.

Figure 8 shows the CH_4 and N_2 loadings on the adsorbent and the absolute loading changes for both CH_4 and N_2 over one complete cycle. The hypothetical loadings from isotherms (if there were no mass transfer resistance) over the course of a cycle at the location of the three temperature sensors are shown in

SI.Figure 2 and SI.Figure 3. These calculated loadings of CH_4 and N_2 on the adsorbent reveal the underlying reasons for the observed temperature variations at each point in the bed throughout the cycle. Figure 8.a exhibits that there were slight changes in the adsorption loading of CH_4 on the adsorbent at the three locations during the whole cycle and Figure 8.b indicates that while there were small N_2 loading changes at locations T1 and T6 there was pronounced loading change at position T11. Figure 8.c shows that loading changes for N_2 was much larger than that for CH_4 in each step of the cycle, which indicates that the temperature changes in the bed were mainly caused by the adsorption and desorption of N_2 . The negligible change in CH_4 adsorption and the manifest change in N_2 adsorption over the cycle indicates that N_2 was indeed the preferentially adsorbed component in this system. The real CH_4 and N_2 loading changes shown in Figure 8 correspond very well with the temperature changes of T1, T6 and T11 in Figure 7.b. The hypothetical loadings of CH_4 and N_2 displayed in SI.Figure 2 and SI.Figure 3 showed stark contrast to the real loadings of CH_4 and N_2 , which further demonstrates the important role of taking into account the mass transfer resistance in an adsorption process, especially for a slow gas adsorption system.

Figure 8 Evolution of (a) CH₄ and (b) N₂ loading amount (w) on the adsorbent over a cycle at three temperature sensor locations: T1, T6 and T11; c) the absolute change amount of loading (Δw) over a cycle for both CH₄ and N₂.

3.4 Capacity Ratio

While variations to the feed step time (t_f) and light reflux flow rate (R_L) had some impact on the separation performance observed in the experiments, the limited range over which they could be varied did not lead to the identification of a clear optimum. Accordingly, the simulations were used to efficiently explore a wider range of conditions to identify and understand the conditions under which separation performance improved. May et al. [35] provided a method for optimizing the design of practical DR PSA cycles in which the practical bed capacity ratio $\mathbb{C}$ is evaluated to determine the extent to which the bed is being used for a given combination of t_f and R_L . The definition of $\mathbb{C}$ is shown in Eqn. 4.

$$\mathbb{C} \equiv \frac{y_H R_H t_F}{n_A^{gas} + n_A^{ads}} + \frac{y_F F t_F}{(n_A^{gas} + n_A^{ads})(1 - Z_F)} \quad \text{Eqn. 4}$$

with

$$n_A^{gas} = (y_H - y'_H)(p_H V_{bed} \varepsilon / (\mathfrak{R} T)) \quad \text{Eqn. 5}$$

$$n_A^{ads} = m_{ads} (Q_A - Q'_A) \quad \text{Eqn. 6}$$

Here y_H and y_F denote the heavy component fraction in the heavy product and feed, respectively, R_H denotes the heavy reflux flow, t_f the feed time, F the feed flow, z_F the axial feed location, p_H the high pressure, V_{bed} the bed's volume, ε the bed void, $\mathfrak{R}$ the ideal gas constant, T the bed temperature, m_{ads} the mass of the adsorbent and Q_A and Q'_A represent the adsorption amount of A corresponding to y_H and y'_H where y'_H is the average mole fraction of component A throughout the bed prior to the start of the purge step. The heavy reflux flow is in practice controlled by adjusting the light reflux flow rate for a given heavy product flow rate.

Figure 9 shows the variations of CH₄ mole fraction in the light and heavy products with capacity ratio $\mathbb{C}$ as t_f and R_L were varied independently (with the other held constant). The effect of t_f and R_L on y_H and $\mathbb{C}$ has

been well documented by May et al. [35] for equilibrium based separations but has not been reported for kinetic based separations. For a kinetic based DR PSA process, t_F and R_L need to be carefully optimized to achieve the best separation performance because of the additional competition between components sorption rates and equilibrium capacities that does not have an as noticeable impact on equilibrium based adsorption processes. The t_F was varied in the range of (60 – 300) s with an interval of 60 s for a feed flow rate of 0.4 SLPM, with an H/F ratio at 0.25 and light reflux rate R_L at 0.37 SLPM. The t_F range was deliberately chosen to be close to the characteristic time that the uptake of N_2 was higher than that of CH_4 . Overall, the effect of t_F on product purities was limited over the range studied with only about 0.014 variation in $(1-y_L)$ and 0.041 in $(1-y_H)$. However, there does seem to be an optimal t_F for CH_4 purity $(1-y_L)$ and recovery at 180 s with a corresponding optimum value of C (denoted C_{opt}) at 0.14. The R_L was varied in the range of (0.05 – 0.6) SLPM at a feed flow rate of 0.4 SLPM with H/F ratio at 0.25 and feed step time t_F of 180 s. The effect of R_L on CH_4 mole fraction in products is much more pronounced than that of t_F with a variation in $(1-y_L)$ of 0.025 and a variation in $(1-y_H)$ of 0.076 between the minimum and maximum values, with C_{opt} occurring at a value of 0.11 when a light reflux flow rate of 0.15 SLPM. These low values of C_{opt} indicate that only a small section of the bed can be used for separation before the front of the N_2 mass transfer zone breaks through into the light gas product.

Figure 9 CH_4 mole fraction in a) the light product and b) the heavy product as a function of bed capacity ratio C ($H/F=0.25$). R_L was held at 0.37 SLPM when t_F was varied; and t_F was 180s when R_L was changed.

3.5 Effect of Purge Pressure

All of the above experiments and simulations were performed with the low pressure column (P_L) fixed at 100 kPa, which was the lowest value achievable in the experiments due to the capacity limitation of the diaphragm compressor used. However, desorption pressure is known to have a significant impact on the product purity and recovery achieved in a pressure swing adsorption process. We therefore explored the effect of P_L on the separation performance via numerical simulation. These simulation studies were carried on the basis of Run 34 in Table 3: CH_4 in the feed was changed to exactly 75 mol%, the H/F ratio was fixed at 0.25, and the compressor inlet flow rate was adjusted to achieve (30 – 80) kPa in the low pressure column. All other parameters used in the varying P_L simulations were the same as those in Run 34. Simulation results for methane purity in the heavy and light product are shown in Figure 10, along with the corresponding methane recovery. Clearly, methane purity in the light product increases with decreasing P_L as does methane recovery. The results in Figure 10 reveal that a P_L lower than 40 kPa can achieve a separation performance of 90 mol% CH_4 in the light product stream and recovery of 90% of the CH_4 in the feed. At 40 kPa, the energy consumption and the productivity of the process are 22.3 kJ per mole of CH_4 produced and 0.48 mole CH_4 per kilogram of adsorbent per hour, respectively. These values are greater than those reported in the numerical simulation work by Effendy et al [22] because the feed N_2 content in this work was higher (25 mol%) than those (10 – 20 mol%) in Effendy's work and in general the higher the feed N_2 content, the greater the energy consumption and the lower the productivity [22]. We plan to consider a more extensive comparison between DR PSA and the more conventional approach of Effendy et al in future work.

Figure 10 Effect of purge pressure in the low pressure column, P_L , in a range of (30 – 80) kPa on the separation performance of the PH-B cycle on the basis of Run 34 (modified to have exactly 75 mol% CH_4 in feed and $H/F = 0.25$).

4. Conclusions

A DR PSA cycle utilising a kinetically selective adsorbent was investigated for the first time via experiment and simulation. The carbon molecular sieve adsorbent MSC-3K 172 which is kinetically selective for N_2 over CH_4 was used to separate a gas mixture of 75 mol% CH_4 + 25 mol% N_2 . The experimental results showed that there was little difference between the four DR PSA cycle configurations although in general the PH-B configuration exhibited a better separation performance compared to the other three configurations. A numerical simulation model for the PH-B configuration was constructed and validated using the experimental results of the PH-B configuration, and then used to study the effects of key process parameters when varied beyond the ranges achievable in the experiment. The simulation results of the gas loadings on the adsorbent showed that the MSC-3K 172 was indeed kinetically nitrogen selective when proper feed step time close to the characteristic adsorption time was selected, and the mass transfer resistance in an adsorption process should not be neglected for a slow gas adsorption system. Evaluation of the bed capacity ratio as a function of feed step time and light reflux rate revealed an optimum of $C_{opt} \approx 0.1$, indicating only a small section of the bed was actually used for the separation. Nevertheless, by lowering the pressure in the light purge column to 40 kPa it was possible to achieve a separation performance of 90 mol% CH_4 in the light product with 90% CH_4 recovery.

Acknowledgements

This research was supported by the Department of Environment Regulation of Western Australia through its Low Emissions Energy Development (LEED) Fund and by the Australian Research Council through GL's Discovery Early Career Researcher Award (DE140101824), and the Industrial Transformation Training Centre program (IC150100019).

References

- [1] IEA, World energy outlook 2017, International Energy Agency.
- [2] R. Neuwirth, Natural gas processing-Nitrogen removal from natural gas, VDM Verlag Dr. Müller Aktiengesellschaft & Co. KG2008.
- [3] T.E. Rufford, S. Smart, G.C.Y. Watson, B.F. Graham, J. Boxall, J.C. Diniz da Costa, E.F. May, The removal of CO₂ and N₂ from natural gas: a review of conventional and emerging process technologies, *Journal of Petroleum Science and Engineering* 94–95 (2012) 123-154.
- [4] K. Lokhandwala, M.B. Ringer, T.T. Su, Z. He, I. Pinnau, J.G. Wijmans, A. Morisato, K. Amo, A. Da Costa, R.W. Baker, R. Olsen, H. Hassani, T. Rathkamp, Nitrogen removal from natural gas, Membrane Technology and Research, Inc., Menlo Park, CA 94025, 1999.
- [5] J.C. Kuo, K.H. Wang, C. Chen, Pros and cons of different nitrogen removal unit (NRU) technology, *Journal of Natural Gas Science and Engineering* 7 (2012) 52-59.
- [6] J.W. Yoon, H. Chang, S.-J. Lee, Y.K. Hwang, D.-Y. Hong, S.-K. Lee, J.S. Lee, S. Jang, T.-U. Yoon, K. Kwac, Y. Jung, R.S. Pillai, F. Faucher, A. Vimont, M. Daturi, G. Ferey, C. Serre, G. Maurin, Y.-S. Bae, J.-S. Chang, Selective nitrogen capture by porous hybrid materials containing accessible transition metal ion sites, *Nat Mater* 16 (2017) 526-531.
- [7] B. Majumdar, S.J. Bhadra, R.P. Marathe, S. Farooq, Adsorption and diffusion of methane and nitrogen in Barium exchanged ETS-4, *Industrial & Engineering Chemistry Research* 50 (2011) 3021-3034.
- [8] R.S. Pillai, S.A. Peter, R.V. Jasra, Adsorption of carbon dioxide, methane, nitrogen, oxygen and argon in NaETS-4, *Microporous and Mesoporous Materials* 113 (2008) 268-276.
- [9] A. Jayaraman, A.J. Hernandez-Maldonado, R.T. Yang, D. Chinn, C.L. Munson, D.H. Mohr, Clinoptilolites for nitrogen/methane separation, *Chemical Engineering Science* 59 (2004) 2407-2417.
- [10] C. Braunbarth, H.W. Hillhouse, S. Nair, M. Tsapatsis, A. Burton, R.F. Lobo, R.M. Jacubinas, S.M. Kuznicki, Structure of strontium ion-exchanged ETS-4 microporous molecular sieves, *Chemistry of Materials* 12 (2000) 1857-1865.
- [11] S.M. Kuznicki, V.A. Bell, I. Petrovic, P.W. Blosser, Separation of nitrogen from mixtures thereof with methane utilizing barium exchanged ETS-4, Engelhard Corporation, Iselin, N. J., United States, 1999.
- [12] X. Ning, W.J. Koros, Carbon molecular sieve membranes derived from Matrimid® polyimide for nitrogen/methane separation, *Carbon* 66 (2014) 511-522.
- [13] A. Jayaraman, R.T. Yang, D. Chinn, C.L. Munson, Tailored clinoptilolites for nitrogen/methane separation, *Industrial & Engineering Chemistry Research* 44 (2005) 5184-5192.
- [14] K.F. Butwell, W.B. Dolan, S.M. Kuznicki, Selective removal of nitrogen from natural gas by pressure swing adsorption, Engelhard Corporation, Iselin, NJ(US), United States, 2001.
- [15] S.M. Kuznicki, V.A. Bell, I. Petrovic, B.T. Desai, Small-pored crystalline titanium molecular sieve zeolites and their use in gas separation processes, Engelhard Corporation, Iselin, N.J., United States, 2000.
- [16] R.P. Marathe, K. Mantri, M.P. Srinivasan, S. Farooq, Effect of ion exchange and dehydration temperature on the adsorption and diffusion of gases in ETS-4, *Industrial & Engineering Chemistry Research* 43 (2004) 5281-5290.
- [17] Y.S. Bae, C.H. Lee, Sorption kinetics of eight gases on a carbon molecular sieve at elevated pressure, *Carbon* 43 (2005) 95-107.
- [18] S. Cavenati, C.A. Grande, A.E. Rodrigues, Separation of methane and nitrogen by adsorption on carbon molecular sieve, *Separation Science and Technology* 40 (2005) 2721-2743.
- [19] G. Watson, E.F. May, B.F. Graham, M.A. Trebble, R.D. Trengove, K.I. Chan, Equilibrium adsorption measurements of pure nitrogen, carbon dioxide, and methane on a carbon molecular sieve at cryogenic temperatures and high pressures, *Journal of Chemical & Engineering Data* 54 (2009) 2701-2707.
- [20] T.L. Saleman, G. Xiao, G. Li, E.F. May, A robust dynamic column breakthrough technique for high-pressure measurements of adsorption equilibria and kinetics, *Adsorption* 23 (2017) 671-684.
- [21] A.I. Fatehi, K.F. Loughlin, M.M. Hassan, Separation of methane-nitrogen mixtures by pressure swing adsorption using a carbon molecular sieve, *Gas Separation & Purification* 9 (1995) 199-204.
- [22] S. Effendy, C. Xu, S. Farooq, Optimization of a pressure swing adsorption process for nitrogen rejection from natural gas, *Industrial & Engineering Chemistry Research* 56 (2017) 5417-5431.

- [23] Y. Jiang, J. Ling, P. Xiao, Y. He, Q. Zhao, Z. Chu, Y. Liu, Z. Li, P.A. Webley, Simultaneous biogas purification and CO₂ capture by vacuum swing adsorption using zeolite NaUSY, *Chemical Engineering Journal* 334 (2018) 2593-2602.
- [24] G. Xiao, Z. Li, T.L. Saleman, E.F. May, Adsorption equilibria and kinetics of CH₄ and N₂ on commercial zeolites and carbons, *Adsorption* 23 (2017) 131-147.
- [25] C. Tian, D. Li, Z. Ding, Z. Han, D. Zhang, Experiment and simulation study of a dual reflux pressure swing adsorption process for separating N₂/O₂, *Separation and Purification Technology* 189 (2017) 54-65.
- [26] Y. Shen, Y. Zhou, D. Li, Q. Fu, D. Zhang, P. Na, Dual-reflux pressure swing adsorption process for carbon dioxide capture from dry flue gas, *International Journal of Greenhouse Gas Control* 65 (2017) 55-64.
- [27] T.S. Bhatt, A. Sliepcevich, G. Storti, R. Rota, Experimental and modeling analysis of dual-reflux pressure swing adsorption process, *Industrial & Engineering Chemistry Research* 53 (2014) 13448-13458.
- [28] T.S. Bhatt, G. Storti, R. Rota, Optimal design of dual-reflux pressure swing adsorption units via equilibrium theory, *Chemical Engineering Science* 102 (2013) 42-55.
- [29] D.T. Kearns, P.A. Webley, Modelling and evaluation of dual reflux pressure swing adsorption cycles: Part II. Productivity and energy consumption, *Chemical Engineering Science* 61 (2006) 7234-7239.
- [30] D.T. Kearns, P.A. Webley, Modelling and evaluation of dual-reflux pressure swing adsorption cycles: Part I. Mathematical models, *Chemical Engineering Science* 61 (2006) 7223-7233.
- [31] A.D. Ebner, J.A. Ritter, Equilibrium theory analysis of dual reflux PSA for separation of a binary mixture, *AIChE Journal* 50 (2004) 2418-2429.
- [32] J.A. McIntyre, C.E. Holland, J.A. Ritter, High enrichment and recovery of dilute hydrocarbons by dual-reflux pressure-swing adsorption, *Industrial & Engineering Chemistry Research* 41 (2002) 3499-3504.
- [33] D. Diagne, M. Goto, T. Hirose, Parametric studies on CO₂ separation and recovery by a dual reflux PSA process consisting of both rectifying and stripping sections, *Industrial & Engineering Chemistry Research* 34 (1995) 3083-3089.
- [34] T.L. Saleman, G. Li, T.E. Rufford, P.L. Stanwix, K.I. Chan, S.H. Huang, E.F. May, Capture of low grade methane from nitrogen gas using dual-reflux pressure swing adsorption, *Chemical Engineering Journal* 281 (2015) 739-748.
- [35] E.F. May, Y. Zhang, T.L.H. Saleman, G. Xiao, G. Li, B.R. Young, Demonstration and optimisation of the four dual-reflux pressure swing adsorption configurations, *Separation and Purification Technology* 177 (2017) 161-175.
- [36] Y. Zhang, T.L.H. Saleman, G. Li, G. Xiao, B.R. Young, E.F. May, Non-isothermal numerical simulations of dual reflux pressure swing adsorption cycles for separating N₂ + CH₄, *Chemical Engineering Journal* 292 (2016) 366-381.
- [37] Y. Zou, G. Xiao, G. Li, W. Lu, E.F. May, Advanced non-isothermal dynamic simulations of dual reflux pressure swing adsorption cycles, *Chemical Engineering Research and Design* 126 (2017) 76-88.
- [38] D.M. Ruthven, S. Farooq, K.S. Knaebel, *Pressure swing adsorption*, VCH Publishers, Inc., New York, 1994.

- Nitrogen rejection from methane was achieved with a kinetic DR PSA process.
- A non-isothermal numerical model was shown capable of simulating kinetic DR PSA cycles.
- A feed with 75 % CH₄ +25% N₂ was separated to achieve 90% CH₄ purity and 90% recovery.
- Simulations provide insight into the separation mechanism of a kinetically N₂ selective adsorbent.

ACCEPTED MANUSCRIPT