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# Separation of $He/N_2/CH_4$ ternary mixtures by a triple-reflux pressure swing adsorption process

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## Abstract

Conventional pressure swing adsorption (PSA) processes can only produce one high purity product in a single stage, whereas the state-of-art dual-reflux PSA (DR-PSA) can produce two high purity products simultaneously. However, multi-component gas separation is often required in the industry, targeting at recovering several valued products at the same time. In this study, we propose a novel adsorption process, namely Triple-Reflux PSA (TR-PSA), to separate three components simultaneously. A middle product outlet and a middle reflux stream were introduced to the adsorption columns of a conventional DR-PSA process to separate ternary mixtures of nitrogen, methane, and helium. Non-isothermal dynamic models were built to investigate the impacts of operating parameters particularly the location of the middle reflux/product stream and the middle reflux flowrates. Results showed that the TR-PSA process successfully separated ternary mixtures obtaining three enriched products simultaneously in a single stage, yielding a separation performance comparable to that of the double-stage DR-PSA with significantly lower capital and energy cost.

Topic heading: Separations: Materials, Devices and Processes

Keywords: pressure swing adsorption, gas separation, ternary mixture, natural gas, helium

## Introduction

Helium (He) is a non-renewable noble gas, which has a wide range of applications in the space industry, scientific research, medical facilities, and many other critical areas with increasing market demand[1,2]. Hence, helium has been admitted as an indispensable strategic resource[2,3]. As the concentration of He in the air is only 5.2 ppm (part per million), helium production by air separation is extremely energy intensive[4]. The helium reserve on the Earth is also quite limited, and most commercially viable helium sources are from helium bearing natural gas (NG) fields, which contains up to 1 − 8 vol.% helium[5]. Currently, concentrated helium is primarily obtained during the production of liquefied natural gas (LNG) as a by-product.

LNG production facilities are commonly operated at cryogenic conditions, containing a liquefaction unit (with an operating temperature around -112 K), a heavy hydrocarbon removal unit and a nitrogen rejection unit (NRU)[6]. The LNG process produces three main streams: the LNG product, the end-flash gas, and the $N_2$ vent gas. Both the end-flash gas and $N_2$ vent gas, consisting primarily of nitrogen and a few percent of methane and helium, can be used as the feed gas and injected into a helium extraction unit (HeXU), generally integrated with the NRU, to obtain the crude helium (molar fraction is commonly ≥50%) product [2,7]. Such HeXU is typically operated by cryogenic processes, which requires even lower operating temperatures (below -93 K) and more restrictions of impurity quantity than LNG processes. Therefore, the use of additional HeXU will significantly increase the capital and operating cost of the LNG production facilities.

Pressure swing adsorption (PSA) has been widely used in various gas separation processes due to its small footprint, high separation efficiency and flexibility. Various process innovations have been reported to improve the separation performance of

PSA over the years, such as layered PSA (LPSA) process using multiple adsorbents in superimposed layers in the columns[8,9], multi-column PSA/VSA (vacuum swing adsorption) with pressure equalization (PE) step[10], PSA process involving a displacement step by a more adhesive gas[11], pressure temperature swing adsorption (PTSA)[12], integrated adsorption and absorption process[13] and the dual reflux PSA (DR-PSA)[14].

The Dual-reflux PSA (DR-PSA) with a lateral feed and two reflux streams was first proposed by Hirose[15] and Leavitt[16] to overcome the process limitations (stripping or enriching limitation[14]) and achieve both high purity and recovery. The four standard DR-PSA configurations were identified by Kearns et al.[17], which are schematically shown in Fig. 1, i.e. PH-A, PL-A, PH-B and PL-B. Following the seminal DR-PSA apparatus demonstrated by Diagne et al.[14,18,19], extensive experimental results have indicated the potential and efficacy of DR-PSA processes at the separation of different binary mixtures, such as air separation[20,21], hydrocarbon concentration[22-28] and $CO_2$ capture[29-32].

Several simulation studies on DR-PSA have been reported, ranging from simplified analytical models[17,33-38] to rigorous non-isothermal numerical models [26-28,39-44]. Based on the equilibrium theory[45], simplified analytical models revealed critical insights into the operating parameters and separation performance of DR-PSA. However, the simplified assumptions of isothermal behavior, no axial pressure drop, complete separation and local equilibrium lead to inaccurate predictions and very limited application. The first non-isothermal numerical model of the DR-PSA process was constructed by Zhang et al.[40] to simulate the separation of $CH_4$ and $N_2$ using Norit RB3 activated carbon as adsorbents. The accuracy of this model was validated by experiments[24], and the root mean square deviations (RMSD) of the $CH_4$

concentrations were only 0.3 and 2.4 mol.% for the light and heavy products, respectively. Therefore, the rigorous non-isothermal numerical model is reliable for predicting the $CH_4/N_2$separation performance of DR-PSA.

Despite the success of DR-PSA for separating binary mixtures, a single-stage PSA process that can separate ternary mixtures and produce three product gases is yet to be developed. In this study, we proposed a novel triple-reflux PSA (TR-PSA) process, which is accomplished by introducing a middle product stream and a middle reflux stream along the adsorption columns of a conventional DR-PSA process, as shown in Fig. 2. The TR-PSA process is then demonstrated using non-isothermal numerical simulations in Aspen Adsorption. Ternary mixtures containing different concentrations of $CH_4$, $N_2$ and He, representing various industrially important gases, were used as feedstocks to investigate the characteristics of the TR-PSA cycles. A ternary mixture consisting of 70 mo.% $N_2$, 20 mol.% $CH_4$ and 10 mol.% was utilized to conduct parametric studies to gain further insight into the impacts of operating parameters on the separation performance of the TR-PSA process. The findings of TR-PSA may be extended to the design of multiple reflux PSA with more than one side-draw products under the same principle.

# Simulation Method

## Adsorption Isotherm Parameters

The Langmuir isotherm equation (Eq. 1) was used to describe the adsorption isotherms of pure $CH_4$ and $N_2$ on Norit RB3, with isotherm parameters calculated by Zhang et al.[40]. Due to its highly inert nature, the adsorption capacity of helium at ambient temperature on carbonaceous adsorbents is negligible. Here, the isotherm parameters of He was determined by fitting the reported experimental data[46] with the Langmuir isotherm equation (Eq.1). Single-component isotherm parameters of $CH_4$,

He, and $N_2$ on this adsorbent are summarized in Table 1. These parameters were used in the extended Langmuir model (Eq. 2) to describe the competitive adsorption of $CH_4$, He and $N_2$ in gas mixtures.

$$Q^* = \frac{IP_1 \cdot exp\left(IP_2/T\right) \cdot p}{1 + IP_3 \cdot exp\left(IP_4/T\right) \cdot p} \quad \text{Eq.1}$$

$$Q_i^* = \frac{IP_{1,i} \cdot exp\left(IP_{2,i}/T\right) \cdot p_i}{1 + \sum_i \left(IP_{3,i} \cdot exp\left(IP_{4,i}/T\right) \cdot p_i\right)} \quad \text{Eq.2}$$

Fig. 3 shows the isotherms of $CH_4$, He and $N_2$ on activated carbon at 293 K, calculated using the isotherm parameters. The adsorption of $CH_4$ on this adsorbent is much stronger than that of He and $N_2$. The adsorption capacity of helium on Norit RB3 is close to zero, which is tally with the actual situation.

## Pressure Flow Network

The process flow diagram applied for the model construction and numerical simulation is depicted in Fig. 4. Each of the two identical columns is segmented into several sections in this model to represent side feed and side draws, the length of each section is determined according to the feed position, middle product extraction location and middle reflux inlet position. There are four external gas streams: "Feed", "Heavy product", "Light product", and "Middle product", which are specified as non-reversible flow with constant pressure. At CSS, the flowrate of feed gas is equal to the sum of flowrates of heavy, light and middle products due to the constraining of overall material balance. The flowrates of feed gas, heavy product and light product are specified directly, whereas the flowrate of middle product is automatically controlled by a proportional-integral-derivative (PID) controller (C1). The internal material cycle contains three reflux streams: the light, middle and heavy reflux streams. As for the internal material balance, the heavy reflux flowrate is constrained by the light and

middle reflux stream, which is ensured by introducing the PID controller (C2). C2 is used to satisfy the internal material balance by altering the volumetric flowrate through the compressor during the FE/PU step and to maintain a constant flowrate of around 1.5 x $10^{-4}$ $m^3/s$ (varied based on the pressure profiles of each simulation) for pressure reversal during the PR/BD step. C3 is only adopted when running the cases of DR-PSA process. The operating mode of each valve was varied at different steps of the TR-PSA cycle as listed in the supplementary Information (Table S.1). Three product tanks (i.e., $B_H$, $B_L$ and $B_M$ in Fig. 4) are used as surge tanks to buffer pressure and composition fluctuations. Other void tanks are added due to the "Pressure setter – Flow setter – Pressure setter" connection requirement in Aspen Adsorption[47] and represent the piping manifolds. Volumes for each of void tanks used in this model are summarized in the Supplementary Information (Table S.2).

The simulation parameters are listed in Table 2. As the adsorption of helium is negligible, the impact of its adsorption kinetics is insignificant. The mass transfer coefficient of helium is set at 0 $s^{-1}$. The simulation was initialized by setting the gaseous and adsorbed phase compositions everywhere within the PF network to be equal to the feed gas. The initial temperature throughout the network was specified as the ambient temperature (293 K). The initial pressures were set to be equal to either that of the low- or high-pressure column.

The governing equations of the adsorption column, model assumptions and equations for calculating component recoveries ($R_i$) are summarized in the Supplementary Information. These governing equations were discretized using the Upwind Differencing Scheme 1 (UDS1), a first-order differential scheme based on the first-order Taylor expansion with 100 grid nodes per adsorption column, which can ensure the accuracy of the calculated results, as can be inferred from Fig. S.2. The implicit

Euler integration method was adopted to solve the differential algebraic equation group with the MA48 linear solver and the mixed Newton nonlinear solver[47]. The error tolerance, used to determine convergence, is set as $10^{-5}$ for absolute and relative error tolerance. The cyclic steady state (CSS) criterion is the relative variation in the total loading and total solid temperature between two consecutive cycles lower than the CSS test tolerance[47], set as $10^{-5}$. The TR-PSA process simulation usually reached CSS after around 300 cycles (45,000 s integrator time), taking approximately 10 hours for computation of real time with 6 simulations running in parallel on an AMD 3900X 12-core processor. At CSS, the overall material balance error $\left|100\% \times (\text{in} - \text{out}) / \text{in}\right|$ was roughly 0.2% for all simulations, whereas the component material balance errors $\left|100\% \times (\text{in} - \text{out}) / \text{in}\right|$ of $CH_4$, He and $N_2$ were around 0.5%, 0.1% and 0.2%, respectively.

## Model Verification

The TR-PSA numerical model was first simplified to a standard DR-PSA simulation by closing all valves associated with the middle reflux/product stream, and utilized to simulate DR-PSA experiments reported by Saleman et al.[24] for the separation of $CH_4/N_2$ mixtures. Fig. 5 shows the comparison of simulated and experimental product compositions at CSS across 15 runs (run 4 – 18, where the $CH_4$ molar fraction of feed gas was 10.4 mol.%). The average root mean squared deviations (RMSD) between the experimental and predicted values of $CH_4$ molar fraction in the heavy product ($y_{H,CH4}$) and light product ($y_{L,CH4}$) were as low as 0.018 and 0.004, respectively, indicating the high accuracy of our model.

# Results and Discussion

## Conventional DR-PSA Cycle

The separation of the $CH_4/N_2$/He mixture was investigated with a conventional DR-PSA process using the method described in 2.3. Seven simulations were conducted with varying FE/PU step durations ($t_{FE/PU}$) from 30 s to 120 s to provide a reference for evaluating the new TR-PSA cycles. As shown in Fig. 6a, the molar fraction of He in the light product ($y_{L,He}$) remains relatively constant, achieving an enrichment ratio of 1.1. The $y_{L,CH4}$ increases gradually with the longer $t_{FE/PU}$ due to the gradual breakthrough of $CH_4$. Fig. 6b shows that increasing $t_{FE/PU}$ from 30 s to 120 s leads to the reduction of $y_{H,CH4}$ from 0.833 to 0.546 and the increase of both $y_{H,N2}$ and $y_{H,He}$ from 0.252 to 0.421 and 0.058 to 0.084, respectively. These results suggest that the conventional single-stage DR-PSA process is challenging to separate ternary mixtures because the medium component (nitrogen in this study) can significantly contaminate the light product (i.e., helium) as they are collected together in the same product tank, which can be avoided by adding another product stream and tank to separately collect the $N_2$ and He products or be solved by introducing a second stage of DR-PSA process to further separate the $N_2$/He mixtures.

Further insights into this process can be found in Fig. 7. For each component, profiles are given for 0 s, 15 s, and 30 s elapsed. As illustrated in Fig. 7a, the axial concentration profiles show high $CH_4$ concentration at the heavy end and high $N_2$ concentration at the light end. The feed gas enters the adsorption column during the FE step, leading to a discontinuity of composition at $Z$=0.5, where the compositions of the feed gas and upstream reflux are different.

Fig. 7b clearly shows the spatial difference for the front of the concentration profiles during the PU step. It can be seen that helium accumulates at the top of the high-

pressure column at the start of the PU step, and the concentration decreases sharply as the PU step proceeds. The $CH_4$ adsorption front reaches the light end of the adsorption column at $t$ =30 s, and hence, further extension of FE/PU step will lead to the breakthrough of $CH_4$. As shown in Figure 7b, the maximum concentration positions of $N_2$ and helium are quite different, Z of 0.8 and 0.9, respectively, at time 0 s. Therefore, we speculate that helium and nitrogen could be collected separately if an extra gas product line is added to the side of the column near the light end. It is also believed that accordingly the purity of $N_2$ and He can be significantly increased.

## TR-PSA Cycle

A middle product stream was introduced to the side of the conventional DR-PSA columns to side draw the $N_2$-rich gas and allow for side purge at the same location, hence the name triple-reflux (TR) PSA. The side-draw outlet was located at a position in the upper part of the adsorption column to collect a middle product ($N_2$ in this case) from the high-pressure column during the FE/PU step, and part of the middle product was injected into the low-pressure column as the middle reflux stream, i.e., the triple-reflux strategy. Parametric studies were conducted to investigate the effects of operating parameters such as feed step duration ($t_{FE/PU}$), heavy product to feed ratio ($H/F$), light product to feed ratio ($L/F$), the locations of feed inlet ($Z_F$), middle product outlet ($Z_{M,out}$) and middle reflux inlet ($Z_{M,in}$), the light reflux flowrate ($R_L$), and the middle reflux flowrate ($R_M$) on separation performance. In all cases, the feed flowrate was fixed at 1.25 SLPM (standard litre per minute) and the PR/BD step time was constant (45 s).

### Effect of Feed Step duration

Three ternary mixtures with different concentrations were used as the feed gas, containing the following compositions: (a) 3% He, 10% $CH_4$ and 87% $N_2$; (b) 5% He,

15% $CH_4$ and 80% $N_2$, and (c) 10% He, 20% $CH_4$ and 70% $N_2$. The effect of $t_{FE/PU}$ was studied by varying the FE/PU step duration between 30 s and 90 s. In all cases, the *H*/*F* ratio and *L*/*F* ratio were set to the same values as the molar fraction of methane and helium in the feed gas stream, respectively. The recovery of each component is equal to the purity in corresponding product streams, as described in the supplementary information.

The separation performance of the three groups of mixtures shows a similar trend, the purities of $CH_4$, He and $N_2$ in the corresponding product streams decrease with the increasing $t_{FE/PU}$, as illustrated in Fig. 8. For three different feed gases, the best purity results were all achieved at $t_{FE/PU}$ =30 s, the concentrations of $CH_4$ in the heavy, He in the light and $N_2$ in the middle product were enriched from 10% to 62.9%, from 3% to 39.0% and from 87% to 94.6%, respectively, for feed gas (a); from 15% to 67.9%, from 5% to 42.9%, and from 80% to 91.5%, respectively, for feed gas (b); and, from 20% to 70.3%, from 10% to 47.9%, and from 70% to 85.9%, respectively, for feed gas (c).

Fig. 9 shows the axial composition profiles in the adsorption column at the end of each stage for $t_{FE/PU}$ =30 s case and 90 s case with the feed compositions being 10% He, 20% $CH_4$ and 70% $N_2$. As shown in Fig. 9 a, the molar fraction of $CH_4$ at *Z*=0 (the heavy end) in the $t_{FE/PU}$ =30 s case is much higher than that in the $t_{FE/PU}$ =90 s case, leading to the higher $CH_4$ purity in the heavy product (70.3% versus 53.5%). The sharp increase of $CH_4$ concentration and dramatic decrease of He concentration at *Z*=0.9 were caused by the injection of the middle reflux stream due to the mixing. At the end of the PR step, as illustrated in Fig. 9 b, the He accumulates at *Z*=1, i.e., the light end, and higher He concentration can be obtained in $t_{FE/PU}$ =30 s case. The peak of $N_2$ concentration is located at the upper part of the adsorption column, moving from *Z*=0.7 to *Z*=0.9 during the PU step. The accumulated He is extracted from the high-pressure

column during the following PU step and collected as the light product. The $N_2$ concentration peaks at the Z values of 0.7 and 0.6 in the 30 s and 90 s cases, respectively. Fig. 9 c indicates the breakthrough of $CH_4$ in the high-pressure column. The adsorption fronts of $CH_4$ in both cases exceed the middle product outlet position, resulting in the severe loss of $CH_4$. During the BD step, the pressure in the column decreases, allowing the desorption of $CH_4$. Therefore, at the end of the BD step, the $CH_4$ concentration in the lower part of the column is high, especially at the heavy end, as presented in Fig. 9 d.

Fig. 10 indicates the bed temperature profile over a cycle at CSS calculated at three different nodes, T1 located at the top of the adsorption column (next to the void tank 6 in Fig. 4), T2 is at the middle of the column, and T3 is at the bottom of the column (next to void tank 10 in Fig. 4). The simulated temperature swing trend is consistent with the reported experimental results[24]. The highest temperature variation can be found at the middle of the column (T2), roughly 9 K and cannot be ignored. The high temperature during the PU step is due to the methane adsorption front passing through the middle of the bed, which agrees with the axial concentration profiles illustrated in Fig. 9. The decrease in temperature during the FE step is mainly caused by the desorption of methane. The temperature trend at the bottom of the column (T3) is similar to that of T2 but with generally lower values, caused by the alteration of internal flow direction at different steps and the thermal effect of adsorption/desorption process[24]. During the desorption steps (BD and FE, the endothermic steps), T3 is at the downstream position and the cold stream flows downward; in contrast, during the adsorption steps (PR and PU, the exothermic steps), T3 is at the upstream location and the hot stream flows upward, as the flow direction shown in Fig. 9. The temperature at the top of the column (T1) varies to a much less extent than T2 and T3

because this part of column is mainly occupied by nitrogen and helium, which have lower enthalpies of adsorption.

To further enhance the separation performance of the TR-PSA process, the aforementioned $CH_4$ breakthrough phenomenon must be avoided and a further parametric study is required. The feed gas containing 10% He, 20% $CH_4$ and 70% $N_2$ was selected to conduct the following parametric study.

**Effect of feed inlet position**

For the TR-PSA and DR-PSA cycles, the feed gas is injected into the column at a lateral intermediate position. The concentration of components in the feed gas stream is generally different from that in the upstream reflux flow, resulting in the so-called "mixing problem", which manifests as the discontinuity of axial concentration curves at the injection position. The mixing problem has been reported and investigated in the open literature [23,42,44,48] and have been confirmed to have negative impacts on the separation performance of the process. The effect of feed position ($Z_F$) was investigated by changing the $Z_F$ between 0.4 and 0.9. As shown in Fig. 10, when the feed position moves towards the light end, the $CH_4$ product purity rises first, reaching a maximum of 70.6% at $Z_F$ =0.6, followed by a slight decline. The purity of He and $N_2$ product shows a similar trend, except that the optimum purity is 48.2% at $Z_F$ =0.6 for helium product and 86.2% at $Z_F$ =0.7 for nitrogen product, respectively. The impact of the $Z_F$ on product purity is minimal, within ±0.6% for $CH_4$ purity in the heavy product, ±0.2% for He purity in the light product and ±0.2% for $N_2$ purity in the middle product. As shown in Fig. 9a, the perturbation at $Z$=0.9 (the middle reflux inlet position) is apparently more server than at 0.5 (the feed inlet position). Therefore, the lateral injection of middle reflux stream dominates the effect on axial concentration distribution, making the impact of feed inlet position can be ignored. However, the $Z_F$

determines the left boundary of the middle reflux inlet position ($Z_{M,in}$). Since the $N_2$ concentration of middle reflux is always higher than that of the feed flow, the middle reflux inlet position should be closer to the light end of the column and above the feed location, as depicted in Fig. 2.

**Effect of Middle outlet/inlet Position**

The impact of the middle product outlet position ($Z_{M,out}$) on purities of three product streams is displayed in Fig. 11. Results indicate that the $Z_{M,out}$ has a significant impact on the separation performance of the TR-PSA process. When the $Z_{M,out}$ value is decreasing (i.e. the middle outlet position moving from the light end to heavy end), the He purity of light product increases sharply from 13.2% to a plateau of roughly 76.8%. Meanwhile, the $CH_4$ purity of heavy product reduces steadily from 79.2% to 30.3%. The maximum $N_2$ purity (87.1%) is obtained at $Z_{M,out}$ =0.8. This can be explained by analyzing the axial concentration profiles, as shown in Fig. 7c, methane occupies the bottom half part of the column, whereas helium accumulates at the top of the column. As indicated in Fig. 7b (at the end of the PR step, namely, the start of the PU step) and Fig. 7c (at the end of PU step), the peak of nitrogen concentration is between the range of Z=0.7 – 0.9 during the PU step ( $N_2$ product is extracted from the high-pressure column). Hence, the maximum $N_2$ product purity was obtained when $Z_{M,out}$ is around at 0.8, the middle position of the range 0.7 – 0.9. When the $Z_{M,out}$ moves forwards to the heavy end, methane will gradually dominate the gas composition, leading to more methane escaping with the middle product and ultimately reducing the purity of the heavy product gas due to the constraint of component material balance. Conversely, more helium is lost when the $Z_{M,out}$ approaches closer to the light side, revealing a tradeoff between the recovery of methane and helium. It should be noted that the case of $Z_{M,out}$ =1.0 is equivalent to collecting light and middle products together

since the $N_2$ and He are already mixed in the tank (void tank 6 or 7 in Fig. 4) before being split into two product streams, hence, the results of this case are equivalent to those of the conventional DR-PSA cycle. The notable difference between results at $Z_{M,out}$ =0.9 and 1.0 demonstrates the importance of collecting $N_2$ and He separately to enhance the separation performance of TR-PSA process.

Fig. 12 shows the purities of $CH_4$, He and $N_2$ in its product streams with different middle reflux inlet positions ($Z_{M,in}$). When the $Z_{M,in}$ increases (the middle inlet position shifts up to the light end) from 0.5 to 1.0, the $CH_4$ product purity increases by 6.2%. The He product purity reduces gradually with an increasing $Z_{M,in}$. The $N_2$ product purity first ascends slowly with the increasing $Z_{M,in}$, peaks at $Z_{M,in}$ =0.8 with a value of 86.5%, and then decreases slightly. The impact of middle reflux inlet position on the separation performance is due to the previous mentioned “mixing problem”. When reducing the $Z_{M,in}$, the middle reflux stream will be admitted to the column at a position near the heavy end, the impact of perturbation on heavy product will be predictably more significant and leading to the decrease in $CH_4$ product purity, in contrast, the increase of $Z_{M,in}$ will have a more apparent impact on the He product purity. It is worthy to note that the case of $Z_{M,in}$ =0.5 and 1.0 are two particular conditions, where the middle reflux stream is mixed with feed gas and light reflux stream in the void tank, respectively, and then flows into the adsorption column. The results under these operating conditions indicate the primary factors that affect the separation results are the concentration and inlet position of the lateral inflow gas, rather than the number of inflowing gas streams.

**Effect of Heavy/Light Product to Feed Flow Ratio**

The ratios of the heavy product to feed ($H/F$) and light product to feed ($L/F$) are crucial operating parameters, which determine the theoretical boundary of heavy and light

product purity, described by Eq. S.15 – 16 in the Supplementary Information. The effects of *H*/*F* and *L*/*F* on the separation performance were investigated separately by varying the molar flowrate of the heavy or light product. The overall material balance was ensured by modifying the molar flowrate of middle product stream, which was automatically controlled by the PID controller. Since the heavy/light product to feed flow ratio will differ from the molar fraction of $CH_4/N_2$ in the feed gas, the recovery of each component cannot be directly represented by its purity in the corresponding product stream (as described by Eq. S. 9 – 11). Therefore, the additional recovery results will be provided in the following discussions.

The arrows in Fig. 13 indicate to which target the TR-PSA process is adjusted by varying the *H*/*F* ratio. In this part of simulation, the flowrate of light product was constant at 0.125 SLPM (i.e., *H*/*F* = 0.1). As shown in Fig. 13a, raising the *H*/*F* ratio from 0.1 to 0.4 causes a decrease in the purity of $CH_4$ product from 69.0% to 48.5%, which is limited by the component material balance of $CH_4$. The $N_2$ purity in middle product gas rises from 78.7% to 93.0% with the increasing *H*/*F* ratio. The *H*/*F* ratio has minimal impacts on the helium product purity, leading to only a decrease of 2% in the light product purity when the *H*/*F* ratio ascends from 0.1 to 0.4. Fig. 13 b describes that the recovery of $CH_4$ increases dramatically from 36.9% to 95.5% with the growth in *H*/*F* ratio. Increasing the *H*/*F* ratio reduces the $N_2$ recovery from 90.3% to 63.9%, due to the rising $N_2$ concentration in the heavy product gas and the higher heavy product flowrate, which results in a massive loss of $N_2$. Since the flowrate of helium product is fixed here, the variation of recovery should be consistent with the purity (refer to Eq. S.10 in Supplementary Information), reducing roughly by 2%. The *H*/*F* = 0.3 can be regarded as the optimum condition that both high $CH_4$ purity and recovery can be obtained.

Fig. 14 reflects the impact of *L*/*F* ratio on the separation performance of the TR-PSA process. Here, heavy reflux flowrate was set constant at 0.25 SLPM (i.e., *H*/*F* = 0.2). As shown in Fig. 14, decreasing the *L*/*F* ratio contributes to the elevation of He purity in light product (increase proportionally from 28.6% to 58.5%) at the sacrifice of He recovery (decrease by 71.2%). When increasing the *L*/*F* ratio, the purity of $N_2$ product ascends from 82.8% to 88.0% and then remains stable, whereas the $N_2$ recovery decrease gradually due to the reduction of middle product flowrate. The influence of *L*/*F* ratio on $CH_4$ purity and recovery can be ignored with a variation of only 2%.

When the *L*/*F* ratio increases, more helium is extracted from the system to the light product stream, hence, we can observe the slight decrease of helium concentration in the heavy stream, as listed in Table 3. However, even for the case of *L*/*F* = 0.3, the concentration of He in the heavy product stream is still a bit high, accounting for 47.7% of the total helium loss. The massive He escaping from the heavy end is probably due to the relatively high flowrate of reflux stream from the high-pressure column (light reflux flowrate is 1 SLPM and middle reflux flowrate is 2.5 SLPM), making the breakthrough of helium be unavoidable.

Since the adsorption of He in the column is negligible, it is challenging to prevent the escape of helium from the heavy end during the FE step (i.e., the low-pressure column). To minimize the loss of He, we need to find the appropriate *H*/*F* and *L*/*F* ratios, which can yield relatively high product purity and recovery of both $CH_4$ and He. Additionally, identifying the proper light and middle reflux flowrates, which can concurrently satisfy the regeneration requirement of the adsorption column and can avoid the severe breakthrough of He at the heavy end, is another effective method.

**Effect of Light and Middle Reflux to Feed flow Ratio**

The reflux ratio is a crucial operating parameter for the separation performance of gases using the TR-PSA process. Saleman et al.[24] suggested that the main role of the light reflux flow for the DR-PSA process is to assist the desorption of loaded heavy component from the low-pressure bed, meanwhile, an equivalent amount of heavy reflux flows into the high-pressure bed due to the internal flow balance leading to an increase in the usage rate of adsorption beds[25]. There is generally an optimum light reflux flowrate ensuring adequate desorption without causing the breakthrough in each bed. In the TR-PSA process, the internal flow cycle contains three streams, i.e., the light reflux, middle reflux and heavy reflux. The heavy reflux flowrate is highly constrained by flowrates of light and middle reflux and adjusted directly by a PID controller. Therefore, here we only separately investigate the influence of light reflux and middle reflux to process performance. The light reflux stream is introduced from the light product tank with the high concentration of He, and the impact of light reflux ratio ($R_L/F$) is investigated by changing the flowrate specification of light reflux stream. Fig. 15 shows that the helium product purity rises to the peak (45.2%) at $R_L/F$ = 0.2, followed by the gradual decline when raises the $R_L/F$ ratio. The maximum $N_2$ purity is 95.9% at $R_L/F$ = 0.5. The purity of $CH_4$ in the heavy product goes up steadily with the increasing $R_L/F$ ratio. The variation trend of recovery as a function of the light reflux to feed ratio should be the same as the purity. The ratio of results between recovery and purity is constant, 1.5 for $CH_4$, 2 for He and roughly 0.714 for $N_2$ (with neglectable fluctuations caused by the minimal material balance error of simulations), which can be deduced from Eq. S. 9 – 11.

The compositions of three product streams are summarized in Table 4. The light reflux stream assists the regeneration of the $N_2$-loaded adsorbent, thus facilitating the

separation of $N_2$ and He in the PU step (in the high-pressure bed), explaining why the growth of light reflux flowrate leads to the increase in helium purity when the $R_L/F$ is lower than 0.2. However, further raising the $R_L/F$ ratio leads to an elevated helium concentration in the heavy product (from 1.8% to 4.3%), exacerbating the helium fugitive from the heavy end. Although increasing the $R_L/F$ helps to improve the $CH_4$ purity, its negative impact on light product should also be considered as helium is also an important target gas in this study. Hence, $R_L/F$ = 0.5 (i.e., $R_L$ =0.625 SLPM) is regarded as the optimum value to obtain both relatively high $CH_4$ purity and He purity and will be used in the subsequent investigation to optimize the middle reflux flowrate. The effect of middle reflux to feed ratio was studied by varying the molar flowrate of middle reflux ($R_M$). Fig. 16 illustrates that both the highest product purity and recovery of $CH_4$ (60.6% and 90.8%, respectively) can be obtained at $R_M/F$ ratio of 2.0. The $N_2$ purity and recovery peak at 95.9% and 68.2% when $R_M/F$ =1.5, respectively. Increasing the $R_M/F$ ratio leads to a gradual reduction in He product purity (from 46.9% to 42.6%) and recovery (from 95.1% to 85.3%), suggesting that an appropriate $R_M/F$ ratio is crucial for ensuring both high recovery of methane and helium. $R_M/F$ =0 is a particular operating condition, which means that the middle reflux flowrate is zero, i.e., a special DR-PSA process with $N_2$ side-drawn product stream but without the middle reflux stream. According to the preliminary simulations results (Table S.3), it is challenging for this process to balance the capture between $CH_4$ and He due to that the regeneration of adsorbents in low-pressure (FE) column and pushing partial $CH_4$ product gas flowing into the high-pressure (PU) column as the heavy reflux stream can only be accomplished by the light reflux. Since the heavy reflux flowrate is only constrained by the light reflux flowrate, a high light reflux flowrate is generally required to satisfy the threshold heavy reflux flowrate for providing adequate $CH_4$ to be

adsorbed in the PU column to elevate the degree of $CH_4$ enrichment, which simultaneously leads to the severe breakthrough of He in the FE column. However, in the TR-PSA process, heavy reflux flowrate is constrained by flowrates of light reflux and middle reflux, therefore, the middle reflux stream can buffer the conflict between the high heavy reflux flowrate demand and the low light reflux flowrate requirement, balancing between the enrichment of $CH_4$ and capture of He better than the process without the middle reflux stream.

The reflux flowrates also have a significant impact on the energy consumption of the compressor (estimated as a single-stage isentropic compressor in this research) in per cycle, as described in the supplementary information (Eq. S17). The specific energy consumption for per mole captured $CH_4$ and He shows approximately as a linear function of the $R_M/F$ ratio, as plotted in Fig. 17. When the $R_M/F$ ratio increases from 0.0 to 3.0, both specific energy consumptions are nearly doubled. When $R_M/F$ =0, there is still a certain amount of compressor duty, mainly caused by the energy consumption for the pressure reversal between two columns and pressurizing the heavy reflux gas (due to the presence of light reflux flow) from low pressure (1 bar) to high pressure (5 bar). Here, we take the separation performance at $R_M/F$ =1.0 as the optimum results, where a heavy product containing 60.0 % $CH_4$ with a recovery of 90.4% and specific energy consumption of 0.274 $MJ \cdot mol^{-1}$ captured $CH_4$, a light product containing 45.3 % He with a recovery of 91.3% and specific energy consumption of 0.543 $MJ \cdot mol^{-1}$ captured He and a middle product containing 95.8 % $N_2$ can be obtained.

**Comparison between TR-PSA and 2-stage DR-PSA processes**

The simulation of the 2-stage DR-PSA process was conducted by combining two DR-PSA units in series. The parameters of adsorption columns were the same as the TR-

PSA unit, as summarized in Table 2. Fig. 18 displays the schematic diagram of 2-stage DR-PSA process, the light product stream obtained from the first-stage DR-PSA unit was used as the feed gas in the second-stage DR-PSA unit, where the helium and nitrogen mixture were separated into the He dominant product and $N_2$ dominant product. The feed flowrate and step duration of 2-stage DR-PSA cycle was set to be the same as the TR-PSA cycle, i.e., feed flowrate is 1.25 SLPM, FE/PU step time is 30 s and PR/BD step time is 45 s. As discussed previously, the product to feed flow ratio will determine the upper limit of product purity, hence, in the simulation of 2-stage DR-PSA process, the flowrates of $CH_4$-dominant and He-dominant product streams were adjusted to be the same as in the TR-PSA cycle. Therefore, the main optimization of 2-stage DR-PSA process was tuning the reflux flowrate. For the first stage, an optimized light reflux flowrate was identified to obtain both high $CH_4$ purity and low He concentration in the heavy product to minimize the flow of $CH_4$ into the second stage and to avoid excessive He lost in the first stage. Meanwhile, an optimal reflux flowrate can be determined to obtain the highest helium purity for the second stage. Here, only the optimum result of 2-stage DR-PSA cycle was selected for comparison with the TR-PSA cycle, and all simulation results of 2-stage DR-PSA process were provided in the Supplementary Information with detailed operating conditions. At CSS, the overall material balance error of 2-stage DR-PSA simulations is around 0.2%, whereas component material balance error is 0.8%, 0.6% and 0.4% for $CH_4$, He and $N_2$, respectively.

Fig. 19 highlights the achieved performance and specific work of both TR-PSA and 2-stage DR-PSA processes. The 2-stage DR-PSA process achieved a bit higher $CH_4$ product purity (61.4% versus 60.0%) and $CH_4$ recovery (92.1% versus 90.4%). Whilst the TR-PSA process could obtain slightly better product purity and recovery of He

(45.3% purity with a recovery of 91.3 %) than the 2-stage DR-PSA process (purity is 44.8% and recovery is 89.7%). Overall, the separation performance of TR-PSA is comparable to that of 2-stage DR-PSA process in terms of the capture of $CH_4$ and He. As for the comparison of compressor duty, TR-PSA process only requires a cycle work of 49.6 kJ/mol (feed), which is significantly (30%) lower than the specific work of the 2-stage DR-PSA process (64.3 kJ/mol (feed)) due to the use of one compressor in TR-PSA versus two in the 2-stage DR-PSA system. Therefore, for the conditions considered in this work, TR-PSA shows remarkable advantages compared to 2-stage DR-PSA in terms of capital investment and energy consumption and guarantees a comparable separation performance.

## Conclusion

In this work, we have developed and demonstrated a novel triple-reflux pressure swing adsorption (TR-PSA) process to obtain three high purity products from ternary mixtures within a single stage. A non-isothermal, non-adiabatic numerical model of the TR-PSA cycle was developed using Aspen Adsorption to investigate its performance for separating the mixtures of He, $CH_4$, and $N_2$. Parametric studies were performed to investigate the effect of concentration of the feed gas, feed step duration ($t_{FE/PU}$), feed inlet position ($Z_F$), middle inlet/outlet position ($Z_{M,out}$ and $Z_{M,in}$), heavy/light product to feed ratio ($H/F$ and $L/F$) and the reflux flowrate to feed ratio ($R_L/F$ and $R_M/F$) on the separation performance. Results showed that the TR-PSA process could effectively separate ternary mixtures into three high-purity products by a single-stage PSA process. For the separation of a ternary mixture containing 10% He, 20% $CH_4$ and 70% $N_2$, we can obtain a heavy product with 60.0 % purity and 90.4% recovery of $CH_4$, a light product containing 45.3 % He with a recovery of 91.3% and a middle product of 95.8 % $N_2$ with a recovery of 68.9%, with the specific work of 49.6 kJ $mol^{-1}$ (feed).

The TR-PSA process can deliver comparable separation performance of the 2-stage DR-PSA process with significantly lower capital and energy costs. Based on the concept of this study, the design of "multi-reflux" might be further extended to accomplish the separation of gas mixtures with more than three components as long as the concentration front of each component is sharp enough.

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## Notation

| | | | |
|---|---|---|---|
| $C_{pai}$ | specific heat capacity of the adsorbed gas | $R_M$ | standard volumetric flow rate of middle reflux |
| $C_{ps}$ | specific heat capacity of the adsorbent | $r_p$ | particle radius |
| $C_{pw}$ | specific heat capacity of the wall | $t_{FE/PU}$ | feed/purge step duration |
| $C_{vg}$ | specific gas phase heat capacity at constant volume | $t_{PR/BD}$ | pressurization/blowdown step duration |
| $c_i$ | molar fraction of component *i* | $T$ | gas temperature |
| $D_B$ | internal diameter of column | $T_{env}$ | environmental temperature |
| $F$ | standard volumetric flow rate of feed | $T_s$ | adsorbent temperature |
| $H$ | standard volumetric flow rate of heavy product | $T_w$ | column wall temperature |
| $H/F$ | heavy product to feed flow rate ratio | $V_i$ | the volume of component *i* |
| $h_b$ | heat transfer coefficient between column and ambient | $v_g$ | superficial gas velocity |
| $h_{gs}$ | heat transfer coefficient between gas and solid | $W_r$ | wall thickness |

| | | | |
|---|---|---|---|
| $h_w$ | heat transfer coefficient between gas and wall | $x$ | axial distance coordinate |
| $IP_{Xi}$ | isotherm parameter $X$ for component $i$ | $y_{F,i}$ | the concentration of component $i$ in the feed gas |
| $k_i$ | constant mass transfer coefficient of component $i$ | $y_{H,i}$ | the concentration of component $i$ in the heavy product |
| $k_g$ | heat conductivity of gas | $y_{M,i}$ | the concentration of component $i$ in the middle product |
| $k_s$ | heat conductivity of adsorbent | $y_{L,i}$ | the concentration of component $i$ in the light product |
| $k_w$ | heat conductivity of wall | $Z$ | dimensionless axial position along the bed |
| $L$ | standard volumetric flow rate of light product | $Z_F$ | feed inlet position |
| $L/F$ | light product to feed flow rate ratio | $Z_{M,in}$ | middle reflux inlet position |
| $M$ | standard volumetric flow rate of middle product | $Z_{M,out}$ | middle product outlet position |
| $m_{ads}$ | the mass of the adsorbent | $\alpha_p$ | specific particle surface area per unit length of bed |
| $M_W$ | molecular weight of gas mixture | $\Delta H_i$ | enthalpy of adsorption for component $i$ |
| $n_i$ | molar of component $i$ | $\Delta M$ | overall material balance error |
| $P$ | gas pressure | $\Delta M_i$ | material balance error for component $i$ |
| $P_H$ | high pressure | $\varepsilon_i$ | bed voidage |
| $P_L$ | low pressure | $\varepsilon_p$ | particle voidage |
| $p_i$ | partial pressure of component $i$ | $\mu_g$ | viscosity of gas mixture |
| $Q_i$ | adsorbent loading of component $i$ per unit mass of adsorbent | $\rho_b$ | bulk density of adsorbent |
| $Q_i^*$ | adsorbent loading of component $i$ per unit mass of adsorbent in equilibrium with its partial pressure in gas phase | $\rho_g$ | gas molar density |
| $R$ | universal gas constant | $\rho_w$ | column wall density |

| | | | |
|---|---|---|---|
| $r$ | radial coordinate of the adsorbent | $\psi$ | particle shape factor |
| $R_L$ | standard volumetric flow rate of light reflux | | |

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## List of Figure Captions

Fig. 1 Schematic diagram of DR-PSA configurations: feed to high- (PH) or low-pressure (PL) column and pressure reversal with the heavy (i.e., the more adsorbable, A) or light (i.e., the less adsorbable, B) adsorbate.

Fig. 2 Schematic diagram of the TR-PSA process. FE: feed. PU: purge. PR: pressurization. BD: blowdown. Valves in solid represent close.

Fig. 3 Isotherms of pure $CH_4$, He and $N_2$ on Norit RB3 activated carbon at 293 K.

Fig. 4 Process flow diagram of the TR-PSA model during FE/PU step in the PL-A configuration. Solid and open valves indicate close or open positions, respectively.

Fig. 5 Comparison of experimental and simulated $CH_4$ molar fraction in light and heavy products.

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Fig. 7 Concentration profiles of gas phase inside the adsorption column during FE (a) and PU (b) step for a conventional DR-PSA cycle with following operating parameters: $R_L/F$ = 2.5, $H/F$ = 0.2, $t_{FE/PU}$ = 30 s, $t_{PR/BD}$ = 45 s and $Z_F$ = 0.5.

Fig. 8 The impact of $t_{FE/PU}$ on the purity of $CH_4$, He and $N_2$ in the corresponding product streams, feed compositions are: a) 3% He, 10% $CH_4$ and 87% $N_2$; b) 5% He, 15% $CH_4$ and 80% $N_2$; c) 10% He, 20% $CH_4$ and 70% $N_2$. Operating parameters: $Z_F$ = 0.5, $Z_{M,out}$ = $Z_{M,in}$ = 0.9, $R_L/F$ = 1 and $R_M/F$ = 2.

Fig. 9 Axial composition profiles in the column at the end of FE (a), PR (b), PU(c) and BD (d) steps. The solid line indicates $t_{FE/PU}$ = 30 s case, and the dashed line indicates $t_{FE/PU}$ = 90 s case. Other operating parameters: $Z_F$ = 0.5, $Z_{M,out}$ = $Z_{M,in}$ = 0.9, $R_L/F$ = 1 and $R_M/F$ = 2. Annotation of gas streams: 1) feed flow in; 2) mid reflux flow in; 3) light reflux flow in; 4) heavy product flow out; 5) heavy reflux flow in; 6) mid product flow out; 7) light product flow out and red/blue indicates gas streams entering/leaving the column.

Fig. 10 Temperature profile over a cycle at CSS, feed compositions are 10% He, 20% $CH_4$ and 70% $N_2$. Operating parameters are as follows: $Z_F$ = 0.5, $Z_{M,out}$ = $Z_{M,in}$ = 0.9, $t_{FE/PU}$ =30 s, $R_L/F$ = 1 and $R_M/F$ = 2.

Fig. 11 Purities of $CH_4$, He and $N_2$ in the corresponding product streams under varying $Z_F$. Operating parameters: $Z_{M,out}$ = 0.9, $Z_{M,in}$ = 0.9, $t_{FE/PU}$ =30 s, $H/F$ =0.2, $L/F$ =0.1, $R_L/F$ = 1 and $R_M/F$ = 2.

Fig. 12 Purities of $CH_4$, He and $N_2$ in the corresponding product streams under varying $Z_{M,out}$. Other operating parameters are set as: $Z_F$ = 0.5, $Z_{M,in}$ = 0.9, $t_{FE/PU}$ =30 s, $H/F$ =0.2, $L/F$ =0.1, $R_L/F$ = 1 and $R_M/F$ = 2.

Fig. 13 Purities of $CH_4$, He and $N_2$ in the corresponding product streams under varying $Z_{M,in}$. Other operating parameters are set as flows: $Z_F$ = 0.5, $Z_{M,out}$ = 0.9, $t_{FE/PU}$ =30 s, $H/F$ =0.2, $L/F$ =0.1, $R_L/F$ = 1 and $R_M/F$ = 2.

Fig. 14 The product purity (a) and recovery (b) of $CH_4$, He and $N_2$ as a function of $H/F$ ratio. The arrows indicate the direction in which the $H/F$ ratio should be varied to bias the separation performance favouring the $CH_4$ purity or the $CH_4$ recovery. Operating parameters: $Z_F$ = 0.5, $Z_{M,in}$ = $Z_{M,out}$ = 0.9, $t_{FE/PU}$ =30 s, $L/F$ = 0.1, $R_L/F$ = 1 and $R_M/F$ = 2.

Fig. 15 The product purity (a) and recovery (b) of $CH_4$, He and $N_2$ as a function of $L/F$ ratio. The arrows indicate the direction in which the $L/F$ ratio should be varied to bias the separation performance favouring the He purity or the He recovery. Operating parameters: $Z_F$ = 0.5, $Z_{M,in}$ = $Z_{M,out}$ = 0.9, $t_{FE/PU}$ =30 s, $H/F$ = 0.2, $R_L/F$ = 1 and $R_M/F$ = 2.

Fig. 16 The impact of $R_L/F$ on the product puritiy (a) and recovery (b) of $CH_4$, He and $N_2$. Operating parameters: $Z_F$ = 0.5, $Z_{M,in}$ = $Z_{M,out}$ = 0.9, $H/F$ = 0.3, $L/F$ = 0.2 and $R_M/F$ = 2.

Fig. 17 The product purity (a) and recovery (b) of $CH_4$, He and $N_2$ as a function of $R_M/F$ ratio. Operating parameters: $Z_F$ = 0.5, $Z_{M,in}$ =$Z_{M,out}$ = 0.9, $t_{FE/PU}$ =30 s, $H/F$ = 0.3, $L/F$ = 0.2 and $R_L/F$ = 0.5.

Fig. 18 Specific energy consumption for per mole captured $CH_4$ and He as a function of $R_M/F$ ratio. Constant operating parameters: $Z_F$ = 0.5, $Z_{M,out}$ = 0.9, $t_{FE/PU}$ =30 s, $H/F$ = 0.3, $L/F$ = 0.2 and $R_L/F$ = 0.5.

Fig. 19 Schematic diagram of the double-stage DR-PSA process (two PL-A configurations).

Fig. 20 Comparison of optimal separation performance and specific work of TR-PSA and 2-stage DR-PSA processes. Operating parameters for the TR-PSA cycle: $Z_F$ = 0.5, $Z_{M,out}$ = $Z_{M,in}$ = 0.9, $t_{FE/PU}$ =30 s, $H/F$ = 0.3, $L/F$ = 0.2, $R_L/F$ = 0.5 and $R_M/F$ = 1.0. Operating conditions for the 2-stage DR-PSA cycle: feed positions are fixed at exact middle of the adsorption bed for both stages, light reflux flowrate is 1 SLPM for first stage and 0.4 SLPM for the second stage, $t_{FE/PU}$ =30 s, methane product flowrate is 0.375 SLPM (i.e., $H/F$ = 0.3) and helium product flowrate is 0.25 SLPM (i.e., $L/F$ = 0.2).