Dynamic Simulation and Optimization of Nitrogen Rejection and Helium Recovery by Dual Reflux Pressure Swing Adsorption for Liquefied Natural Gas Production

Yuan Zou

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Summary

The demand for natural gas as an energy source is expected to grow substantially in future because natural gas presents many environmental advantages over conventional oil and coal fuels. Virtually all natural gas contains some level of nitrogen impurity, which lowers the heating value and needs to be rejected to meet sales gas specifications. Natural gas is also the only viable source for production of helium, a unique gas with a wide range of industrial, scientific and medical applications. Both nitrogen and helium are difficult diluents to separate from natural gas with cryogenic distillation being the conventional technology applied. Pressure swing adsorption (PSA) is a proven technology for small scale operation to save vast capital costs, but there remains scope to develop higher performance PSA processes to improve the gas plant efficiency.

A review showed the potential of an emerging dual reflux PSA process (DR PSA), which recycles both products simultaneously, to facilitate more efficient recovery and refinery of hydrocarbons than the conventional PSA cycles because its separation power is not confined thermodynamically by the pressure ratio input. It was also identified that the DR PSA models presented in the literature are simplified to isothermal conditions and indicate a specific opportunity for improvement in prediction accuracy. In this work, dynamic simulations of DR PSA process were constructed, with the fixed bed dynamics involving rigorous energy balance across over gas, solid and bed wall phases. It was benchmarked against a set of most detailed results of DR PSA experiments available in literature, and shown to be capable of comprehensively reproducing a real DR PSA process. The cycle sequence of the model was fully automated by a customized program which included a pressure control algorithm allowing for self-estimation of the speed of the gas compressor required for a certain cycle configuration.

The DR PSA model was improved with addition of bed pressure regulating modules to adapt specifically a pilot scale DR PSA unit constructed at UWA, for which experiments were targeted at commercially available, non-proprietary adsorbents that have the potential for CH₄ + N₂ separations. The reliability and robustness was verified by benchmarking against two sets of experimental CH₄ + N₂ separations, which respectively, involved the test of equilibrium
The performance of DR PSA upgrading of subquality natural gas (75 % CH₄ + 25 % N₂) was comparably assessed with simulation between the most promising adsorbents Norit RB3 and CMS 3K-172, through conducting a series of cycle optimizations. It was found that an optimum would occur at a moderate feed time or light reflux flow rate, at which the breakthrough was reduced to a minimum. The adjustment of heavy product flow rate could be used to shift the separation towards more extract or raffinate oriented nature as required. Specially, with the insights provided by the simulation, a set of parametric variations of sorption rate revealed that the kinetic separation of methane and nitrogen mixture using CMS 3K-172 was strongly limited by the slow sorption rate of nitrogen rather than its selective adsorption over methane. More importantly, this adsorbent comparison demonstrated that for the N₂ rejection application, an equilibrium CH₄ selective adsorbent in a DR PSA process works as well or better than a kinetically N₂ selective adsorbent. That is, the magnitude of selectivity, rather than the choice of component to be physically eliminated, dictates the DR PSA separations.

The optimized Norit RB3 cycle of DR PSA separation of 75 % CH₄ +25 % N₂ mixture was further modified in bed geometry and tested in simulation at an industrial flow scale. A review of industrial method for adsorption bed sizing identified that the determination of bed height, as a summation of saturate zone and mass transfer zone (MTZ) heights, was the key step. In this work, we presented a second and simplified method to replace the saturated zone with an effective bed capacity which included the MTZ effect and feed condition corrections, and the pressure drop can be checked graphically through the simulated ΔP-L_{bed} correlations. This method was found adequate for the DR PSA separation of CH₄ + N₂ mixtures, suggesting it as an effective tool of using the simulation outcome towards industrial commission of DR PSA
techniques. The choice of feed inlet position was examined with simulation, and by means of bed composition distribution, the existence of an optimal feed inlet position at the exact middle of the bed was confirmed.

The last chapter presented a preliminary simulation of a four step DR PSA cycle using Norit RB3 as the adsorbent to recover helium from a nitrogen-rich stream at feed helium compositions representative of the light ends from a cryogenic nitrogen rejection unit. The impact of N₂ presence as a heavy component in the feed was found to be akin to that of CH₄ through the separations of binary feed containing 4 % helium in CH₄ or N₂, which under several cycle conditions yielded a helium raffinate up to 40 % purity with 68 % He recovery. Better performance, comparable to that obtained by cryogenic distillation, could be expected through a combination of reduced feed time and light reflux flow rate. For a ternary system comprising of 4 % He, 26 % CH₄ and 70 % N₂, the study on the cyclic evolution of composition distribution suggested that improvements could also be made by introducing a nitrogen vent port to a selected bed axial position to mitigate its contamination of the helium raffinate.
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Nomenclature

\( a_p \) = specific particle surface per unit volume bed \([m^2(\text{particle area})/m^3(\text{bed})]\)

\( C \) = gas phase concentration \([\text{kmol/m}^3]\)

\( c_i \) = concentration of component \( i \) \([\text{kmol/m}^3]\)

\( C_{p_{\text{a,i}}} \) = specific heat capacity of adsorbed phase of component \( i \) \([\text{MJ/kmol/K}]\)

\( C_{p_s} \) = specific heat capacity of adsorbent \([\text{MJ/kmol/K}]\)

\( C_{p_w} \) = specific heat capacity of wall \([\text{MJ/kg/K}]\)

\( C_{V_g} \) = specific heat capacity of gas phase at constant volume \([\text{MJ/kmol/K}]\)

\( D_B \) = bed layer diameter \([\text{m}]\)

\( D_{m,i} \) = molecular diffusivity of component \( i \) \([m^2/s]\)

\( E_x \) = axial dispersion coefficient of component \( i \) \([m^2/s]\)

\( F_F \) = feed flow rate \([\text{sccm}]\)

\( F_H \) = heavy product flow rate \([\text{sccm}]\)

\( F_{HR} \) = heavy reflux flow rate \([\text{sccm}]\)

\( F_L \) = light reflux flow rate \([\text{sccm}]\)

\( F_{LR} \) = light reflux flow rate \([\text{sccm}]\)

\( H_{\text{amb}} \) = wall-ambient heat transfer coefficient \([\text{MW/m}^2/\text{K}]\)

\( H_{gs} \) = gas-solid heat transfer coefficient \([\text{MW/m}^2/\text{K}]\)

\( H_w \) = gas-wall heat transfer coefficient \([\text{MJ/m}^2/\text{s}]\)

\( IP_{*,i} \) = isotherm parameter of component \( i \), units depend on isotherm

\( j \) = column j-factor for heat or mass transfer

\( k_g \) = gas phase thermal conductivity \([\text{MW/m/K}]\)

\( k_s \) = adsorbent thermal conductivity \([\text{MW/m/K}]\)
\( k_w \) = wall thermal conductivity [MW/m/K]

\( M \) = mole weight of bulk gas [kg/mol]

\( MTC \) = mass transfer coefficient [s\(^{-1}\)]

\( P \) = gas phase pressure [kPa]

\( P_C \) = gas cylinder pressure [kPa]

\( P_{FT} \) = feed tank pressure [kPa]

\( P_H \) = maximum operating pressure [kPa]

\( P_L \) = minimum operating pressure [kPa]

\( P_{PT} \) = product tank pressure [kPa]

\( \text{P}_{\text{ratio}} \) = pressure ratio [-/-]

\( R \) = universal gas constant [8.3145 kJ/kmol/K]

\( R_{C2} \) = recovery of ethane [%]

\( R_{N2} \) = recovery of nitrogen [%]

\( R_S \) = ratio of sorption rate [-/-]

\( r_p \) = radius of adsorbent particle [m]

\( sfac \) = particle shape factor

\( T_{amb} \) = ambient temperature [K]

\( T_{Feed} \) = feed temperature [K]

\( T_g \) = gas phase temperature [K]

\( T_{HR} \) = heavy influent temperature [K]

\( T_{LR} \) = light influent temperature [K]

\( T_p \) = adiabatic compressor outlet temperature [K]

\( T_s \) = adsorbent temperature [K]
$T_V$ = isothermal valve outlet temperature [K]

$T_w$ = wall temperature [K]

$t_{F/PU}$ = feed/purge step time [s]

$t_{BD/EQ/PR}$ = BD/EQ/PR step time [s]

$v_g$ = superficial velocity of gas phase [m/s]

$w_i$ = solid loading of component $i$ [kmol/kg]

$w_i^*$ = solid loading at equilibrium of component $i$ [kmol/kg]

$W_T$ = wall thickness [m]

$y_{Feed,i}$ = feed mole fraction of component $i$ [-/-]

$z/L$ = dimensionless feed position [-/-]

**Greek letters**

$\varepsilon_i$ = inter-particle void fraction [-/-]

$\varepsilon_b$ = bed void fraction [-/-]

$\rho_g$ = gas phase mole density [kmol/m$^3$]

$\rho_s$ = bulk density of adsorbent layer [kg/m$^3$]

$\chi_{char}$ = characteristic length for a sphere

$\mu$ = dynamic viscosity [Pa.s]

$\Psi$ = particle shape factor

**Dimensionless numbers**

$Nu_w$ = Nusselt number for gas wall heat transfer

$Pe_H$ = Peclet number for gas wall heat transfer

$Pr$ = Prandtl number

$Re$ = Reynolds number
Abbreviations

ACM = Aspen Custom Modeler

CSS = cyclic steady state

DR PSA = dual reflux pressure swing adsorption

GPSA = Gas Process Supplier Association

HP/LP/FE = heavy purge/light purge/feed purge

BD/EQ/PR = blow down/equalization/pressurization

LNG = liquefied natural gas

MFC = mass flow controller

MTZ = mass transfer zone

NGL = natural gas liquids

NRU = nitrogen rejection unit

PID = proportional-integral-derivative

SLPM = standard liter per minute

SP = set point for PID controller
1.1 Overview of natural gas

The earliest record of commercial use of natural gas could date back to ancient China, where natural gas was obtained from shallow wells, transported in bamboo pipes, and used as a fuel to heat an evaporator containing brine for salt production. In the late 17th and early 18th centuries, gas manufactured from coal was used in both Britain and United States for streetlights and house lighting. The next record of commercial use of natural gas occurred in 1821, William Hart drilled a shallow well in Fredonia, New York, and transported natural gas in wooden pipes to local houses and stores. Although in the following years a number of small scale local programs involved use of natural gas, it was not until after the World War Two, when the engineering advances allowed for construction of safe and robust pipelines over long-distance for gas transportation, the large scale industrial activity exploiting gas started to boom.\(^1\)\(^2\)

Natural gas is primarily used as an industrial and residential fuel, and in addition it is also a source of hydrocarbons for petrochemical feedstock and a major source of elemental sulfur, an important industrial chemical. The gas usage is expected to expand widely in near future due to the environmental advantages over conventional fossil fuel, such as coal and oil. Carbon dioxide, a major greenhouse gas linked to global warming, produced from combustion of natural gas is approximately 30-40 % less than the production from coal and oil.\(^2\)\(^3\) Nitrogen oxides, which are greenhouse gases and a source of acid rain, are sourced from both atmosphere nitrogen and nitrogen compound in fuel. As natural gas is free of most nitrogen compounds present in both coal and oil, the production of nitrogen oxides from natural gas is as low as 20 % of that from burning coal and oil.\(^2\) As compared with oil and coal, particulate formation in gas is significantly less, an important environmental consideration because in addition to being an air pollutant, high concentration of particulates may pose serious health problems. Although a considerable quantity of sulfur presents in wellhead gas, the pipeline gas quality specifications requires almost complete removal of sulfur before pipelining and sale. On the whole, natural gas produced significantly less pollutants than the competitors, and as a cleaner energy source, the demand is expected to grow significantly in the near future.
1.2 World picture for natural gas

Of the primary energy resources on current market, dry natural gas (natural gas with liquid constituents removed) is of equivalent importance as coal, accounting for 23.5 % of total energy usage, with crude oil remains the leading fuel. Russia and Iran possess almost half of the world’s gas reserves, with other major proven gas reserves reside primarily in Qatar, Saudi Arabia, United Arab Emirates, and United States, respectively. Gas reserves located in remote regions, where the reserve size does not justify the cost of infrastructure required to bring it to market, are not economically attractive and thus are excluded from this report. Note that the proven reserve estimates depend on the gas prices; increased gas prices will cause the proven reserve estimates also to rise.

It is noteworthy that gas production capability varies significantly among regions. The North America (principally the United States) accounts for 29 % of the world’s dry gas production, ranking at the second across the world, although only 5 % of the total global gas reserves resides in this region. While possessing 36 % of the world gas reserves, Eastern European areas has just slightly higher dry gas production than North America. It is also reported that about 13 % of gross gas production is flared or vented in Africa, a considerably high number as compared with the world’s average, which if excludes Africa, is only 2.3 %. The primary reason for this high loss in Africa is the lack of infrastructure in many of the developing nations. Thus, effort is required to reduce flaring or venting by constructing gas processing facilities that can convert the crude gas to a quality product at high energy density, i.e. liquefied natural gas.

1.3 Important impurities in natural gas

Conventionally, natural gas was obtained from deep reservoirs, either associated with crude oil (associated gas), or from reservoirs containing little or no oil (non-associated gas). As oil rejection or separation is generally required at the casinghead or wellhead before entering gas plant, associated gas produced in this fashion is often referred to as casinghead gas or wellhead gas. Non-associated gas is sometimes referred to as dry gas. This name might be misleading as the dry gas can still contain significant quantity of natural gas liquids. In
addition, there is another class of natural gas reservoir, where due to the high pressure and temperatures, material present is in a very dense fluid form rather than as a gas or liquid.

Traditionally, both associated and unassociated gas obtained from well varies significantly in composition. Water is all the common impurity present in the gas at wellhead condition, with concentration ranging from trace amounts up to saturation, but typically is not included in the composition analysis. It is common practice that the plant inlet condition assumes the feed gas is saturated with water unless dehydration is performed beforehand. A number of impurities present in the well gas can dictate the processes required, which is listed as follows.

Water. Water must be removed to meet the pipeline specifications or to enter the cryogenic section of the plant. Field operations sometimes dry the gas to avoid hydrate formation as well as to reduce corrosion.

Sulfur species. The total concentration of sulfur species contained in natural gas is usually less than 3%. Hydrogen sulfide concentration higher than 3% may cause formation of carbonyl sulfide, carbon disulfide, elemental sulfur and mercaptans.

Mercury. Some gases may contain trace amount of mercury, either in elemental form or as organometallic compounds. Concentrations range from 0.01 to 180 µg/Nm³. As elemental mercury may cause mechanical failure to brazed aluminum heat exchangers used in cryogenic applications due to amalgam formation, conservative design requires mercury removal to a level of 0.01 µg/Nm³.

NORM. Natural gas contains radon, a naturally occurring radioactive material (NORM), at low concentrations ranging from 1 to 1450 pCi/l. Radon rarely pose a health problem because it has a short half-life, about 3.8 days. However, the daughter products from radon decay some of which are more stable and can pose long-term radioactive threat.

Diluents. Although not often, some gases may contain undesired components at extreme level. For example, according to Hobson and Tirastso (1985), wells that contains as much as 92% carbon dioxide, 88% hydrogen sulfide, and nitrogen have been observed.5

Oxygen. Of all the natural gas impurities, oxygen is the only contaminant that is not a naturally occurring. The major source of oxygen is from leaking pipelines and open valves.
and other system compromises in the gathering system that operates below atmosphere pressure. Thus, the best approach for treating it is to prevent its introduction into the processing system. Even at low concentration of 50 ppm, oxygen may pose a problem in gas processing, such as enhancing pipeline corrosion and leading to formation of daughter products that are linked to the major system corrosions and performance degenerations. For example, reacting with amines in gas treating, which ultimately leads to heat stable salt formation; reacting with glycols to form corrosive acidic compounds; reacting with hydrocarbons in the adsorption system during the high temperature regeneration step to form water, which reduces regeneration effectiveness and thus reduces the bed capacity.

1.4 Processing and principal products

Purification, separation and liquefaction are three basic processes involved in the production of pipeline quality gas, liquefied natural gas (LNG) and salable petrochemicals from raw natural gas. Since the principal use of natural gas is as a fuel, purification of gas processing is required to remove material, valuable or not, that inhibits the distribution of natural gas to industrial or residential consumers for fuel. Note that gas plants are rarely dedicated to gaseous fuel production only. Raw natural gas contains a considerable quantity of valuable components that can be used either as petrochemical feedstock or as industrial gas. Separation is generally required to split out these materials for better profits. Furthermore, although a less common process, liquefaction is becoming more important world widely in gas fields located in remote regions. Liquefaction plays a key role as a means of increasing energy density for storage and transportation.

1.4.1 Overview of gas plant process

Gas plants play a variety of roles in the oil and gas industry. The desired end product dictates the process required. To make the gas marketable, the undesired diluents N₂, H₂S, CO₂ are removed. Of these components, nitrogen is the most difficult to remove because, to make the process economical, it requires cryogenic distillation when large volumes are processed.
Figure 1-1 shows the block schematic of a gas plant that integrates various gas processing steps. Blocks of nitrogen rejection and helium recovery highlighted in red are less common processes. Note that it is uncommon for a gas plant to include all the processes steps shown above. In fact, the combination of desired end product, feed compositions and conditions dictate the required processes in gas plant.

Raw gases obtained from reservoirs usually go to field operation that includes preliminary dehydration, CO₂ and H₂S removal and compression before entering a gas plant. Once the gas enters the plant, it goes into inlet receiving section where condensed water and solids are rejected and hydrocarbon liquids go on to liquid processing. Water must be removed to avoid hydrate formation as well as to reduce corrosions. The requirement of inlet compression stems from the fact that the cryogenic-liquids recovery processes are pressure driven, where high pressure is critical. Gas treating step are commonly required in gas industry to remove acid gases H₂S and CO₂ along with other sulfur impurities. Water-based scrubber is a popular method to remove the impurities, although some other solvents and processes are used. Gas treated in this fashion is usually saturated with water or contains too much water to enter the cryogenic sections. Consequently, dehydration is required to remove water to a level as low as 10 ppm. Two conventional methods for water removal are physical absorption and adsorption (principally TSA), and some nonconventional processes such as desiccant and membrane processes are emerging. The removal of mercury is mandatory in gas industry due to two major problems associated with mercury, environmental pollutant and amalgam formation.
with aluminum. The cryogenic section of the gas plant provides the major fractionation duty to produce sales gas and natural gas liquids, as well as to recover helium if the feed helium concentration is sufficient. Cryogenic distillation process is usually expensive and energy intensive, and sometimes is finished with PSA or membrane processes to ensure very low impurity levels.

1.4.2 Principal products

Although pipeline quality gas is the major product of gas plants, a number of natural gas components can be separated out as a standalone product for use in local market. Following is an overview of the principal products from gas plants in the United States.²

Methane. As a fuel, pipeline quality natural gas predominantly contains methane, which at the same time, is also an important chemical feedstock for production of ammonia and methanol.

Ethane. Gas plants and refineries contribute the primary production of ethane used in the United States, and the remainder comes from imports. Ethane can be either left in the gas for fuel, or used in the production of ethylene, a feedstock for polyethylene.

Propane. The majority of the propane used in the United States comes from gas plant and gas refineries, and the imports are responsible for the remainder. Almost half of the produced ethane is used as a petrochemical feedstock, with the remaining principally distributed for residential use.

Ethane-propane mix. Ethane-propane mix is primarily the light ends constituents remaining in the production of butanes and some portion of propane when NGL is fractionated into various hydrocarbon streams. While the as-produced butanes and propane are shipped to local market by truck, the ethane-propane mix is transported via pipeline to industrial customers for chemical or refining feedstocks.

Isobutane. Gas plant production of isobutane accounts 42% of the total supply in the United States, refineries contributes about 5% and imports accounts for 12%. The remaining supply on the market comes from isomerization plants where n-butane is
converted to isobutane. Isobutane is an important petrochemical and industrial feedstock in the production of methyl tertiary butyl ether, reformulated gasoline and propylene oxide.

N-butane. Approximately 63% of the domestic production of n-butane comes from gas plants, refineries are responsible for 31 %, and imports accounts for the remainder. Two primary uses of n-butane are as blending component in gasoline, and as a chemical feedstock for the isomerization to isobutane.

Natural gas liquids. The term natural gas liquids (NGL) is used to designate all hydrocarbon liquids produced either in the fields or gas plants. NGL includes ethane, propane, butane, and natural gas line, a mixture comprising mostly pentanes and heavier hydrocarbons. NGL is sometimes also referred to as “Y-grade” or “raw product”.

Natural gasoline. According to the GPA product specification, this term is used to refer to a NGL subset mixture that consists of mostly pentanes and heavier hydrocarbons. Some major use of natural gasoline includes direct blending into gasoline, C5/C6 isomerization and production of ethylene.

Sulfur. Approximately 85 % of the sulfur supply on market comes from gas processing plant that convert hydrogen sulfide to elemental sulfur. The major uses of sulfur are rubber vulcanization, as a feedstock for the production of sulfuric acid, and manufacture of black gunpowder.

1.5 Nitrogen rejection for gas updating

Nitrogen, a naturally occurring diluent in natural gas, need to be rejected or separated out as industrial gas to meet the total 3 % inert component specifications on pipeline quality gas. Although a less common process in industrial gas plant, nitrogen rejection is becoming more important as the industrial practitioners shift to lower quality feedstocks. Nitrogen rejection is typically required when the following circumstances arise:

Subquality gas upgrading. Natural gas obtained from gas wells varies significantly in compositions. The gas research institute classified natural gas from 48 states in the US as high quality gas and subquality gas. The subquality gas is defined as one that contains more than 2 % CO₂, 4 % N₂ and 4 ppmv H₂S. According to the Gas research institute’s
survey of gas reserves (Meyer, 2000), it was found approximately 16 % of the unassociated gas reserves at that time were subquality in nitrogen, and consequently will require blending to lower the nitrogen concentrations or require nitrogen rejection to meet the pipeline quality gas specification.  

EOR operation. Gas plants strip out CO₂ and N₂ from raw natural gas. The upgraded natural gas is marketed and the CO₂ and N₂ are rejected to the formations for enhanced oil recovery operation. In N₂ EOR project, an air separation plant may be built to provide N₂ at the project beginning. As early as 1998, it was reported that approximately 12 % of the total oil supply in the United States market were furnished by enhanced oil recovery methods. Of the total production, about 55 % was from thermal methods, 28 % was from carbon dioxide flooding, 12 % was from natural gas flooding, and nitrogen flooding was responsible for 5 %. Although with relatively small fraction of production, the nitrogen EOR operation contributed 5,100 m³/d, about 32,000 barrels oils per day.

Helium recovery. Helium is a difficult diluent to remove in natural gas unless nitrogen rejection is used. As with nitrogen rejection, the helium recovery process is cryogenic, which generates crude helium product at 40 - 70 % purity in the light ends from distillation tower when a nitrogen rich overhead stream from NRU (nitrogen rejection unit) is fractionated.

1.5.1 Cryogenic distillation

Conventionally, cryogenic distillation, adsorption and membrane separation are three basic methods used in gas plants for nitrogen removal. The choice of processing method depends on the gas throughput requested. At high throughput, cryogenic distillation is most economical and provides higher throughput of nitrogen rejection. As compared to cryogenic distillation, pressure swing adsorption (PSA) and membrane processes are relatively simple to operate and are economically feasible at low gas volumes. Most gas plants use cryogenic distillation to remove nitrogen in natural gas, either with single column design at low feed N₂ concentrations or using a dual-column when the feed N₂ concentration is 20 % or higher. With the addition of a recycle compressor, the dual-column could be adapted to operations at lower N₂ concentrations.
Feeding 15% N2 at -150 °F and 250 psig.

Figure 1-2 shows the schematic of a dual-column cryogenic distillation design of nitrogen rejection unit. A demethanizer by use of conventional turbo expander generates a feed stream containing 15% N2 at -150 °F and 235 psig. Before entering the high pressure column, this feed stream flows through two heat exchangers (cooled against the bottom reflux and overhead product from this column, respectively) and an expansion valve to cool the stream to about -200 °F. The bottom product from this high pressure column is cooled by pressure reduction to approximately -240 °F. This stream, along with the overhead of a second low pressure column, is recycled to a heat exchanger at the top of the high pressure column to provide necessary reflux. The overhead product of the high pressure column is cooled by three heat exchangers, reduced in pressure and fed to the low pressure column operating at 15 psig. The overhead from this column contains 98% nitrogen and the bottom product contains 98% methane.

In situations where the nitrogen in feed is at low concentration, a single column design may be used, which, because of relatively lower nitrogen rejection throughput, is less energy intensive than the two-column design. Detailed review of the single column cryogenic process for nitrogen rejection is available in some publications. Although a maturely developed technology, the cryogenic distillation is complex and prohibitively expensive for small scale developments of LNG facilities.
1.5.2 Adsorption separations

Although a new technology relative to cryogenic distillation, adsorption separation is widely used in industrial gas plants, often serves for final purification or used with the cryogenic distillation in a hybrid separation process to improve the system efficiency. It is important to note that two types of adsorption are physical adsorption and chemisorption. In physical adsorption, van der Waals force, the attractive and repulsive force that holds liquid or gas molecules together and give them structure, contributes the formation of physical bond between the adsorbed species and the solid surface. In chemisorption, a much stronger bond, also referred to as a chemical bond, occurs between the adsorbed species and solid surface, often accompanied with significant heat generation. In this review, only physical adsorption is discussed for the natural gas system. Physical adsorption is an equilibrium process like the vapor-liquid system and can be described with following equation:

\[ w_i = f(c_i, p_i) \]  

Eq. 1-1

where \( w_i \) refers to the equilibrium concentration that is the maximum concentration of condensed component (adsorbate) on the solid surface. The relationship between the equilibrium concentration of the adsorbate and its relevant concentration \( c_i \) (if liquid) or partial pressure \( p_i \) (if gas) in the bulk phase is described using a function \( f \), which is called isotherm. The total pressure or concentration has minor effect on the adsorption equilibrium.\(^{12}\) In gas system, factors that dictates the amount adsorbed include the adsorbent itself, the adsorbate, the temperature, and the partial pressure of the adsorbate. Once the adsorbent and adsorbate are selected, the temperature and partial pressure become the governing variables.

For large scale separation applications, cyclic batch operation process, in which the adsorbent bed is alternatively statured and regenerated, is mostly used. Cyclic batch adsorption processes differ from each other mainly in the methods by which the adsorbent is regenerated during the desorption cycle. Four basic methods are in common use although combinations of two or more methods may also be used with advantage in particular situations.

Thermal/Temperature swing. In a thermal/temperature swing process, the adsorbent of the bed is regenerated by heating, usually with a stream of hot fluid (gas or less commonly
liquids), to a temperature at which the adsorbed species desorb and is removed from the bed in the fluids stream. Thermal swing processes are generally preferred for strongly adsorbed species and for systems containing several adsorbates of widely different adsorption affinities. Such a process are applicable to both gas and liquid system.

Pressure swing. In pressure swing operation, the bed temperature is essentially maintained constant. The bed regeneration is accomplished by dropping the bed pressure, which causes the adsorbed species to desorb, and then purging the bed at low pressure, normally with a small fraction of raffinate product stream. Apparently, this regeneration method is restricted to gas system. The pressure swing process is well suited to rapid cycling and thus has the advantage of maximizing the efficiency of adsorbent usage, with several large scale separation applications such as, heatless air drier, air separation processes, and hydrogen purification.

Purge gas stripping. In a purge gas stripping process, a stream of non-adsorbing inert gas is essentially used to purge the bed operating at constant pressure and temperature, which flushes the adsorbed species away from the bed. This process is therefore only suited to the separation where the adsorbed species is weakly held, otherwise the quantity of purge gas required could not be justified. Furthermore, the flushing effluent normally contains the desorbate at very low concentration so this process is normally applicable to the situation where the desorbate is not to be recovered.

Displacement desorption. As with purge gas stripping, the bed temperature and pressure are essentially maintained constant in displacement desorption operation. The essential difference between the displacement desorption and purge gas stripping is that in displacement desorption, instead of an inert purge, a stream of purge gas containing competitively adsorbing species is used. This method is applicable to both gas and liquid systems.

Thermal and pressure swing are probably the most common system. The choice of possible regeneration method for a particular system depends on the economic factors as well as some technical considerations. This review here is restricted to a few general considerations which
provide initial guidance regarding the choice between thermal and pressure swing method, as listed in Table 1-1:

**Table 1-1 Summary of factors dictating the choice between thermal and pressure swing regeneration method. (Adapted from Ruthven D.M., 1984)**

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal swing</td>
<td>Favor the desorption of strongly adsorbed species; a small change of T gives a large change of $Q^*$, Extract product may be recovered at high purity</td>
<td>Thermal aging of adsorbent Heat loss means inefficiency in energy usage Time delays in heating and cooling; unsuitable for rapid cycling so adsorbent cannot be used with maximum efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Applicable to both gas and liquid systems</td>
<td>In liquid system high latent heat of interstitial liquid must be added</td>
</tr>
<tr>
<td>Pressure swing</td>
<td>Good for recovery of raffinate product at high purity</td>
<td>Very low operating pressure may be required</td>
</tr>
<tr>
<td></td>
<td>Rapid cycling means efficient use of adsorbent</td>
<td>Mechanical energy more expensive than heat</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Low extract product purity</td>
</tr>
</tbody>
</table>

In natural gas system, it is common practice to dry the gas using temperature swing adsorption (TSA), because the separation meet two general criterions; trace amount of adsorbate (water) is removed to very low level and the adsorption heat is very high. For nitrogen rejection, PSA may be the choice for bulk removal of nitrogen gas from methane, because the bulk concentration of nitrogen is high and the adsorption heat is low.
As discussed previously, the cyclic batch adsorption process used in a gas plant always involves two steps, adsorption to produce purified product and regeneration to prepare the bed for further use. Two bed is essentially required for continuous operation. In practice, more than two beds are often used in a gas plant. For example, in industrial natural gas dehydration operation, four beds are usually used; two are in adsorption service while one is put in regeneration mode, and the fourth one serves as a spare. Description of multi-bed PSA systems that involve much complicated cycle sequence and internal refluxes arrangements are reported in detail in some publications. We here present a brief interpretation of PSA fundamentals with a simplified two bed system, as shown in Figure 1-3. This system is designed for use in the separation of a binary mixture of compounds A and B. Assume adsorbate A is strongly adsorbed relative to adsorbate B. Once the feed enters the bed operating at ambient temperature and high pressure, two steps are involved in adsorbing the gas component. The first step is to have the component contact the solid surface and the second step is to have it travel through the pathways inside the adsorbent and then condense at the adsorption site to form adsorbed layers. The second step is relatively slow due to the existence of mass transfer resistances contributed by a set of factors, such as film transfer resistance, macro-pore and/or micro-pore diffusion resistances. Consequently, the solid adsorbent takes longer to come to equilibrium with the gas phase than in absorption process. As component A is more strongly adsorbed than component B, A is enriched on the solid surface of adsorbent and thus the A concentration in the gas leaving the bed is reduced. Such a
process that produces highly purified B is called stripping or raffinate or purification process. Breakthrough occurs when the bed is saturated with the adsorbed A, which is in equilibrium with feed gas A at partial pressure P1, and the bed is switched to regeneration mode.

The regeneration of the bed is simply accomplished by reducing the total pressure of the bed, which causes the gas to desorb, and purging the bed with a small fraction of product stream. Purge is essential for an efficient separation and the reversed-flow purge ensures that the more strongly adsorbed components are pushed back towards the bed inlet and thus do not contaminate the raffinate product during the next cycle. As the desorbate effluent from the bed contains A at higher concentration than the feed, such a process is sometimes referred to as enriching or extracting process. The isotherm indicates that the final A concentration on the regeneration bed is reduced to what will be in equilibrium with the purge gas A at partial pressure P2. The residual A that loads when the bed is put back into adsorption service is at equilibrium pressure P2, which means during the next adsorption step the bed will produce a raffinate product containing a small fraction of A at partial pressure P2. If the purge gas is free of A, the bed will be mostly regenerated with zero partial pressure of A. Consequently, the bed is capable of produce raffinate product at very low level of A.

1.5.3 Membrane separations

In natural gas system, membrane process is primarily used for dehydration, fuel-gas conditioning and bulk CO2 removal. Presently, CO2 removal is by far the most important applications. From a thermodynamics perspective, the driving force for movement through the membrane is the difference of chemical potential, \( \mu \), for a certain component on both sides of the membrane. In gas system, if ideal gas behavior is assumed for the diffusing gas component (subscripted with i), the following equation applies:

\[
\frac{y_{i,feed}}{y_{i,permeate}} \frac{P_{i,feed}}{P_{i,permeate}} > 1 \tag{1-2}
\]

\[
\frac{y_{i,feed}}{y_{i,permeate}} \frac{P_{i,feed}}{P_{i,permeate}} \leq 1 \tag{1-3}
\]

Where \( y \) is the mole fraction and \( P \) is the total pressure, Equation (1-3) indicates that the maximal separation achieved is governed by the pressure ratio \( \frac{P_{feed}}{P_{permeate}} \).
The pros and cons of the membrane systems was reviewed by Kohl and Nielsen and Echt et al.\textsuperscript{19-20} The following summarizes their conclusions:

**Advantages**

- Low capital investment when compared with solvent systems
- Ease of operation: process can run unattended
- Ease of installation: Units are normally skid mounted
- Simplicity: No moving parts for single-stage units
- High turndown: The modular nature of the system means very high turndown ratios can be achieved.
- High reliability and on-stream time
- No chemicals needed or generated
- Good weight and specie efficiency

**Disadvantage**

- Economy of scale: little availability of economy of scale because of their modular nature
- Clean feed: Pretreatment of the feed to the membrane to remove particulates and liquids is generally required
- Gas compression: Considerable recompression to ensure sufficient driving force may be required for either or both the residue and permeate streams

In regards to the natural gas system, the following disadvantages also apply:

- Generally higher hydrocarbon losses than solvent systems
- Difficult to meet H\textsubscript{2}S specifications
- Well suited to bulk removal; membranes alone cannot be used to meet ppmv specifications

Nevertheless, membranes are probably the safest and most environmental friendly of the processes for gas treating. No chemicals are needed, no waste disposal by-products are generated, and membranes operate at low pressures and usually ambient temperatures. Offshore applications tend to favor membrane systems in particular, because of unattended operation, no chemicals involved and good weight and space efficiency.\textsuperscript{2}
Cryogenic nitrogen removal is complex and prohibitively expensive at modest scale. Membrane based system is a proven and economical solution. Figure 1-4 shows a NitroSep™ membrane process that produces pipeline quality or pipeline acceptable gas and a nitrogen rich fuel. The proprietary membranes are significantly more permeable to methane, ethane and other hydrocarbons than to nitrogen. The inlet gas containing 8-15% N₂ is compressed and enters a separator, where any condensate formed is removed and the feed gas is passed across a first set of membrane modules. The permeate that contains 4% N₂ is sent to pipelines and the nitrogen rich residue gas is passed to a second set of membrane modules. These modules produce a residue gas containing 50% N₂ and a nitrogen depleted permeate containing 10-20% N₂. The residue gas is used as a fuel and the permeate is mixed with the incoming feed for further recovery.

From the nitrogen rejection processes reviewed above, cryogenic distillation is the leading nitrogen rejection technology for large scale gas plants, but adsorption and membrane process are commercially available for small scale applications. There remains scopes of developing more efficient N₂ removal technologies based on CH₄ or N₂ selectivity based rapid cycling PSA or membrane systems.
1.6 Helium recovery from natural gas

1.6.1 World production and usage of helium

Helium, a chemically inert gas that has extremely low boiling point (4K) and small molecular size, is distinctively important for a broad range of medical, scientific and industrial applications. In 2010, the world demand for helium is 30,000 t, which is equivalent to a value of USD$ 1billion. As the economies of many developing nations in Asia rise (principally China and India), it can be predicted that the demand for helium will continue to grow at 5-8 % annually. In 2003, of the world total helium production, approximately 84 % comes from the United States, and the remainder is furnished by Algeria, Poland and Russia. However, in recent years two large helium facilities have been constructed and commissioned, one in Darwin, Australia, which started production in Mar, 2010, and the other in Qatar, which became operational in 2005. Both plants were designed to process off-gas from base-load LNG facilities. At full production, the Darwin plant is capable of producing 150 MMscf (4.2 MMm³) of helium per year and the Qatar is capable producing 300 MMscf (8.5 MMm³) of helium per year.

Helium is primarily used as a coolant for modest-scale equipment operating at high energy throughput, such as magnetic resonance imaging equipment in hospital and particle accelerator in high energy physical research. Some other uses are as carrier gas for analytical instrument, as blanket gas for welding, as blending component of breathing mixtures and atmosphere control. Specially, produced helium has replaced water as the preferred reactor coolant in nuclear power plant.

Although air contains a large amount of helium, recovery of helium from air would be very expensive and inefficient because the helium concentration in air is prohibitively low (5.24 ± 0.05 ppm). The only practical source is from certain natural gas fields. The best of these fields still contains relatively small quantities of helium, with helium rich gas field typically defined as one that contains more than 0.3 % helium. Gas fields that contains more than 5 % helium is not common.
1.6.2 Recovery methods

Cryogenic distillation is the most common method in use for industrial helium recovery from natural gas. Few gas plants are dedicated primarily to helium extraction only. The helium recovery facility is typically an addition to the gas plant. Figure 1-5 shows the conventional helium recovery and refinement processes and the locations of the helium concentration units in a gas plant. The feed gas from gas gathering system is firstly compressed and pretreated for acid gas removal and then trace quantity of mercury is removed before dehydration. The helium recovery unit is closely integrated with the nitrogen rejection unit in a cold box where, through cryogenic distillation, nitrogen is removed to produce pipeline quality gas while helium is recovered in the non-condensable light ends, which usually contains 50-70% helium. This crude helium is sent to storage or further refined in a series of low temperature separations, followed by a final PSA purification process to produce high quality product (99.995% He). A waste stream is recycled and combined with the incoming feed gas for further recovery. The helium produced may be either liquefied and stored in liquid nitrogen-shielded containers and shipped by truck as a liquid or compressed and stored as a high pressure gas.

![Figure 1-5 Block schematic of recovery of helium from natural gas. (Adapted from Rufford et al., 2014)](image)

The choice of cryogenic distillation design for helium recovery depends mainly on the feed flow rate and compositions, including whether the quantity of helium contained in the feed
could justify the cost of the additional infrastructure required to bring it market. Figure 1-6 shows a typical but modern two-column design for helium recovery from natural gas by use of cryogenic fractionation. The clean natural gas is cooled against the product streams in a heat exchanger and fed to the high pressure column. A condenser provides the reflux for this column and the low pressure column, respectively. The non-condensable overhead that contains mostly helium is passed into a crude helium separator, from which the helium is drawn as crude product and leaves the plant after warming. The bottoms, with some of the nitrogen removed, serves as the feed to the low pressure column, where the methane-nitrogen separation is performed. The bottom reboiler of this column produces a methane-rich residue which is pumped to elevated pressure and vaporized and finally leaves the plant after warming. The reboiling duty in the low pressure column necessary to produce the sales gas is furnished by the condensing nitrogen overhead from the high pressure column. This heat exchanger is possible because the column pressures are such that the condensing point of the nitrogen in the overhead from the high pressure column is higher than the boiling point of methane rich stream in the bottom reflux from the low pressure column.

![Schematic of helium recovery process combined with nitrogen rejection by use of two column-cryogenic distillation.](image)

Figure 1-6 Schematic of helium recovery process combined with nitrogen rejection by use of two column-cryogenic distillation. (Adapted from Häussinger et al., 2000)\(^ {11}\) Arrows in blue indicates the helium route through the plant.

Das et al. reported a pilot scale PSA system for helium purification from a 0.06 vol% helium feed containing N\(_2\), CH\(_4\), CO\(_2\) and heavier hydrocarbons. The PSA unit comprised of three
beds loaded with Lithium exchanged low silica X-zeolite (LiLSX) as the adsorbent, and was programed to operate through four stages, with each stage associated with a seven step cycle to physically eliminate selected impurities. The helium purity in final product was increased to a level of or better than 99.0 vol% with 61% He recovery. Their achievements indicates that scopes exists to develop more efficient PSA processes for He recovery and purification from natural gas based on the emerging carbon and/or nitrogen selective adsorbents.

1.7 Research motivations and objective

Currently, cryogenic distillation is probably the most common method in use for bulk removal of nitrogen from natural gas to produce pipeline quality gas and NGL, as well as to extract helium if required. Adsorption processes is widely used for final stage purification to produce high quality product (e.g. 99.995% purity He), but so far there is no alternative commercial processes that is competitive with cryogenic distillation for nitrogen removal and helium recovery from subquality gas sources at flow rate characteristic of large LNG facility operations. In some other industrial applications, such as air separation, hydrogen purifications, PSA process is a proven solution for modest scale operations to achieve large capital savings and energy reduction as compared to cryogenic distillation. Das et al. reports a pilot scale PSA unit that is capable of producing high purity helium product from natural gas feed containing 6% helium. Also, PSA separations of nitrogen methane mixtures by use of various solid adsorbents, either equilibrium or kinetic selectivity based, are reported in a large quantity of recent publications. Scope exists to optimize these conventional PSA processes by operating at lower temperatures, using improved adsorbent or to develop enhanced PSA cycles that is not limited by the selection of operating pressures, which is known as thermodynamics constraints. A dual reflux PSA cycle, which recycles a portion of both its raffinate and extract product, is proven to be free of this constraint, and the potential has been demonstrated for bulk and/or trace impurities removal from natural gas to achieve high purities and recoveries. However, constructing and testing an experimental PSA rig could be very expensive. Even at pilot scale, the large quantity of gases required to yield qualitative results would be prohibitive, in particular when helium is used. The objective of this research is to design and optimize a dual reflux PSA process for nitrogen rejection and helium recovery.
from natural gas using commercial simulation software, which serves as a step towards the goal of developing high performance PSA processes to improve the LNG plant efficiency.
Chapter 2 Literature review and Non-isothermal Dynamic Simulations of Dual Reflux Pressure Swing Adsorption

Abstract

Dynamic simulations of Dual Reflux Pressure Swing Adsorption (DR-PSA) cycles were constructed and benchmarked against the most detailed set of experimental DR-PSA data available in the literature (up until 2015), which involved the separation of C$_2$H$_6$ + N$_2$ mixtures. A rigorous energy balance was included in the model in contrast to previously reported dynamic simulations of DR-PSA which have all assumed isothermal operation to simplify the numerical solution of the governing equations. At cyclic steady state, the standard deviations of the model’s predictions from the experimental data were: 2.4 K for the nine bed temperatures, which ranged from (286 to 307) K; 0.003 mole fraction in a rich product stream with an average ethane composition of 0.63 mole fraction; and 9 kPa for the bed pressures, which ranged from (20 to 180) kPa. This non-isothermal DR PSA simulation was demonstrated to be capable of comprehensively reassessing a real DR PSA process.

2.1 Literature review

Pressure swing adsorption (PSA) technology has been widely applied for industrial separation and purification of gaseous mixtures. Conventional, a PSA cycle is based on the Skarstrom design with a twin-bed system and can be deployed in either stripping or, less commonly, enriching configurations. The stripping configuration feeds to the high pressure bed and recycles a portion of purified light product to the low pressure bed to produce heavy product. However, in such a configuration, enrichment of the heavy component concentration from the feed to the heavy product stream is limited by the ratio of that component’s sorption capacities at the high and low pressures; upon the assumption of linear equilibrium isotherms this limit is equivalent to the pressure ratio used in the cycle and has been referred to as the “thermodynamic constraint”. Likewise for the enriching configuration, which inverts the feed injection and product recycle relative to the stripping configuration, the cycle’s pressure ratio constrains the achievable purity of the light product. This constraint can be overcome

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through the use of a combined PSA cycle that recycles both product streams and uses intermediate feed injection, known as dual reflux PSA (DR PSA). Such cycles have been demonstrated to be free of the enrichment constraints set by pressure ratios and are thus theoretically capable of producing both products in high purity and are constrained only by material balance.\textsuperscript{33, 35-36} Detailed reviews of the history and development of DR-PSA cycles are available in the literature.\textsuperscript{32-34, 36-48}

To the best of our knowledge, the feasibility of the DR PSA process was first experimentally demonstrated by Diagne et al.\textsuperscript{33} By testing a set of feed of air containing up to 20 % CO\textsubscript{2} with molecular sieve 13X, they demonstrated that simultaneous enriching and stripping of CO\textsubscript{2} by a DR PSA process was feasible and unconstrained by the pressure ratios. By optimizing the feed position, reflux ratios, flow rates and pressure ratios, it was further shown that the CO\textsubscript{2} could be concentrated to above 95 % in the heavy product stream and removed to below 3 % in the light product.\textsuperscript{37-38} McIntyre et al. experimentally investigated the possibility of enriching dilute hydrocarbons in a N\textsubscript{2} dominant feed by using a laboratory-scale DR PSA rig loaded with BAX carbon.\textsuperscript{36, 42} By applying a pressure ratio of 8, a feed containing 0.75 vol% ethane in nitrogen was enriched to 68.4 vol% in the heavy product with a corresponding recovery of 99.6 %. The ethane concentration in light product could be stripped to as low as 30 ppm. Furthermore, McIntyre et al.\textsuperscript{36, 42} reported extensive details regarding the dynamic pressure and temperature profiles within the columns as well as effluent compositions, which provide the opportunity to benchmark predictive models of DR PSA cycles. Very recently Bhatt et al.\textsuperscript{47} reported the use of a laboratory-scale DR-PSA apparatus containing Norit RB1 activated carbon to separate a 0.05CH\textsubscript{4} + 0.95N\textsubscript{2} mixture into product streams containing up to 60 % CH\textsubscript{4} and 98.4% N\textsubscript{2}, respectively.

The published modeling work on DR PSA system basically falls into two categories. One was developed on the basis of equilibrium theory, and solved by the method of characteristics; the other one, known as dynamic modeling, was solved by numerical integration of all the governing equations. The first equilibrium model for a DR PSA system was reported by Ebner and Ritter.\textsuperscript{40} The model assumed non-dispersive plug flow, no axial pressure drop, isothermal operation, and uncoupled linear isotherms for a binary mixture. By stipulating two pure products be generated, the model was able to solved over a wide range of parameters, even
with pressure ratio as low as 1.1. Later, Kearns and Webley identified four typical cycle configurations with different feed injection and pressure inversion methods and analyzed them using equilibrium models, identifying an optimum feed position that maximized the utilization of the bed volume.\textsuperscript{34} They also used this equilibrium model to investigate the work–productivity tradeoff as a function of feed composition.\textsuperscript{41} Most recently, Bhatt et al. used equilibrium models of DR PSA cycles model to demonstrate a graphical design method to predict optimal operation conditions in terms of feed position and capacity ratios.\textsuperscript{49}

Although the equilibrium model provides preliminary guidance and useful insights into DR PSA cycles, the model is highly idealized and inherently limited in its ability to provide insight into key issues of practical importance. It assumes a priori that pure product streams will be generated and cannot, therefore investigate the factors that impact achievable enrichment ratios which are of critical interest. Furthermore, such analytic models generally preclude consideration of realistic phenomena such as nonlinear adsorption isotherms, heat effects, gas phase dispersion and sorption kinetics. In contrast, the numerical solution of dynamic models allows much more realistic simulations to be considered and can in principle be adequately general to enable a detailed optimization approach to the design and operation of DR PSA processes.\textsuperscript{50} The first dynamic modeling of DR PSA process was published by Diagne et al., as a comparison with their experimental separations of diluted CO\textsubscript{2}/air mixtures.\textsuperscript{39} Although only material balance equations were considered and isothermal operation was assumed, the model yielded good agreement with the experimental data. Sivakumar and Rao developed an isothermal model of DR PSA cycles that included axial dispersion and pressure drop effects and hence a more realistic column concentration profile could be depicted.\textsuperscript{43-45} This model was used to investigate separations involving non-competitive and competitive adsorption, as well as a modified cycle design intended to increase the achievable product purities by mitigating the effects of transient variations in product composition during the feed-purge step. They demonstrated that by introducing additional steps to the DR PSA cycle and only producing one product stream at a time, the purities of both products could be in excess of 99 mol\%, for both equilibrium and kinetically controlled systems. By eliminating energy balance considerations and implementing the model directly into FORTRAN, their simulations were able to run relatively quickly (1 hour). However, mass balance errors of up to 1.5 % were present in these
simulations and had to be reset after each cycle.

Bhatt and co-workers reported the development of an isothermal dynamic model implemented in the commercial software Aspen Adsorption, which they benchmarked against their own experimental data for CH\textsubscript{4}-N\textsubscript{2} separations and subsequently the data of McIntyre et al. for C\textsubscript{2}H\textsubscript{6}-N\textsubscript{2} separations.\textsuperscript{42, 47} The computational load was also lowered by using the so-called “single-bed approach” where only one bed is simulated and the effect of the second bed is determined using the “interaction modules” feature available in the Aspen software. In this approach, all the properties of a selected stream leaving the first bed are recorded and then reproduced as an input stream to the first bed at a subsequent and appropriate point in the cycle. Hence only one single bed was actually simulated, yielding an approximated result which is less accurate than that using the twin bed approach. Nevertheless, even with the use of the interaction units, a simulation of 1500 cycles still required between 3 and 14 days to run. Bhatt et al. also used their isothermal dynamic model to investigate the effect of axial feed position for the C\textsubscript{2}H\textsubscript{6}-N\textsubscript{2} separations.\textsuperscript{47}

However, while isothermal dynamic models are generally able to reproduce pressures, flow rates and gas compositions observed in laboratory scale DR PSA apparatus, the omission of energy balance considerations means that their applicability to the analysis of industrial scale units is limited. Even for the laboratory-scale experiments of McIntyre et al. the bed temperatures varied by 25 K at cyclic steady state.\textsuperscript{42} Moreover, key experimental information about the location of the adsorption front that is available from measurements of the bed’s axial temperature profile is particularly useful for optimizing the cycle timing to ensure maximum use of the bed while avoiding breakthrough of the other component; such information, however, cannot be considered with isothermal dynamic models. Similarly, non-isothermal dynamic models enable investigation of the effect of reflux stream temperatures on separation performance: the temperatures of these streams are process variables that could have a significant impact on the performance of a large-scale DR-PSA unit and/or be manipulated to improve the effectiveness of the separation. In this work, we developed a robust numerical DR PSA model with rigorous material, momentum and energy balance on the platform of Aspen Adsorption (Adsim). Interaction modules were not used and both beds were simulated. The robustness and reliability of the model was validated by comparison with
the published experimental data of McIntyre et al. in terms of cyclic pressure, composition profiles and bed temperatures. Limiting values of the mass transfer coefficient required to simulate the experimental results were established. Subsequently the model was used to investigate the impact of reflux temperature on the DR PSA separation efficiency.

2.2 Model development

The non-isothermal DR PSA model implemented in the Aspen Adsorption software involved the numerical solution of the dynamic material, energy and momentum balance equations as listed in Table 2-1. To achieve this, the following assumptions and/or selections of choices within the Aspen software were made:

i. Material balance: convection with estimated dispersion

The gas phase material balance includes terms for convection, axial dispersion, gas accumulation in inter-particle void space, and adsorption flux to solid surface.

ii. Momentum balance: Ergun equation

Ergun equation counts for pressure drop from both laminar and turbulent flow.

iii. Kinetic model: lumped resistance in form of linear driving force; constant mass transfer coefficient

The mass transfer driving force is a linear function of solid phase loading.


The use of I.A.S.T. here has slightly increased computational load.


The gas phase energy balance includes terms for thermal conduction, convection of energy, accumulation of heat, compression, heat transfer from gas to solid, and heat transfer from gas to the internal wall.

The solid phase energy balance includes terms for thermal conduction accumulation of heat, accumulation of enthalpy in the adsorbed phase, heat of adsorption, and heat transfer from gas to solid.

The wall energy balance includes terms for axial thermal conduction along the wall, heat accumulation within the wall material, heat transfer from the bed to the inner wall, and heat transfer from the outer wall to the environment.

Specifically, a set of considerations are included as follows:

a) Heat of adsorbed phase: constant adsorbed phase heat capacities
b) Heat of adsorbent assumption: constant (value estimated by the method introduced by Whittaker et al.\textsuperscript{51})

c) Form of heat transfer coefficient: estimated (equation 9-12)

d) Form of gas thermal conductivity: based on axial dispersion (equation 8,10,13)

e) Heat transfer to environment: rigorous (considering energy balance for wall)

f) Form of gas-wall heat transfer coefficient: estimated (equation 14-16)

g). Gas phase behaves as an idea gas mixture. (equation 17)

h). Radial concentration and temperature gradients are negligible.

Governing equations based on these assumptions are tabulated in Table 2-1. The boundary value for bed dynamics were computed through the boundary gas tanks which were deployed at the bed inlet and outlet. Boundary conditions were specified at the feed and product streams, shown in Figure 2-1. Intermediate feed injection was realized through the boundary tanks which divided the bed layer into enriching and stripping sections. Feed and product tanks were used as the meet point to deliver and collect gas with the twin beds, and were stabilized by Proportion-Integration-Differentiation (PID) controllers in a fixed pressure gradient across the boundary tanks to avoid disruptive backflows. Feed and product streams were used to provide start and end streams conditions, with feed composition, temperature, gas cylinder pressure specified to the feed stock and ambient pressure specified to the product stocks. The flow rates of feed and product streams were specified using the mass flow controllers, as was the light reflux flow rate. The heavy reflux flow rate was set by an isentropic compressor model, of which the maximum inlet volumetric flow is of significant importance.

To allow control of the reflux stream temperatures prior to them entering each bed’s boundary tank, model heat exchangers that assumes no pressure drop were included immediately after the compressor and light reflux MFC. The heat exchanger models were also important to correct for the idealized assumptions associated with the models available in Aspen Adsorption for the compressor and light reflux valve: without them the heavy reflux temperature could have been as high as 200 °C because of the compressor’s isentropic assumption, while the expansion valve model in the software is isothermal and thus neglects any Joule-Thompson cooling. It may well be that future experimental DR PSA rigs,
particularly those operating an industrial scale, consider implementing heat exchangers to moderate or even control the temperatures of the reflux streams.

Table 2-1 Model equations for the bed layer of the DR PSA model. All symbols used are defined in the Nomenclature section.

(a) Material, momentum and energy balance equations

<table>
<thead>
<tr>
<th>Component balance</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material balance</td>
<td>$-E_{e,i} \frac{\partial^2 c_i}{\partial z^2} + \frac{\partial (v_g c_i)}{\partial z} + \varepsilon_i \frac{\partial c_i}{\partial t} + \rho_s \frac{\partial w_i}{\partial t} = 0$ (2-1)</td>
</tr>
<tr>
<td>Momentum balance</td>
<td>$\frac{\partial P}{\partial z} = \left(1.5e^{-3}(1-\varepsilon_i)^2 \frac{\mu v_g}{(2r_p \psi)^2 \varepsilon_i^3} + 1.75 \times 10^{-5} M \rho_s \frac{(1-\varepsilon_i)^2}{2r_p \psi \varepsilon_i^3} v_g^2\right)$ (2-2)</td>
</tr>
<tr>
<td>Gas phase</td>
<td>$-k_g \varepsilon_i \frac{\partial^2 T_g}{\partial z^2} + C_{vg} v_g \rho_s \frac{\partial T_g}{\partial z} + \varepsilon_i C_{vg} \rho_s \frac{\partial T_g}{\partial t} + P \frac{\partial v_g}{\partial z} + H_{g} \varepsilon_i (T_g - T_w) + \frac{4H_{g}}{D_B} (T_g - T_{amb}) = 0$ (2-3)</td>
</tr>
<tr>
<td>Solid phase</td>
<td>$-k_s \frac{\partial^2 T_s}{\partial z^2} + C_{ps} \rho_s \frac{\partial T_s}{\partial z} + \rho_s \sum_{i=1}^{n} (C_{ps,i} w_i) \frac{\partial T_s}{\partial t} + \rho_s \sum_{i=1}^{n} (\Delta H_i) \frac{\partial w_i}{\partial t} - H_{gs} \varepsilon_i (T_s - T_w) = 0$ (2-4)</td>
</tr>
<tr>
<td>Wall</td>
<td>$-k_w \frac{\partial^2 T_w}{\partial z^2} + \rho_w C_{pw} \frac{\partial T_w}{\partial t} - H_w \frac{4D_B}{(D_B + W_T)^2} (T_g - T_w) + H_{amb} \frac{4(D_B + W_T)^2}{(D_B + W_T)^2 - D_B^2} (T_w - T_{amb}) = 0$ (2-5)</td>
</tr>
</tbody>
</table>

(b) Other correlations

<p>| Isotherms          | $w_i^* = \frac{IP_{i,j} \exp\left(\frac{IP_{i,j}}{T}\right) P_i}{1 + IP_{j,i} \exp\left(\frac{IP_{j,i}}{T}\right) P_i}$ (2-6) |
| Kinetics           | $\frac{\partial w_i}{\partial t} = M \tau C_{w_i} (w_i^* - w_i)$ (2-7) |
| Dispersion coefficient | $E_{e,i} = 0.73 D_{g,i} + \frac{v_g \tau_p}{\varepsilon_i (1 + 9.49 \varepsilon_i D_{g,i})}$ (2-8) |
| Reynolds number    | $Re = \frac{2 r_p M \rho_g v_g}{\mu}$ (2-9) |
| Prandtl number     | $Pr = \frac{\mu C_p}{k_{gs} M}$ (2-10) |</p>
<table>
<thead>
<tr>
<th>Term</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>j-factor</td>
<td>[ j = 1.66 \Re^{-0.51}, \Re &lt; 190 ] [ j = 0.983 \Re^{-0.41}, \Re \geq 190 ]</td>
<td>(2-11)</td>
</tr>
<tr>
<td>gas-solid heat transfer coefficient</td>
<td>[ H_{gs} = jC_p g v_g \rho_g \Pr^{-2/3} ]</td>
<td>(2-12)</td>
</tr>
<tr>
<td>gas phase thermal conductivity</td>
<td>[ k_g = C_p g \sum_i (E_{z,i} v_i) \rho_g \Pr^{-2/3} ]</td>
<td>(2-13)</td>
</tr>
<tr>
<td>Nusselt number for gas-wall heat transfer</td>
<td>[ Nu_w = \frac{H_w \chi_{\text{char}}}{k_g} ]</td>
<td>(2-14)</td>
</tr>
<tr>
<td>Peclet number for gas-wall heat transfer</td>
<td>[ Pe_H = \chi_{\text{char}} v_g \rho_g MC_p g ]</td>
<td>(2-15)</td>
</tr>
<tr>
<td>gas-wall heat transfer coefficient</td>
<td>[ Nu_w \left(1 + \frac{12H_w}{D_s \Pe_H}\right) = -2 \times 10^{-6} (Pe_H)^2 + 0.0477 Pe_H + 22.1 ]</td>
<td>(2-16)</td>
</tr>
<tr>
<td>idea gas law</td>
<td>[ P = CRT_g ]</td>
<td>(2-17)</td>
</tr>
</tbody>
</table>
2.3 Model benchmarking

To verify the reliability and robustness of the model, a series of simulation runs were performed and the results benchmarked against the experimental results reported by McIntyre et al.\textsuperscript{42}. The focus of the benchmarking exercise was on the base-case experiment for which...
the operation pressure range was 26 kPa-184 kPa, corresponding to a pressure ratio about 7, with further details summarized below.

2.3.1 Description of the benchmark cycle

The complete cycle configurations of the four-step DR PSA are shown in Figure 2-2 and the cycle parameters are tabulated in Table 2-2. In Step 1, a feed mixture containing 1.35 mol% ethane in N\textsubscript{2} was introduced into the middle position of Bed-A, which was initialized at the low pressure. Part of the ethane-enriched heavy product effluent from Bed-A was withdrawn as the heavy product stream, while the rest was compressed to high pressure and recycled into Bed-B as a heavy purge stream. Concurrently, a portion of the light effluent stream from Bed-B was withdrawn as the light product stream while the rest was depressurized and recycled to Bed-A as a light purge stream. This step ended after the specified feed/purge time had expired. In Step 2, the feed and product flows were stopped and Bed-A was re-pressurized using the enriched effluent from Bed-B which underwent a counter-current blow down. This step ended when the pressures of the two beds were fully inverted; the amount of time allocated for this blow-down, equalization and pressurization was less than \( \frac{1}{4} \) of the time allocated for Step 1. Step 3 is equivalent to Step 1 except with Bed-A being at high pressure and Bed-B at low pressure receiving the feed stream. Similarly Step 4 is the equivalent of Step 2 except with the labels of the beds reversed.

<table>
<thead>
<tr>
<th>Table 2-2 Cycle parameters of the benchmark DR PSA cycle\textsuperscript{42}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed concentration(ethane), ( y_{\text{Feed}} ) (-/-)</td>
</tr>
<tr>
<td>feed flow rate, ( F_{F} ) (sccm)</td>
</tr>
<tr>
<td>heavy product flow rate, ( F_{H} ) (sccm)</td>
</tr>
<tr>
<td>light reflux flow rate, ( F_{LR} ) (sccm)</td>
</tr>
<tr>
<td>dimensionless feed position, ( z/L ) (-/-)</td>
</tr>
<tr>
<td>high pressure, ( P_{H} ) (kPa)</td>
</tr>
<tr>
<td>pressure ratio, ( P_{\text{ratio}} ) (-/-)</td>
</tr>
<tr>
<td>feed/Purge step time, ( t_{F/P} ) (s)</td>
</tr>
<tr>
<td>BD/EQ/PR step time, ( t_{BD/EQ/PR} ) (s)</td>
</tr>
</tbody>
</table>
Light product
\( (F_L = F_F - F_H) \)

Stripping end
\( z/L = 0 \)

Feed

Enriching end
\( z/L = 1 \)

Heavy product

Step 1:
LP/HP

Step 2:
PR/BD

Step 3:
HP/LP

Step 4:
BD/PR

Figure 2-2. The four steps of the DR PSA cycle used to benchmark the non-isothermal model.
2.3.2 Parameter estimation

Many but not all of the experimental parameters needed to completely specify the simulation were provided in the original work.\textsuperscript{42} Those that weren’t include the isotherm parameters for each adsorbate and the physical properties of the adsorbents and columns. Accordingly, the values of these unknown parameters were either estimated from the relevant literature for similar properties, or were assumed and adjusted to be as physically reasonable as possible and, if the model’s results were sensitive to them, to force optimal agreement between simulation and experiment. The former group are known as fixed parameters and are shown in Table 2-3(a), together with the specifications provided by McIntyre et al.\textsuperscript{42} It is noteworthy that the intra-particle void fraction estimated here is not of significant impact on the simulated bed dynamics, if the bulk density of bed layer, $\rho_s$, was fixed. The latter group are termed the adjustable parameters and, as shown in Table 2-3(b), include the mass and heat transfer coefficients, the ambient temperature and the temperatures of the feed and reflux streams. The most uncertain and crucial was the wall-ambient heat transfer coefficient, which was studied over the range from $1 \times 10^{-6}$ to $1 \times 10^{-4}$ MW/m$^2$/K for benchmark, due to the significant exothermic feature of ethane adsorption on carbon. In contrast, the simulation was expected to be insensitive to the MTC as long as the kinetics were sufficiently fast. For the benchmarking case the stream temperatures were set to be equal to the ambient temperature.

Table 2-3 Simulation parameters estimated for the benchmark DR PSA cycle

(a) Fixed parameters estimated from the available literature

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Equations</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed half-length, $L$</td>
<td>0.435</td>
<td>m</td>
<td></td>
<td>1,2,3,4,5</td>
</tr>
<tr>
<td>wall thickness, $W_T$</td>
<td>0.0016</td>
<td>m</td>
<td>5</td>
<td>42</td>
</tr>
<tr>
<td>bed layer diameter, $D_0$</td>
<td>0.0242</td>
<td>m</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>inter-particle void fraction, $e_i$</td>
<td>0.43</td>
<td>n/a</td>
<td>1,3,8</td>
<td>52-53</td>
</tr>
<tr>
<td>intra-particle void fraction, $e_p$</td>
<td>0.7</td>
<td>n/a</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>bulk density of bed layer, $\rho_s$</td>
<td>284.882</td>
<td>kg/m$^3$</td>
<td>1,4</td>
<td>42</td>
</tr>
<tr>
<td>particle diameter, $d_p$</td>
<td>0.0026</td>
<td>m</td>
<td>2,8,9</td>
<td>54</td>
</tr>
<tr>
<td>particle shape factor, $s_{fac}$</td>
<td>0.86</td>
<td>n/a</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>molecular diffusivity, $D_{m,i}$</td>
<td>$1.00 \times 10^{-05}$</td>
<td>m$^2$/s</td>
<td>1,8</td>
<td>55</td>
</tr>
<tr>
<td>$D_{m, nitrogen}$</td>
<td>$2.00 \times 10^{-05}$</td>
<td>m$^2$/s</td>
<td>1,8</td>
<td></td>
</tr>
<tr>
<td>isotherm parameters $IP_{*,i}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$IP_{1, ethane}$</td>
<td>$8.52 \times 10^{-08}$</td>
<td>kg/kmol/bar</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>$IP_{1, nitrogen}$</td>
<td>$1.65 \times 10^{-06}$</td>
<td>kg/kmol/bar</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>$IP_{2, ethane}$</td>
<td>3331.53</td>
<td>K</td>
<td>6</td>
<td>36, 51</td>
</tr>
<tr>
<td>$IP_{2, nitrogen}$</td>
<td>1575.56</td>
<td>K</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>
### Adjustable parameters for tuning cycle characteristics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>stipulation</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass transfer coefficient, ( MTC(C_2H_6/N_2) )</td>
<td>( 0.02 \leq MTC(C_2H_6&amp;N_2) \leq 0.30 )</td>
<td>1/s</td>
</tr>
<tr>
<td>wall-ambient heat transfer coefficient, ( HTC_{amb} )</td>
<td>( 1 \times 10^{-06} &lt; HTC_{amb} &lt; 1 \times 10^{-04} )</td>
<td>MW/m²/K</td>
</tr>
<tr>
<td>ambient temperature, ( T_{amb} )</td>
<td>( T_{Feed} = T_{amb} )</td>
<td>K</td>
</tr>
<tr>
<td>feed temperature, ( T_{Feed} )</td>
<td>( T_{amb} \leq T_{HR} )</td>
<td>K</td>
</tr>
<tr>
<td>heavy reflux temperature, ( T_{HR} )</td>
<td>( T_{amb} \leq T_{LR} )</td>
<td>K</td>
</tr>
<tr>
<td>light reflux temperature, ( T_{LR} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

(b) Adjustable parameters for tuning cycle characteristics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>stipulation</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>specific heat capacity of adsorbent, ( Cp_s )</td>
<td>( 1.00 \times 10^{-03} )</td>
<td>MJ/kg/K</td>
</tr>
<tr>
<td>specific heat capacity of wall, ( Cp_w )</td>
<td>( 5.00 \times 10^{-04} )</td>
<td>MJ/kg/K</td>
</tr>
<tr>
<td>specific heat capacity of adsorbed phase, ( Cp_{a,i} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Cp_{a,ethane} )</td>
<td>( 0.052 )</td>
<td>MJ/kmol/K</td>
</tr>
<tr>
<td>( Cp_{a,nitrogen} )</td>
<td>( 0.029 )</td>
<td>MJ/kmol/K</td>
</tr>
<tr>
<td>heat of adsorption, ( \Delta H_i )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta H_{ethane} )</td>
<td>(-27.7)</td>
<td>MJ/kmol</td>
</tr>
<tr>
<td>( \Delta H_{nitrogen} )</td>
<td>(-13.1)</td>
<td>MJ/kmol</td>
</tr>
<tr>
<td>adsorbent thermal conductivity, ( k_s )</td>
<td>( 5.00 \times 10^{-07} )</td>
<td>MW/m/K</td>
</tr>
<tr>
<td>wall thermal conductivity, ( k_w )</td>
<td>( 1.60 \times 10^{-05} )</td>
<td>MW/m/K</td>
</tr>
<tr>
<td>wall density, ( \rho_w )</td>
<td>( 7800 )</td>
<td>kg/m³</td>
</tr>
</tbody>
</table>

---

\(a\) Since the separation was equilibrium controlled, the difference in the component mass transfer coefficient was neglected.

2.3.3 Pressure control algorithm

To correctly emulate the experimental steady state bed pressure profiles reported for the benchmarked DR PSA cycle, it was necessary to implement a custom dual control algorithm within the simulation. Experimentally the bed pressures appear to have been controlled on the basis of flow rates (i.e. mass flow controllers) rather than using back pressure regulators. Consequently, the bed pressures did not show a constant pressure plateau during the feed and purge steps, i.e. the bed pressure was continuously increasing or decreasing, creating a maxima and minima on the cyclic pressure profile at the end of each step, respectively. Replicating these experimental bed pressures in the simulation is difficult because of the interaction between the compressor and the product flow controller. In their isothermal dynamic simulation, Bhatt et al. were able to match the bed pressures at the end of the feed (Step 1) and purge (Step 3) stages using mass flow controllers and the interaction units but did
not replicate the curvature exhibited by the experimental pressures during these stages. In such a DR PSA process, the experimentally attainable pressure ratio was determined by the provided speed of the compressor running over a cycle, while the light product flow rate matched the steady state value. Therefore, it can be expected that, on stipulating the cycle time, one may reproduce the same pressure ratio in the simulation as that of the benchmark cycle by finding an appropriate speed for the gas compressor. In the meantime, the light product flow rate also needs temporary adjustment to give the desired maximum operating pressure, in order to fully attain the benchmarked pressure window.

To achieve this, we developed a dual convergence algorithm to adjust the maximum inlet volumetric flow of the compressor $V_{in_{\text{max}}}$ and the light product flow rate $F_L$ in the process of achieving the desired pressure window in simulation. As shown in Figure 2-3, at the end of each cycle, the deviation of maximum pressure and pressure ratio from the reference value was calculated respectively, and was used to activate the adjustment in either $V_{in_{\text{max}}}$ or $F_L$ for the next cycle based on a comparison of magnitude of the deviations. Following this algorithm, $V_{in_{\text{max}}}$ will be determined when the simulated pressure window reaches the desired value and $F_L$ has been returned to match the steady state experimental result.
2.3.4 Benchmark results & discussions

To converge numerically to its cyclic steady state (CSS) convergence, the benchmark simulation required approximately 500 cycles, which took about 24 hours on a computer with an Intel i7M chip running at 2.20 GHz and an RAM of 4 GB. The DR PSA cycle parameters calculated during the transient stages of the simulation bear no relation to those in the experimental transient. The attainment of CSS for the simulation was assessed using the relative changes in solid loading and temperature of all bed layers over each cycle. Such relative changes were computed to be 0.00208 % and 0.00395 % for cycle 400-401, and 0.00205 % and 0.00393 % for cycle 450-451 in a run of 500 cycles. In comparison, the published experiments used temperature change of 0.168 % as the criterion of cyclic steady state.

The separation performance of the benchmark simulation was analyzed and compared with experiment once CSS was achieved. Figure 2-4 shows how within the first 10 cycles of the simulation the ethane feed concentration of 1.35 mol% was increased by a factor of 11 in the
heavy product stream and reduced by a factor of 4 in the light product (nitrogen-rich) stream. At CSS, the simulation produced a cycle-averaged ethane product purity of 62.3 %, an ethane recovery of 84.1 %, a cycle-averaged nitrogen product purity of 99.8 %, and a nitrogen recovery of 99.3 %. These correspond well to the experimental results of 63.2 %, 84 %, 99.8 % and 99 %, respectively. Furthermore, the variation of ethane concentration in the heavy product stream across the feed stage of the steady state cycle matched the reported experimental profile as shown in the inset of Figure 2-4. The standard deviation of the two simulated product purities from the experimental values over a full cycle was 0.026 mole fraction, which on a relative basis corresponds to 2.8 % of the heavy product’s ethane fraction.

![Graph showing cyclic evolution of ethane concentration in the heavy product and light product streams respectively.](image)

Figure 2-4 Cyclic evolution of ethane concentration in the heavy product and light product streams respectively, with a 1.35 mol% ethane in feed. For clarity, curves before the break denote the first 10 cycles (110 s/cycle) of the simulation and curves after the break show cycle 490–500, where the simulation had reached CSS. For comparison the corresponding experimental CSS values are also listed, with the inset showing concentration of ethane in heavy product during the 45 s feed step of cycle 500.

To obtain the above separation performance, the control of operating pressure is of critical importance. By using the pressure control algorithm, the desired pressure profile of a published real DR PSA process could be reproduced through the convergence of two controlling variables as discussed previously. Figure 2-5(a) shows that by running a batch of
successive cycles, the inlet volumetric flow of compressor $V_{in_{max}}$, which controlled the attainable pressure ratio, converged to 11.04 L/min with an initial guess at 4.8 L/min, giving a steady cyclic pressure ratio of 7. This converged value was comparable with the work capacity of real compressor commercially available for laboratory usage. In the meanwhile, the light product stream $F_L$, which controlled the maximum adsorption pressure, also converged to the desired value at 572.97 sccm, fulfilling the overall cycle mass balance (Figure 2-5(b)). Notice that $F_L$ was undergoing periodical minor overshoots over the desired convergence value, which was due to the exceeding of desired maximum pressure that was corrected by temporarily increasing $F_L$ as automatically controlled by the algorithm. This minor correction of $F_L$ reflects the change of component composition in the simulated twin-bed when undergoing cyclic pressure swing operation. Such a composition change was only a small effect that did not disrupt the attainment of CSS for the system. Nevertheless, the convergence of the two controlling variables indicated that the desired pressure window of the cycle was stabilized, which is shown in Figure 2-5(c). Eventually at CSS, the simulated pressure profile closely tracked both the pressurizing and depressurizing trajectories of the corresponding experimental data, giving a well matched maximum pressure of ~184 kPa and minimum pressure of ~26 kPa in a pressure ratio at ~7, as shown in Figure 2-6(a). The standard deviation of the simulated bed pressures from the experimental values over a full cycle was 9.15 kPa, which on a relative basis corresponds to an average of 7.3 % of the bed pressure. This is a significant improvement over the pressure profile generated from Bhatt et al., particularly for the stages when the two columns are reaching maximum pressure ratios; therein they attained an approximation of pressure trajectories with R.M.S.D. of 15.64 kPa from the experimental value, while we achieved 1.34 kPa of a much better match, as shown in Figure 2-6(b). 47
Maximum inlet flow capacity, $V_{\text{in, max}}$ (L/min)

Flow rate of light product, $F_L$ (sccm)

(a) adjusted

(b) converged

Cycle (-)
Figure 2.5 Convergence of the modeling DR PSA process to the reference cyclic steady state through pressure control algorithm.

(a) Convergence of the maximum pump inlet flow rate $V_{in_{Max}}$ as required to achieve the steady-state pressure ratio of the experimental cycle.

(b) Temporary adjustment and value return of the light product flow rate $F_L$ as required to achieve the steady-state maximum bed pressure.

(c) Stabilization of the simulated pressure cycles to the target experimental values.42
Figure 2-6 Evaluation of simulated cycle characteristics of pressure profiles at CSS for the DR PSA model of this work.

(a) Pressure trajectories with time from simulation of this work and the reference.\textsuperscript{42}

(b) Deviations of the simulated pressure trajectories from the reference value in comparison with the corresponding simulation result from Bhatt et al.\textsuperscript{47}

The most important test of the non-isothermal simulation was its ability to reproduce the experimental CSS variations in temperature along the bed over the course of the cycle. Two of...
the adjustable parameters listed in Table 2-3(b), $HTC_{amb}$ and $T_{amb}$, were tuned manually according to the following criteria: (a) the average bed temperature across the cycle should be slightly higher than the ambient temperature, and (b) the peak temperatures achieved in the cycle should be reproduced as closely as possible. The optimal values that satisfied these criteria were $HTC_{amb} = 10 \text{ W m}^{-2} \text{ K}^{-1}$ and $T_{amb} = 297.4 \text{ K}$. Figure 2-7(a) shows a comparison of the temperatures of five nodes across the bed corresponding to the locations of five of the ten thermometers used to monitor the experimental bed temperatures. The nodes corresponding to T1, T3, and T5 were located around the stripping end of the bed. In this region the temperature variation was slight periodical variation, which ranged from 295 K to 301 K with an average of 300 K, matching the experimental values well (R.M.S.D. = 0.98 K). In contrast the nodes corresponding to T7 & T9 which were located near the enriching end of the bed exhibited significant temperature fluctuations over a cycle with peak-to-peak values of 308 K and 287 K, respectively, clearly indicating the non-isothermal nature of the adsorption cycle. Nevertheless, the simulated bed temperatures in this enriching region of the bed were good agreement with the corresponding experimental data (R.M.S.D. = 2.64 K). The standard deviation of all the simulated bed temperatures from the corresponding experimental values over a full cycle was 2.35 K, which on a relative basis corresponds to an average of 0.5 % of the bed temperature.

Of course, representing the physical heat transfer characteristics of the experimental rig is problematic: no details about the thermal insulation (if any) around the columns was provided by McIntyre et al.\textsuperscript{36, 42} and, furthermore, it is likely that the heat loss rate from the ends of the column to the environment would be much faster than that from the middle. Thus attempting to describe the heat transfer characteristics of the apparatus with a single number will inevitably lead to some differences between the experimental and simulated bed temperatures. This may explain why the curvature of the simulated bed temperatures with time is larger than that observed experimentally, particularly in the enriching section of the bed during the pressurization and heavy purge stages of the cycle. A value of 10 W/m$^2$/K was found to be the optimal $HTC_{amb}$ for the best benchmark results. Tuning up or down the $HTC_{amb}$ would move the thermal characteristics of the apparatus towards more isothermal or adiabatic, which respectively, corresponds to a minor or major temperature fluctuation in the simulated bed.
The adjustment of $T_{\text{amb}}$ would affect the temperature gradient built across the apparatus, which, depending on the $HTC_{\text{amb}}$, would also vary the rate of the wall-ambient heat transfer.

Figure 2-7 Evaluation of simulated cycle characteristics of column temperature profile at CSS for the DR PSA model of this work.
(a) Temperature trajectory with time in comparison with the reference experimental data.  
(b) Variation of simulated column temperature along axial bed length during depressurization and low pressure purge stage in half cycle.
The results obtained for the benchmark simulation were found to be largely independent of the value of the mass transfer coefficients used in the simulation for N₂ and C₂H₆ provided they were sufficiently large and both greater than 0.2 s⁻¹. This is consistent with the fact that the adsorption of both the components onto an activated carbon could be expected to be an equilibrium rather than kinetically-limited process. The limiting value of the MTCs at which the simulation exhibited a sensitivity to the sorption kinetics was investigated in a parametric study relative to the benchmarked case. Once this was established, a second parametric study was conducted with the non-isothermal model investigating the impact of the reflux temperatures.

2.4 Conclusions

A dynamic model of DR PSA system was built on the platform of Aspen Adsorption (Adsim). Bed dynamics was derived from rigorous mass, momentum and energy balance assumptions. Gas void tanks were deployed at the bed inlet and outlet to determine the dynamic boundary pressures of bed and also allow intermediate feed injections. Feed and product tanks were used at steady pressure to avoid disruptive backflows to the bed. The cyclic operation of the DR PSA model was automated by self-coded algorithm in Aspen Custom Modeler language (ACM). The reliability and robustness of the DR PSA model was verified by benchmarking against a published DR PSA experiment. By reasonably estimating the key parameters, the as-reproduced cycle characteristics in terms of product purity, pressure and temperature profile could quantitatively match the corresponding published data, giving a comprehensive reassessment of the real DR PSA process.
Chapter 3 Simulation Investigation of DR PSA Separation of Methane and Nitrogen Mixtures

Abstract

The non-isothermal model developed in Chapter 2 was modified to adapt to a pilot DR PSA rig that was constructed in our laboratory (Saleman et al., 2015) for CH$_4$ + N$_2$ separations. Modules of proportional-integral-derivative (PID) controller were used to achieve constant bed pressure control during the adsorption and regeneration step. The reliability and robustness of the model was verified by benchmarking against two sets of experimental DR PSA results of CH$_4$ + N$_2$ separation, which respectively, involved the test of Norit RB3, the CH$_4$ equilibrium selective adsorbent, and CMS 3K-172, the N$_2$ kinetically selective adsorbent. At cyclic steady state, similarity of model predictions with experimental records in terms of cycle characteristics of pressure, temperature and flow rate profiles was qualitatively established and then good agreement of product purities was found over a wide range of flow regime and feed composition. The feasibility and potential of kinetic DR PSA separation of methane and nitrogen mixture using CMS 3K-172 was demonstrated, through elucidating a set of parameter effect of feed time, flow rate of light reflux and heavy product, and sorption rate on the separation performance relative to a benchmarked cycle. The comparison of these two adsorbent revealed that it is the magnitude of selectivity rather the component matters for the DR PSA separation of CH$_4$ + N$_2$ mixture. This simulation study of DR PSA technique can serve as a useful tool for process design, reduction of cost for laboratory and/or plant trials and enhanced understanding of process behavior.

3.1 Introduction

Although Ritter’s report indicates a promising adsorption process, their cycle was focused on the enrichment of diluted heavy hydrocarbons associated with a sharp equilibrium selectivity. The bulk removal of nitrogen from natural gas presents a more challenging separation because of the similar properties and molecule size between methane and nitrogen. Saleman et al. reported a pilot scale DR PSA rig constructed at UWA to experimentally test...
the nitrogen rejection tasks with various feed composition and flow regime conditions. With commercial activated carbon Norit RB3 being the adsorbent, they demonstrated the potential of DR PSA technology to reduce CH₄ emissions at relatively low energy cost with potential applications in recovery of low grade CH₄ recovery from coal mine ventilation and polish N₂-rich waste from LNG production facilities. With our rigorous non-isothermal model developed in Chapter 2, we here adapted this pilot rig into simulation for use in predicting and optimizing the DR PSA cycles for CH₄ + N₂ separation, which can serve as a useful tool for process design guidance for industrial practitioners. In Section 3.2, we presented a description of model adaptation focused on the pressure control details typically used on our experimental DR PSA rig. In section 3.3, the model was verified through benchmarking against the published experimental results of CH₄ + N₂ separation with Norit RB3 being used as the equilibrium CH₄ selective adsorbent.

In adsorption processes, it is more energy efficient to remove the trace component rather than the dominant component in the feed. Thus in the natural gas system, using a nitrogen selective adsorbent for low quality fuel upgrading tends to favor the processing economics of PSA units. However, there is no viable adsorbent available at low cost to have nitrogen equilibrium capacity over methane. Carbon molecular sieve is a class of carbonaceous adsorbent with relatively small micro-pore size distribution that can be produced from many different organic sources: bituminous coals, bones, coconut shells, etc. This kind of adsorbent does not have high equilibrium capacity, but is known to offer significant kinetic selectivity between compounds of similar molecular size and properties, e.g. air separations. The difference of molecular size between nitrogen (3.64 Å) and methane (3.8 Å) indicates the possibility of the kinetic separation of nitrogen-methane to be performed. Fatehi et al. have shown that a 60 % and 92 % methane feed balanced with nitrogen, can be respectively, increased to 76 % and 96 % by a PSA unit containing carbon molecular sieve. However, the methane recoveries were prohibitively low.

Our DR PSA experiments have demonstrated its capability of upgrading low quality fuels using carbon molecular sieve CMS 3K-172, a nitrogen selective adsorbent with up to 100 kinetic selectivity over methane. However, to the author’s knowledge, such a kinetic separation has rarely been assessed in comparison with an equilibrium selectivity-based
process, which is however essentially important for the economic merits of any separation process to be determined. By simulation means we here provided detailed insights into the potential of this kinetic separation through a series of parameter effect study towards a performance optimum, which included key cycle operating inputs as well as artificial variation of kinetic selectivity. On the basis of the best cycle condition being identified, we were then able to comparably assess the adsorbent performance between Norit RB3 and CMS 3K-172 to determine which one represents the better choice of cycle inputs for DR PSA upgrading of low quality fuels. These research tasks were completed in the following steps: Section 3.4 presented a model verification of this kinetic separation by benchmarking against our experimental results available; Section 3.5 shows a set of parameter effect on one benchmarked cycle; in Section 3.6, with the optimal cycle condition available, these two adsorbents were conclusively compared.

3.2 Model development

The construction of a dynamic DR PSA model simulating the rig of Saleman et al. was based on the outcome of the model previously developed that simulates Ritter’s rig. The major difference of these two models is that in this work, instead of allowing for varying bed pressures across the cycle, the simulated twin-bed is maintained at steady pressure during the adsorption and regeneration step by use of PID controller modules. The flow diagram for this model is identical to that described in Chapter 2, except that two sets of PID controller modules are added to the twin-bed system to regulate the bed pressure during the adsorption and regeneration step. Specifically, one set is deployed at the compressor, regulating the inlet volumetric capacity of the compressor sucking gas from the regeneration bed, and the other is deployed at the outlet control valve of the high pressure bed to regulate the amount of light effluent flowing to the light product. By prescribing desired set point of operating pressure, these PID controllers can serve as the realistic back pressure regulators to achieve steady bed pressure.

The constant flow rate of feed, heavy product and light reflux were prescribed via the mass flow controller modules, whereas the flow rate of heavy reflux and light product are free variables, which was respectively, manipulated by the PID controller in accordance with the mass balance of the bed for the attainment of desired low and high pressure set point. The feed
and product module (shown as hollow arrows in the flow diagram) were used to provide start
and end stream conditions, and with feed composition, cylinder pressure (or any pressure value
that is sufficiently high above the adsorption pressure), and ambient temperature specified to
the feed module and ambient pressure specified to the product modules. The corrected
temperature of the two reflux streams were specified via the heat exchanger, and was assumed
to be ambient temperature.

3.3 Simulation benchmark of Norit RB3 test

To verify the robustness and reliability of the model, two sets of benchmarking exercises were
conducted against the experimental DR PSA results of CH₄ + N₂ separations, which
respectively, involved the test of Norit RB3, the methane equilibrium selective adsorbent and
CMS 3K-172 adsorbent, the nitrogen kinetically selective adsorbent. Details of benchmark
setup and performances of both adsorbents are described in the following two sections,
respectively.

3.3.1 Description of the benchmarked cycle

The benchmark exercise of Norit RB3 involved 24 simulation runs of DR PSA cycles that
operated with the same operating pressure and cycle step time but varied in feed composition
and flow regime. Table 3-1 lists the cycle parameters for these benchmark runs.

<table>
<thead>
<tr>
<th>Table 3-1 Cycle parameters for benchmarking Norit RB3 runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed concentration (methane), y_{Feed} (-/-)</td>
</tr>
<tr>
<td>feed flow rate, F_r (SLPM)</td>
</tr>
<tr>
<td>heavy product flow rate, F_{H} (SLPM)</td>
</tr>
<tr>
<td>light reflux flow rate, F_{LR} (SLPM)</td>
</tr>
<tr>
<td>dimensionless feed position, z/L (-/-)</td>
</tr>
<tr>
<td>high pressure, P_{H} (kPa)</td>
</tr>
<tr>
<td>low pressure, P_{L} (kPa)</td>
</tr>
<tr>
<td>pressure ratio, P_{ratio} (-/-)</td>
</tr>
<tr>
<td>feed/Purge step time, t_{F/P} (s)</td>
</tr>
<tr>
<td>BD/EQ/PR step time, t_{BD/EQ/PR} (s)</td>
</tr>
</tbody>
</table>

a. The operating pressure for simulation used the average value of what was measured at the
top and bottom of the respective experimental column. This also applies to the benchmark
exercise of CMS 3K-172 test.
Figure 3-1 A four step cycle configured with low pressure feed injection and heavy reflux pressure reversal for the separation of \( \text{CH}_4 + \text{N}_2 \) mixture by use of activated carbon Norit RB3 as the adsorbent. (The dash streams denote alternative approaches to feed injection and pressure reversal. Being different from Ritter’s cycle shown in Chapter 2, the flow rate of heavy reflux and light product here are outputs of PID controllers that regulate the bed pressure.)

\[ F_L = \text{OP}, \text{PID}(P_{\text{High}}) \]

\[ F_{HR} = \text{OP}, \text{PID}(P_{\text{Low}}) \]
A four step cycle was used (Figure 3-1) and is described as follows: In step 1, the feed gas was injected to column A at low pressure. A methane-rich heavy effluent from column A was compressed to high pressure, and with a portion drawn as heavy product, the remainder was recycled as a heavy reflux to column B for adsorption purge. A portion of nitrogen-rich effluent from column B was drawn as light product while the rest was depressurized and recycled as light reflux to regenerate column A. This step ended when specified time expired.

In step 2, column B was put in concurrent blowdown mode to re-pressurize column A with the desorbate stream. This step ended when the pressure of the twin-column was completely reversed. Step 3 was equivalent to step 1 except with feed gas injected to column B. Step 4 was equivalent to step 2 except with the column pressures inverted.

The DR PSA cycle configuration described above is referred to as DR-PL-A as first reported by Kearns et al., where ‘PL’ refers to the low pressure feed injection while ‘A’ means the pressure reversal through the enriching end of the twin-bed.24 This nomenclature further distinguishes other three cycle configurations available for the DR PSA system with ‘PH’ referring the high pressure feed injection and a suffix ‘B’ for pressure reversal by light product, i.e., DR-PH-A, DR-PL-B, and DR-PH-B. The DR-PL-A configuration used in test of Norit RB3 adsorbent is akin to our previous work benchmarking against a published experiment of McIntyre et al., except that in this work adsorption and desorption pressure was maintained constant whereas previously ongoing change of the bed pressure was allowed.42

3.3.2 Performance of cycle characteristics

As previously demonstrated, simulation performance of cycle characteristics in terms of bed pressure and temperature is requisite for achieving a good match of separation results. Therefore, we here first verified the simulated CSS pressure and temperature profiles of DR PSA cycles available from publication of Saleman et al.29 In addition, the CSS cycle flow pattern was examined to demonstrate the effectiveness of PID controller modules used to adapt the experimental rig that operates with steady pressure operation during adsorption and regeneration step.

CSS condition was considered to be established when the time invariance of average product purities over each cycle was reached and the changes of solid loading and temperature of all
bed layers was, on a relative basis, less than $1 \times 10^{-5}$, a more rigorous criterion than that used by McIntyre in experiments. If the CSS condition for the simulation was not established by finishing a batch of 500 cycles, a further bath will be executed and then repeat the criterion check. However, the establishment of CSS condition was sooner than anticipated in the CMS 3K-172 cases, usually less than 400 cycles. Also, the component material balance for the simulations was within 2%, with a majority being less than 1%.

Figure 3-2 shows the simulated CSS pressure profile of the DR PSA separation for CH$_4$ + N$_2$ mixture, in comparison with the data measured in experiments. Firstly, it is noteworthy that the initial sharp increase of pressurization trajectories observed in experiments was reduced, characterized by a smooth pressure evolution over the step. This was because the over-flow of heavy purge gas in experiments was avoided in simulation with precise flow rate control being attainable by MFCs. As a result, the simulated pressure reversal step was accomplished at desired values precisely, whereas in experiments a significant pressure overshoot was observed. The minor fluctuation of simulated pressure trajectory at the beginning of adsorption step should be attributed to the prompt response of PID controllers when a feed gas was suddenly injected. Since this fluctuation was so minor, the attainment of cyclic steady state was not disturbed. Secondly and more importantly, by employing the module of PID controllers, the bed effluent could be dynamically regulated so that steady pressure at set points for adsorption and regeneration purge was achieved in simulation, showing a great trajectory match with the experimental records. Notice that while a significant pressure drop was observed in experiments due to the flow confining effect by small connecting elements, the simulated bed was free of such effect and thus had much less pressure drop. Therefore, the simulated bed was set to operate at a pressure equal to an average of the top and bottom pressure measures of the respective experimental bed.
Figure 3-2 Simulated CSS pressure profile of the DR PSA cycle in comparison with data measured in experiment using Norit RB3 as the adsorbent.

Figure 3-3 shows a comparison of CSS temperature changes of the bed top, middle and bottom node corresponding to the locations of three of eleven probes used to monitor the experimental bed temperatures. The middle node exhibited a major temperature fluctuation over a cycle with a peak to peak value from 20 °C to 30 °C, which was consistent with the experimental records. The bottom temperature was relatively lower than that of the middle node because of the regenerative heat exchange effect, where colder stream flowed down during desorption than the hot stream flowed up during adsorption. In contrast, the bed top experienced only slight temperature variations as there was little methane adsorption. As the simulation used a single coefficient for the description of wall-environment heat transfer characteristics, this will inevitably lead to some deviations from the experimental observations, where the heat loss rate from the column middle to environment would be much faster than that from the two column ends. This may explain why the simulated temperature curvature with time is larger than that of the experimental data.
Figure 3-3 Simulated CSS temperature changes at the top, middle and bottom of the bed in comparison with the data measured in experiment using Norit RB3 as the adsorbent.

Figure 3-4 shows the simulated CSS flow profiles in comparison with the corresponding experimental data, including feed, heavy + light product, and heavy + light reflux streams. The flow rate of feed, heavy product and light reflux was prescribed at the MFC modules and maintained constant over the cycle, which thereby, presents mostly agreement with the experimental records. The flow rate of heavy reflux and light product were both free variables and were manipulated by the PID controller modules for the attainment of pressure set point. The two successive descending trajectories of heavy reflux over the cycle corresponded to the cycle segments of pressure reversal and steady pressure purge, respectively. While the former was associated with the flow characteristics of the gas compressor module, the latter was a consequence of the prompt response of PID controller at the step beginning when feed gas was suddenly injected in. This results is consistent with the minor pressure fluctuation step shown in Figure 3-2. Since most heavy purge gas entering the high pressure bed was captured by the adsorbent, there was little to no light product produced at the step beginning. This phenomenon was more prominent in experiments due to the physical difficulty in fine tuning the back pressure regulators. However, the area under the simulated profile was close to that under the flow plot recorded in experiments, showing that a good agreement on the amount of light product produced was achieved.
3.3.3 Separation performance achieved with benchmarked simulation

With the qualitative establishment of similarity of simulated CSS pressure and temperature profiles with the experimental records, verification of simulated separation performance for all the benchmark runs is summarized in Table 3-2 as well as in Figure 3-5.
Table 3-2 summarizes the simulated CSS separation performance, flow rate of light product and heavy reflux for the 24 benchmark runs of DR PSA separation of methane and nitrogen mixture at various conditions, with Figure 3-5 separately display the product purities as a function of various light reflux flow rate. Over the investigated range of feed compositions, the simulated cycle closely reproduced the separation performances, with run 16 19, -21 in particular match the experimental data for the highest nitrogen raffinate purity. Also in consistent with the experiments, there was an increase of the methane enrichment ratio with the decrease of methane feed composition; thereby run 24 reached the highest enrichment ratio at 22 with a methane concentration increase in heavy product from 2.4% to 53%. The average flow rate of light product and heavy reflux calculated by simulation shows good match with respective experimental records. Since physically several data points around the peak of heavy reflux variations were not recorded, this may results in the relatively small average value than that calculated in simulation.

Table 3-2 Summary of simulated product purities and average flow rate of light product and heavy reflux of 24 benchmark runs performed against the respective experiments, which used Norit RB3 as the adsorbent to separate a 1.25 L feed gas containing (2.1%-49.6%) methane at ambient temperature. (The first three columns list the constant cycle condition of each simulation run)

<table>
<thead>
<tr>
<th></th>
<th>Feed CH₄</th>
<th>Heavy Product</th>
<th>Light Reflux</th>
<th>Light N₂</th>
<th>Heavy CH₄</th>
<th>Light Product</th>
<th>Heavy Reflux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>(-/-)</td>
<td>(SLPM)</td>
<td>(SLPM)</td>
<td>(-/-)</td>
<td>(-/-)</td>
<td>(SLPM)</td>
<td>(SLPM)</td>
</tr>
<tr>
<td>run 1</td>
<td>0.496</td>
<td>0.896</td>
<td>2.276</td>
<td>0.910</td>
<td>0.992</td>
<td>0.674</td>
<td>0.659</td>
</tr>
<tr>
<td>run 2</td>
<td>0.496</td>
<td>0.827</td>
<td>3.388</td>
<td>0.795</td>
<td>0.933</td>
<td>0.657</td>
<td>0.683</td>
</tr>
<tr>
<td>run 3</td>
<td>0.496</td>
<td>0.853</td>
<td>2.231</td>
<td>0.879</td>
<td>0.972</td>
<td>0.687</td>
<td>0.725</td>
</tr>
<tr>
<td>run 4</td>
<td>0.104</td>
<td>0.261</td>
<td>2.287</td>
<td>0.990</td>
<td>0.993</td>
<td>0.518</td>
<td>0.457</td>
</tr>
<tr>
<td>run 5</td>
<td>0.104</td>
<td>0.259</td>
<td>2.036</td>
<td>0.992</td>
<td>0.993</td>
<td>0.524</td>
<td>0.462</td>
</tr>
<tr>
<td>run 6</td>
<td>0.104</td>
<td>0.269</td>
<td>1.301</td>
<td>0.997</td>
<td>0.989</td>
<td>0.514</td>
<td>0.448</td>
</tr>
<tr>
<td>run 7</td>
<td>0.104</td>
<td>0.245</td>
<td>2.796</td>
<td>0.980</td>
<td>0.992</td>
<td>0.515</td>
<td>0.484</td>
</tr>
<tr>
<td>run 8</td>
<td>0.104</td>
<td>0.233</td>
<td>0.801</td>
<td>0.993</td>
<td>0.963</td>
<td>0.561</td>
<td>0.402</td>
</tr>
<tr>
<td>run 9</td>
<td>0.104</td>
<td>0.217</td>
<td>2.033</td>
<td>0.980</td>
<td>0.984</td>
<td>0.562</td>
<td>0.521</td>
</tr>
<tr>
<td>run 10</td>
<td>0.104</td>
<td>0.185</td>
<td>2.057</td>
<td>0.967</td>
<td>0.980</td>
<td>0.578</td>
<td>0.578</td>
</tr>
<tr>
<td>run 11</td>
<td>0.104</td>
<td>0.132</td>
<td>2.054</td>
<td>0.944</td>
<td>0.961</td>
<td>0.597</td>
<td>0.646</td>
</tr>
<tr>
<td>run 12</td>
<td>0.104</td>
<td>0.167</td>
<td>1.965</td>
<td>0.960</td>
<td>0.976</td>
<td>0.589</td>
<td>0.615</td>
</tr>
<tr>
<td>run 13</td>
<td>0.104</td>
<td>0.160</td>
<td>1.237</td>
<td>0.964</td>
<td>0.967</td>
<td>0.625</td>
<td>0.580</td>
</tr>
<tr>
<td>run 14</td>
<td>0.104</td>
<td>0.171</td>
<td>2.717</td>
<td>0.952</td>
<td>0.971</td>
<td>0.552</td>
<td>0.558</td>
</tr>
<tr>
<td>run 15</td>
<td>0.104</td>
<td>0.229</td>
<td>2.712</td>
<td>0.976</td>
<td>0.991</td>
<td>0.527</td>
<td>0.424</td>
</tr>
<tr>
<td>run 16</td>
<td>0.104</td>
<td>0.435</td>
<td>1.959</td>
<td>1.000</td>
<td>0.997</td>
<td>0.330</td>
<td>0.258</td>
</tr>
<tr>
<td>run 17</td>
<td>0.104</td>
<td>0.338</td>
<td>1.953</td>
<td>0.999</td>
<td>0.995</td>
<td>0.423</td>
<td>0.324</td>
</tr>
</tbody>
</table>
Table 3-2 (continued)

<table>
<thead>
<tr>
<th>Run 18</th>
<th>0.104</th>
<th>0.084</th>
<th>2.003</th>
<th>0.925</th>
<th>0.943</th>
<th>0.612</th>
<th>0.660</th>
<th>1.207</th>
<th>1.101</th>
<th>6.828</th>
<th>4.451</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 19</td>
<td>0.041</td>
<td>0.252</td>
<td>2.281</td>
<td>1.000</td>
<td>0.999</td>
<td>0.253</td>
<td>0.192</td>
<td>1.079</td>
<td>0.959</td>
<td>4.721</td>
<td>3.423</td>
</tr>
<tr>
<td>Run 20</td>
<td>0.041</td>
<td>0.226</td>
<td>1.534</td>
<td>1.000</td>
<td>0.998</td>
<td>0.278</td>
<td>0.212</td>
<td>1.049</td>
<td>1.001</td>
<td>3.833</td>
<td>2.837</td>
</tr>
<tr>
<td>Run 21</td>
<td>0.024</td>
<td>0.070</td>
<td>2.302</td>
<td>0.999</td>
<td>0.997</td>
<td>0.473</td>
<td>0.357</td>
<td>1.227</td>
<td>1.153</td>
<td>6.478</td>
<td>3.971</td>
</tr>
<tr>
<td>Run 22</td>
<td>0.024</td>
<td>0.053</td>
<td>0.811</td>
<td>0.995</td>
<td>0.987</td>
<td>0.512</td>
<td>0.279</td>
<td>1.220</td>
<td>1.205</td>
<td>4.169</td>
<td>2.501</td>
</tr>
<tr>
<td>Run 23</td>
<td>0.024</td>
<td>0.059</td>
<td>3.775</td>
<td>0.982</td>
<td>0.993</td>
<td>0.398</td>
<td>0.325</td>
<td>1.234</td>
<td>1.077</td>
<td>8.480</td>
<td>5.265</td>
</tr>
<tr>
<td>Run 24</td>
<td>0.024</td>
<td>0.028</td>
<td>2.223</td>
<td>0.979</td>
<td>0.984</td>
<td>0.530</td>
<td>0.513</td>
<td>1.265</td>
<td>1.165</td>
<td>6.756</td>
<td>4.353</td>
</tr>
</tbody>
</table>

Figure 3-5 Comparison of a) nitrogen purity in light product and b) methane purity in heavy product at various light reflux flow rate for the 24 benchmark runs of DR PSA separation of CH$_4$ + N$_2$ mixture using Norit RB3 at various feed compositions ranging from 2.4 % to 49.6 %.
3.4 Simulation benchmark of CMS 3K-172 test

3.4.1 Description of the benchmarked cycle

Table 3-3 lists the cycle parameters used for the batch of CMS 3K-172 benchmarking runs. The benchmarking exercise of CMS 3K-172 was focused on the comparison of different cycle configurations for the DR PSA separation of 75 % CH₄ + 25 % N₂ mixture by kinetic means. A four step cycle was used, which was same as that shown in Figure 3-1, with exception of high pressure feed injection and/or light product pressure reversal when the cycle configuration was varied as required.

| feed concentration(methane), y<sub>Feed</sub> (-/-) | 0.75 |
| feed flow rate, F<sub>F</sub> (SLPM) | 0.4 |
| heavy product flow rate, F<sub>H</sub> (SLPM) | 0.1-0.35 |
| light reflux flow rate, F<sub>LR</sub> (SLPM) | 0.1-2 |
| dimensionless feed position, z/L (-/-) | 0.5 |
| high pressure, P<sub>H</sub> (kPa) | 500 |
| low pressure, P<sub>L</sub> (kPa) | 110 |
| pressure ratio, P<sub>ratio</sub> (-/-) | ~4.6 |
| feed/Purge step time, t<sub>F/t<sub>P</sub></sub> (s) | 60-420 |
| BD/EQ/PR step time, t<sub>BD/EQ/PR</sub> (s) | 30 (A cycles) 20 (B cycles) |

3.4.2 Performance of cycle characteristics

Again, in the previous chapter we have demonstrated that the separation performance of DR PSA cycle can be reasonably benchmarked only after similarity of cycle characteristics to the ones recorded exponentially have been qualitatively established. We therefore in this section assessed the simulation performance of periodical pressure and temperature profiles for the CH₄ + N₂ separation using CMS 3K-172. This comparable analysis was based on normalized pressure and temperature variations plotted along time over a cycle at CSS condition, referring to one presentative cycle which provides the best experimental separation performance.

Figure 3-6 shows the evolution of simulated CSS pressure occurring in each column in comparison with the corresponding experimental values. Note that as the cycle operated with a relatively small flow rate, the pressure drop across the bed is significantly reduced as compared to that measured in the Norit RB test. By use of PID controller modules, the
Attainment of desired pressure set point in simulation is apparent. The little fluctuations of simulated pressure trajectories at the step beginning indicates the prompt response of PID controller when the internal stream loop was suddenly formulated, which resulted in overshoot of column pressure. Also, the simulated pressure trajectory during the BD/PR step is similar to that observed in experiment, as dictated by the flow characteristics of the gas compressor module.

![Simulated pressure profile](image)

Figure 3-6 Simulated periodical pressure profile of the DR PSA cycle at CSS condition in comparison with the experimental data of CMS 3K-172. (Only the top pressure of the simulated column was tracked as the pressure drop was found to be insignificant)

Figure 3-7(a) shows a comparison of simulated CSS temperature changes of three nodes, which respectively, corresponds to the top, middle and bottom location of three of eleven probes used to monitor the experimental bed temperature. Good consistency of model predictions with data measured was established at respective position across a cycle. Note what being different from the Norit RB3 experiments is the bottom temperature fluctuation that is significantly reduced, only in a small peak to peak amplitude of 2 °C, and is close to the thermal condition occurring at the bed top where little adsorption is expected to happen. This result indicates the adsorption of nitrogen on CMS 3K-172 was limited, although this is the preferentially adsorbed component in feed. Figure 3-7(b) displays the net axial temperature changes along the bed across the cycle. The model predictions shows close match with the experimental data over the net temperature increase or decrease developed at the bed bottom during step 1 and 3, which respectively, corresponds to the course of adsorption and
regeneration. Good agreement was also found over step 2 and step 4, where because of the light reflux for pressure reset, little temperature change was observed. It is noteworthy that the axial temperature profile manifests a very broaden mass transfer zone developed along the bed, suggesting a slow nitrogen sorption in general.

Figure 3-7 Comparison of simulated CSS bed temperature with an experimental DR PSA test of CMS 3K-172, performed at 120s feed time and 0.1 SLPM light reflux flow rate and in PHB cycle configuration. a) Temperature changes at the top (T1), middle (T6) and bottom (T11) of the bed over the four steps of the cycle. b) Net temperature changes along the bed in each step.
3.4.3 Separation performance achieved with benchmarked simulation

The product purities achieved with simulation is summarized in Table 3-4 as well as in Figure 3-8, which involved comparison of different cycle configurations, for the kinetic DR PSA rejection of nitrogen using CMS 3K-172. For each cycle configuration tested, a very good match was found between the model predictions and experimental records over a wide range of feed time and light reflux flow rate, with absolute deviations being less than 2% for the heavy product and 5% for the light product (Figure 3-8e-f). In general, the B cycles are shown to offer better enrichment performance than the A cycles, because in the B cycle configuration, methane is retained in the stripping section by using light product to reset the bed pressure. However, there is little difference between the two feed methods, due to the fact of using dual reflux that forms an internal flow loop across both beds. At the best cycle condition, the DR PSA cycle is capable of producing a methane raffinate up to 90 % purity, indicating a promising process for methane purification. However, since the enrichment performance is relatively low in general, nitrogen breaks through to the methane raffinate. This may explain why the separation performance appeared to be insensitive to the variation of feed time and light reflux flow rate. However, product purity patterns in the figure suggest that improvements could be made by using a combination of shorter feed time and lower light reflux flow rate, as a result of increased contact time of favorable uptake of nitrogen and less breakthroughs per cycle.

Table 3-4 Summary of simulated product purities in comparison with corresponding experimental result, which used CMS 3K-172 as the adsorbent to separate a 0.4 SLPM feed containing 25 % nitrogen in methane with different cycle configurations

<table>
<thead>
<tr>
<th>Test</th>
<th>Feed time (s)</th>
<th>Heavy product (SLPM)</th>
<th>Light reflux (SLPM)</th>
<th>Heavy N₂ Expt</th>
<th>Heavy N₂ Model</th>
<th>Light CH₄ Expt</th>
<th>Light CH₄ Model</th>
<th>Dev N₂ (Model-Expt)</th>
<th>Dev CH₄ (Model-Expt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>run1</td>
<td>60</td>
<td>0.322</td>
<td>1.080</td>
<td>0.400</td>
<td>0.359</td>
<td>0.845</td>
<td>0.804</td>
<td>-0.041</td>
<td>-0.041</td>
</tr>
<tr>
<td>run2</td>
<td>60</td>
<td>0.460</td>
<td>1.094</td>
<td>0.357</td>
<td>0.332</td>
<td>0.874</td>
<td>0.827</td>
<td>-0.026</td>
<td>-0.048</td>
</tr>
<tr>
<td>run3</td>
<td>60</td>
<td>0.256</td>
<td>1.068</td>
<td>0.397</td>
<td>0.365</td>
<td>0.856</td>
<td>0.807</td>
<td>-0.032</td>
<td>-0.049</td>
</tr>
<tr>
<td>run4</td>
<td>60</td>
<td>0.114</td>
<td>0.359</td>
<td>0.364</td>
<td>0.380</td>
<td>0.852</td>
<td>0.808</td>
<td>0.016</td>
<td>-0.045</td>
</tr>
<tr>
<td>run5</td>
<td>60</td>
<td>0.110</td>
<td>0.726</td>
<td>0.378</td>
<td>0.394</td>
<td>0.873</td>
<td>0.809</td>
<td>0.016</td>
<td>-0.063</td>
</tr>
<tr>
<td>run6</td>
<td>30</td>
<td>0.303</td>
<td>2.769</td>
<td>0.322</td>
<td>0.318</td>
<td>0.836</td>
<td>0.781</td>
<td>-0.004</td>
<td>-0.055</td>
</tr>
<tr>
<td>run7</td>
<td>30</td>
<td>0.337</td>
<td>0.665</td>
<td>0.300</td>
<td>0.314</td>
<td>0.824</td>
<td>0.782</td>
<td>0.014</td>
<td>-0.041</td>
</tr>
<tr>
<td>run8</td>
<td>60</td>
<td>0.235</td>
<td>1.442</td>
<td>0.403</td>
<td>0.364</td>
<td>0.839</td>
<td>0.788</td>
<td>-0.039</td>
<td>-0.050</td>
</tr>
<tr>
<td>run9</td>
<td>240</td>
<td>0.119</td>
<td>0.367</td>
<td>0.487</td>
<td>0.450</td>
<td>0.863</td>
<td>0.840</td>
<td>-0.037</td>
<td>-0.023</td>
</tr>
<tr>
<td>run</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>run10</td>
<td>300</td>
<td>0.123</td>
<td>0.368</td>
<td>0.450</td>
<td>0.439</td>
<td>0.866</td>
<td>0.842</td>
<td>-0.011</td>
<td>-0.024</td>
</tr>
<tr>
<td>run11</td>
<td>180</td>
<td>0.119</td>
<td>0.368</td>
<td>0.463</td>
<td>0.449</td>
<td>0.878</td>
<td>0.839</td>
<td>-0.014</td>
<td>-0.039</td>
</tr>
<tr>
<td>run12</td>
<td>120</td>
<td>0.116</td>
<td>0.368</td>
<td>0.452</td>
<td>0.436</td>
<td>0.875</td>
<td>0.830</td>
<td>-0.017</td>
<td>-0.046</td>
</tr>
<tr>
<td>run13</td>
<td>120</td>
<td>0.117</td>
<td>0.745</td>
<td>0.416</td>
<td>0.413</td>
<td>0.887</td>
<td>0.828</td>
<td>-0.003</td>
<td>-0.059</td>
</tr>
</tbody>
</table>

**PHA**

| run |  |  |  |  |  |  |  |  |  |
|-----|---|---|---|---|---|---|---|---|
| run1 | 240 | 0.122 | 0.737 | 0.434 | 0.424 | 0.865 | 0.836 | -0.010 | -0.029 |
| run2 | 240 | 0.123 | 0.370 | 0.478 | 0.461 | 0.877 | 0.855 | -0.017 | -0.022 |
| run3 | 300 | 0.122 | 0.371 | 0.469 | 0.461 | 0.880 | 0.856 | -0.008 | -0.024 |
| run4 | 420 | 0.123 | 0.370 | 0.444 | 0.452 | 0.866 | 0.850 | 0.008 | -0.016 |
| run5 | 180 | 0.118 | 0.372 | 0.479 | 0.460 | 0.888 | 0.850 | -0.018 | -0.038 |
| run6 | 120 | 0.117 | 0.366 | 0.454 | 0.442 | 0.879 | 0.839 | -0.013 | -0.040 |
| run7 | 60 | 0.115 | 0.359 | 0.361 | 0.391 | 0.853 | 0.806 | 0.030 | -0.047 |

**PHB**

| run |  |  |  |  |  |  |  |  |  |
|-----|---|---|---|---|---|---|---|---|
| run1 | 300 | 0.121 | 0.348 | 0.472 | 0.488 | 0.863 | 0.852 | 0.016 | -0.011 |
| run2 | 120 | 0.114 | 0.364 | 0.526 | 0.513 | 0.885 | 0.852 | -0.013 | -0.033 |
| run3 | 60 | 0.105 | 0.326 | 0.520 | 0.514 | 0.891 | 0.840 | -0.006 | -0.052 |
| run4 | 180 | 0.116 | 0.357 | 0.510 | 0.508 | 0.879 | 0.856 | -0.002 | -0.024 |
| run5 | 240 | 0.118 | 0.361 | 0.491 | 0.498 | 0.872 | 0.855 | 0.006 | -0.017 |
| run6 | 60 | 0.103 | 0.466 | 0.513 | 0.500 | 0.891 | 0.833 | -0.013 | -0.058 |
| run7 | 60 | 0.103 | 0.653 | 0.498 | 0.475 | 0.887 | 0.825 | -0.023 | -0.062 |
| run8 | 60 | 0.103 | 0.214 | 0.540 | 0.530 | 0.895 | 0.840 | -0.010 | -0.055 |
| run9 | 60 | 0.103 | 0.142 | 0.524 | 0.527 | 0.899 | 0.841 | 0.003 | -0.058 |
| run10 | 120 | 0.109 | 0.147 | 0.575 | 0.549 | 0.903 | 0.859 | -0.026 | -0.043 |
| run11 | 120 | 0.111 | 0.221 | 0.552 | 0.528 | 0.901 | 0.858 | -0.024 | -0.043 |
| run12 | 120 | 0.115 | 0.515 | 0.498 | 0.485 | 0.888 | 0.844 | -0.013 | -0.044 |
| run13 | 180 | 0.112 | 0.138 | 0.579 | 0.533 | 0.907 | 0.860 | -0.046 | -0.046 |
| run14 | 120 | 0.165 | 0.148 | 0.459 | 0.423 | 0.923 | 0.871 | -0.036 | -0.053 |
| run15 | 120 | 0.177 | 0.356 | 0.431 | 0.418 | 0.919 | 0.880 | -0.013 | -0.039 |
| run16 | 120 | 0.176 | 0.190 | 0.445 | 0.413 | 0.928 | 0.877 | -0.032 | -0.051 |
Figure 3-8 Comparison of simulated separation performance of DR PSA cycle in PLA, PHA and PHB configurations with corresponding data measured in experiments, which used CMS 3K-172 as the adsorbent to separate a 0.4 SLPM feed containing 25% nitrogen on a N2 kinetically selective basis. (a-d) purities of nitrogen extract and methane raffinate at various feed time and light reflux flow rate. (e-f) respective absolute deviations between model prediction and experimental data.

3.5 Parameter effect study

Although parameter effect of DR PSA cycle has been reported for a couple of times in recent publications, few of them explicitly addressed the case using kinetically selective adsorbent, where the removal of impurities is facilitated by the difference in sorption rate rather than equilibrium capacity. It could be understood that while the feed step time and operating flow
in a kinetic adsorption system would affect the separation performance in a manner akin to that of an equilibrium system, the effect of sorption rate would completely differ. In such a system, it is the kinetic selectivity required that is decisive to achieve a certain separation requirement. We here presented a set of parameter effect of feed time, flow rate of light reflux and heavy product as well as sorption rate on the kinetic DR PSA separation of CH₄ + N₂ mixture using CMS 3K-172 as the adsorbent, which is attempted for the first time on a kinetic DR PSA separation.

3.5.1 Effect of feed time

As with adsorption process, the feed time in DR PSA separation is of key importance, as an insufficient feed time may result in inadequate usage of the bed volume, while an excessive amount of feed gas treated in a cycle may surpass the top of bed capacity, resulting in significant breakthroughs. In this section, feed time was parametrically varied in a range of (60-300) s with the benchmarked simulation of CMS 3K-172. The objective of this study were to confirm the existence of feed time effect on the kinetic DR PSA separation and to combine the optimal light reflux flow rate towards an optimization.

Figure 3-9 shows the effect of increasing feed time in a range of (60 – 300) s on the performance of the DR PSA cycle that used CMS 3K-172 as the kinetic selective adsorbent to remove nitrogen from a 0.4 SLPM feed containing 75 % methane. It is interesting to see that although the effect of feed time was not significant on the product purities, an optimal feed time was clearly observed at around 180 s. This existence of optimal feed time may be explained by the changes of composition distribution over the bed. When the feed time was short, only a small amount of nitrogen entered into the bed at the end of high pressure purge bed and this resulted in an inadequate usage of bed volume (Figure 3-10a). As the feed time was increased, the nitrogen wave further penetrated into bed and thus the separation performance was increased. In the meantime, there was also an increase of light purge over the bed (Figure 3-10b), and when the feed time was 300 s, this effect dominated the penetration of nitrogen wave and caused more methane to break through into heavy product. As a result, the separation performance was degraded. Therefore, the optimal feed time should correspond to a cycle segment, in which there is neither inadequate nitrogen penetration nor over clean from light purge of the bed. In this study, this optimal duration was found around 180 s, at which
the purity of methane raffinate was improved to 85 % with nitrogen enriched up to 56 % in heavy product.

Figure 3-9 Effect of increasing feed time in a range of (60 – 300) s on the separation performance of the DR PSA cycle using CMS 3K-172 as the adsorbent at 0.25 SLPM light reflux flow rate.
Figure 3-10 Changes of nitrogen composition distribution along the bed at the end of a) heavy pressure purge/feed step and b) low pressure purge step with the increase of feed time from 60 s to 300 s at 0.25 SLPM light reflux flow rate.
3.5.2 Effect of light reflux flow rate

Figure 3-11 shows the effect of increasing the light reflux flow rate in a range of (0.05 – 0.6) SLPM on the separation performance of the DR PSA cycle at the optimal feed time of 180 s, which was attempted to further seek possible improvement of the kinetic separation that used CMS3K as the adsorbent. In analogy to the effect of feed time, an optimum was observed at an intermediate light reflux flow rate of 0.15 SLPM, at which the methane purity in light product was improved to 85.25 % with nitrogen being enriched up to 58.3 % in heavy product. Again, this existence of optimal light reflux flow rate can be interpreted by the changes of composition distribution as shown in Figure 3-12. Since the heavy product is maintained constant, the increase of light reflux should cause the heavy reflux to increase. Thus, there are two competitive effects as the light reflux flow rate was increased, the increase of heavy reflux should cause more adsorption penetration of nitrogen whereas the increase of light reflux should cause more regeneration of the adsorbent. At low light reflux flow rate relative to 0.15 SLPM, the increase of heavy reflux causes more nitrogen to penetrate into the bed (Figure 3-12a). When desorption occurs, this results in higher enrichment of nitrogen as well as better raffinate of methane, which indicates a threshold flow of light reflux is required to ensure minimum usage of bed volume and continuous operation of the DR PSA cycle. At higher light reflux flow rate of (0.2 - 0.6) SLPM, the increasing clean effect of light reflux overcomes the adsorption penetration of nitrogen wave and results in more methane breakthrough into the heavy product, degrading the separation performance. (Figure 3-12b). It is clear now that the effect of light reflux flow rate is akin to that of feed time, as both of which determines the total amount of gas processed on the bed per cycle, at the optimal value of which, the bed volume is of adequate usage while the breakthrough is minimized. Also, the effect of feed flow rate should be akin to that of light reflux. The increase or decrease of feed flow rate affects the amount of gas processed in the bed, which if already optimized at a selected feed time, may lead to a loss of the separation performance. It is thereby sensible to understand that with a sharper adsorption wave front, as could be developed by a higher adsorption selectivity, either equilibrium or kinetic, the separation performance of the DR PSA can be further pushed up at the same operating cost.
Figure 3-11 Effect of increasing light reflux flow rate in a range of (0.05 – 0.6) SLPM on the separation performance of the DR PSA cycle using CMS 3K-172 as the adsorbent at 180 s feed time.
Figure 3-12 Changes of nitrogen composition distribution along the bed at the end of a) high pressure purge/feed step and b) low pressure purge step with the increasing of light reflux from 0.05 to 0.6 SLPM at 180 s feed time.
3.5.3 Effect of heavy product flow rate

Figure 3-13 shows the effect of increase of heavy product flow rate in a range of 0.06 SLPM to 0.18 SLPM, which is equivalent to a heavy product to feed ratio of 0.16 - 1.8, on the separation performance of the kinetic DR PSA process with a feed gas containing 25% nitrogen. As shown in the figure, the effect of increasing the heavy product flow rate was to shift the separation performance towards producing higher purity of methane raffinate but at a cost of decreasing the nitrogen purity in heavy product. At heavy product flow rate of 0.06 SLPM, the nitrogen adsorption wave propagates further into the bed (Figure 3-14a). When desorption occurs, this results in highly enriched nitrogen being purged out as heavy product at a purity of 68 % (Figure 3-14b). Since the light reflux flow rate is constant, the increase of heavy product will cause the heavy reflux flow rate to decrease, which results in the receding of nitrogen adsorption wave, as shown in Figure 3-14a. Thereby, at heavy product flow rate of 1.8 SLPM, desorption of nitrogen is significantly reduced, resulting in a much lower heavy product purity at 41%. However, since the nitrogen wave recedes during the high pressure purge step, less nitrogen makes its way to the light product through the stripping end of the bed, which in turn produces a methane raffinate at higher purity of 87 % (Figure 3-14b). As perfect separation is unable to achieve in practice, the overall material balance of the DR PSA cycle can be adjusted through the flow rate of heavy product to tune the separation performance towards more stripping or enriching oriented nature depending on the requirement.
Figure 3-13 Effect of increasing heavy product flow rate in a range of (0.06 – 0.18) SLPM on the separation performance of the DR PSA cycle using CMS 3K-172 as the adsorbent at 180s feed time and 0.15 SLPM light reflux flow rate.
Figure 3-14 Changes of nitrogen composition distribution along the bed at the end of a) high pressure purge/feed step and b) low pressure purge step with the increase of heavy product flow rate from 0.06 SLPM to 0.18 SLPM.
3.5.4 Effect of sorption rate

The physical sorption rate of nitrogen and methane on CMS 3K-172 is used for the input of mass transfer coefficient in modelling of adsorption kinetics, which serves as the base condition for this parametric study. The data required were experimentally determined with Micromeritics ASAP2020 through carrying out a physisorption measurement at 303 K and were found to be 0.01 s\(^{-1}\) and 0.0001 s\(^{-1}\), respectively. Details of the experimental measurement of physisorption rate with ASAP2020 were described by Jensen et al.\(^{28}\) Here only a brief description of this measurement is provided. The sorption of a pure component on an adsorbent under a static, constant pressure atmosphere condition can be described by the linear driving force model with Eq. 3-1 for time-dependent adsorbate uptake \(F(t)\) and Eq. 3-2 for sorption rate \(\kappa_i\) in s\(^{-1}\).

\[
F_i(t) = \frac{Q_i(t) - Q_i(0)}{(Q_i(\infty) - Q_i(0))} \quad \text{Eq. 3-1}
\]

\[
1 - F_i = \exp(-\kappa_i t) \quad \text{Eq. 3-2}
\]

where \(Q_i(t)\), \(Q_i(0)\), \(Q_i(\infty)\) refers to the measured solid loading of component \(i\) at time \(0\), \(t\) and equilibrium, respectively. The constant pressure assumption is reasonable for the ASAP measurements, and the sorption rate \(\kappa_i\) can be determined by regression of the experimental data to the above equations.

In the parametric variation, firstly the sorption rate of methane was solely varied in a range of \((8 \times 10^{-6} - 10^{-3})\) s\(^{-1}\), which was equivalent to a nitrogen to methane sorption rate ratio of \((1.3 – 1300)\). Separation power, as defined in the following equation (Eq. 3-3), was used to indicate the changes of kinetic selectivity of the DR PSA process.

\[
S(CH_4) = \frac{Y_{N_2,\text{light}}}{1 - Y_{N_2,\text{light}}} \cdot \frac{Y_{CH_4,\text{light}}}{1 - Y_{CH_4,\text{light}}} \quad \text{Eq. 3-3}
\]

Figure 3-15 shows the effect of increasing Rs values on the separation power and methane purity in heavy product produced by the DR PSA cycle from a 0.4 SLPM feed containing 75 % methane. At low Rs = 1.3 relative to the realistic value of 84.5, the cycle exhibits an artificial methane selectivity, indicated by a separation power at 2.4, and methane is enriched from 75 % to 86 % in heavy product rather than being removed to lower level as was observed in the
original case. This result suggests that the role of heavy component is in fact determined by
the adsorption kinetics rather than the equilibrium capacity alone and is switchable between
each component in feed gas via a certain selection of sorption ratio. At higher Rs values, the
separation power drops below one, indicating that the process is shifted to be kinetically
nitrogen selective. As the methane sorption rate is decreased, the kinetic selectivity of nitrogen
over methane is increased and the separation performance is improved. However, the trend
displayed in the figure shows that this improvement is less effective for Rs over 84.5, which is
the realistic ratio obtained by experimental measurement. Therefore, it is clear that the DR
PSA separation of CH₄ + N₂ using CMS 3K-172 is strongly limited by the slow sorption rate
of nitrogen rather than the competitive adsorption of methane.

Figure 3-15 Effect of increasing nitrogen to methane sorption ratio on the kinetic separation
performance of the DR PSA cycle, with CMS 3K-172 being used as the base adsorbent to
separate a 0.4 SLPM feed mixture containing 75 % methane. (The sorption rate of methane
was maintained constant at the realistic value 0.01 s⁻¹ while that of methane was
parametrically varied from 8×10⁻⁶ s⁻¹ to 8×10⁻³ s⁻¹, yielding Rs values ranging from 1.3 to
1350.)

Figure 3-16 shows the effect of solely increasing the nitrogen sorption rate by ten times, which
is equivalent to Rs of 845, on the kinetic DR PSA separation of 75 % methane and 25 %
nitrogen at various light reflux flow rate, with CMS 3K-172 being used as the adsorbent. By
increasing the nitrogen sorption rate, the improvement of separation performance is apparent. The best performance occurs at light reflux of 0.6 SLPM, at which the cycle produces a methane raffinate at purity close to 90% with nitrogen enriched up to 75% in heavy product, whereas realistically a much lower performance was observed. The increase of the optimal light reflux flow rate from the original 0.15 SLPM to 0.6 SLPM implies that at higher nitrogen sorption rate, the bed capacity is increased so that more gas can be treated per cycle. Figure 3-17 shows the changes of nitrogen composition distribution over the bed and further confirms the occurrence of this improvement. At nitrogen sorption rate ten times higher than original, the nitrogen wave propagates further into the bed at the end of high pressure purge step; when dropping the bed pressure, this would give a better enrichment of nitrogen as compared to that at the original sorption rate. Overall, these results suggest that the adsorbent CMS 3K-172 exhibits limited capability in the application of CH₄ + N₂ separation due to the slow sorption rate of nitrogen.

Figure 3-16 Effect of solely increasing sorption rate of nitrogen by ten times on the kinetic separation performance of the DR PSA cycle at various light reflux flow rate, with CMS 3K-172 being used as the base adsorbent and a 0.4 SLPM feed containing 75% methane. (MTC_N₂ 1x notes the original sorption rate of nitrogen whereas MTC_N₂ 10x notes the increased value)
Figure 3-17 Comparison of nitrogen composition distribution over the bed at the optimal light reflux flow rate for the kinetic DR PSA separation of methane and nitrogen. (MTC_N2 1x notes the original sorption rate of nitrogen whereas MTC_N2 10x notes the value increased by ten times)

3.6 Adsorbent performance comparison

The performance of any separation technology is characterized by a balance between purity and recovery. In natural gas system, recovery of methane is usually more preferential than its product purity. In this section, methane purity and recovery were used as the performance criterion to comparably assess the adsorbents of Norit RB3 and CMS 3K-172 for the DR PSA processing of low quality fuel gas (75 % methane in nitrogen).

Figure 3-18 shows a comparison of simulated methane purity and recovery by DR PSA cycles using CMS 3K-172 (triangle) and Norit RB3 (circle) as the adsorbent respectively, from a feed consisting of 75 % methane. Process optimization and intensification was performed through adjustment of key cycle flows, which involved two steps. Firstly, as noted by the solid arrow, feed time and light reflux flow rate were adjusted towards an optimum of separation performance. During this step, the breakthrough of nitrogen was reduced and thus the methane purity in product was increased. The cycle containing Norit RB3 as the adsorbent produces an optimum of methane raffinate at 92 % purity at 90 s feed time and 1.25 SLPM light reflux,
whereas only 85 % methane purity is achieved with CMS 3K-172 at the respective optimal cycle condition. Secondly, as noted by the dot arrow, the flow rate of heavy product was further adjusted to increase the methane recovery on the basis of the optimal cycle. During this step, the overall cycle mass balance was shifted towards producing a lower purity of methane raffinate, making it less likely to breakthrough to the nitrogen product. By increasing the flow rate of heavy product, methane recovery of the Norit RB3 case (hollow circle) was further increased to 99.6 % but at a cost of degrading the methane composition to 87 % in heavy product. In the CMS 3K-172 case (hollow triangle), where nitrogen was kinetically selected over methane, the flow rate of heavy product was decreased to further improve the concentrate the nitrogen extract so that more methane was driven to the light product, resulting in an improved methane recovery at 93%. However, this also came with an extent of nitrogen contamination to the methane raffinate, as dictated by the overall mass balance. On the whole, the adsorbent Norit RB3 shows apparently better capability than CMS 3K-172 in separating CH₄ + N₂ mixture with the DR PSA process. This may be attributed to the higher equilibrium capacity and sorption rate of Norit BR3 than CMS 3K-172 that allows for better usage of the bed volume. The adsorbent CMS 3K-172, on the other hand, is more likely to be applied in the kinetic separation where the sorption rate is sufficiently fast. Nevertheless, it is demonstrated in our work that the separation of CH₄ + N₂ mixture with DR PSA cycle is determined by the choice of adsorbent selectivity rather than the component.
Figure 3-18 Model predictions of methane purity and recovery by DR PSA processes using CMS 3K-172 (triangle) and Norit RB3 (circle) as the adsorbent, respectively, from a feed consisting of 75% methane and 25% nitrogen. The solid arrow notes the direction of methane purity increase towards an optimum through adjusting the feed time and light reflux flow rate, and the dot arrow notes the direction of methane recovery increase towards a balance with methane purity (hollow symbols) through adjusting the heavy product flow rate.

3.7 Conclusions

A dynamic model of dual reflux pressure swing adsorption was adapted from previous work to simulate the laboratory DR PSA system recently developed, with PID controller modules being added to achieve steady bed pressure for adsorption and regeneration step. The robustness of the model was verified through benchmarking against results of experimental DR PSA separation of CH\textsubscript{4} + N\textsubscript{2} from a pilot scale rig, which tested CH\textsubscript{4} equilibrium selective (Norit RB3) and N\textsubscript{2} kinetically selective (CMS 3K-172) adsorbent, respectively, with a feed gas at composition representative of industrial N\textsubscript{2}-rich waste stream or low grade sources of natural gas. A four step cycle was used with feed, light reflux, heavy reflux carried out simultaneously and counter-current blowdown and heavy product pressurization (or co-current blowdown and light product pressurization) carried out simultaneously during different segment of the cycle. Similarity of model predictions with experimental records in terms of cyclic steady state pressure, temperature and flow profiles was qualitatively established and
then good agreement of product purities were found over a wide range of flow regime and feed composition conditions.

Based on the benchmarked CMS 3K-172 cycle, the effect of feed time and light reflux flow rate was parametrically studied and it was found that the separation performance could be optimized at an appropriate value of these two parameters, at which the breakthrough was reduced to a minimum. The effect of increasing the heavy product flow rate was to shift the cycle towards producing a lower nitrogen purity in the heavy product, making it less likely to break through to the methane rich light product as dictated by the overall material balance. This adjustment could be used to shift the separation towards more nitrogen enrichment or methane purification as required. The potential of DR PSA separation of CH$_4$ + N$_2$ mixture using CMS 3K-172 was investigated with simulation via respectively varying the sorption rate of methane and nitrogen. It was found that the separation performance was strongly limited by the sorption rate of nitrogen rather than the competitive adsorption of methane.

The simulation test of Norit RB3 showed that the DR PSA cycle was capable of producing highly enriched methane extract at methane recovery in excess of 99 %, from a feed containing 75 mol % methane in nitrogen, suggesting great potential of future application in upgrading low quality fuel gas. In contrast, the test of CMS 3K-172 exhibited much lower separation performance and thus this adsorbent was less likely to be applied for industrial natural gas processing. This comparison of adsorbent provides evidence that it is the magnitude of selectivity rather than the component that matters for the DR PSA separation. On the whole, this simulation of dual reflux pressure swing adsorption technique can serve as a useful tool for process design, reduction of cost for laboratory and/or plant trials and enhanced understanding of process behaviour.
Chapter 4 Simulation Investigation of Upscale DR PSA Cycles for Natural Gas Upgrading

Abstract

On the basis of adsorbent assessment presented in Chapter 3, this work further investigated the DR PSA simulation of upgrading low quality fuel at industrial flow characteristics with Norit RB3 being used as the adsorbent.29 A three-step bed sizing method for industrial dehydration of natural gas was firstly reviewed, which identified that the calculation of bed height required to accommodate enough adsorbent was the most critical step. A strategy of constructing upscale DR PSA cycle including bed sizing and flow upscaling was presented, which depicted a simple and quick path of using the outcome from laboratory simulation towards future industrial commission of DR PSA technique. An optimal feed inlet position was identified at the exact middle of the bed, through analysis of composition distribution change over the cycle. This work further elucidates the process behavior for future industry practitioners.

4.1 Introduction

Norit RB3, the equilibrium CH$_4$ selective adsorbent, was shown in the previous chapter to have greater potential over CMS 3K-172 in polishing CH$_4$-rich fuel gas with CH$_4$ recovery in excess of 90%. By simulation means, this chapter further presented a design of an upscale DR PSA process for upgrading the low grade fuel gas using Norit RB3 with the optimal cycle condition provided in Chapter 3.

The Engineering Data Book (Gas Process Supplier Association or GPSA, 2004) points out that the combination of feed rate, pressure drop and adsorbent crush strength dictates the adsorption bed geometry.8 Three steps are involved to size the dehydration bed containing molecular sieve as the desiccant to remove water from natural gas, which includes bed diameter estimation, bed height calculation and pressure drop check. Of these steps the calculation of bed height is probably the most crucial because the adsorbent installed should be enough to make up the bed degeneration over three to five years use while ensuring that the
pressure drop builds over the bed height does not exceed a maximum allowable value. Too high a pressure drop plus the bed weight would break down adsorbent particles.

For the dehydration application, the Engineering Data Book suggests that the design bed height is the summation of the saturated zone and mass transfer zone heights. The height of saturated zone, where the adsorbent is in equilibrium with the inlet wet gas, can be estimated by dividing the amount of water to be removed with the sieve bulk density and then the bed diameter. This calculation is relatively straightforward, although it may require correction factors if the inlet gas is not water saturated and/or at elevated temperature. The determination of MTZ, where because of the adsorbing resistance, the adsorbate solid loading declines with height, is complex and requires numerically solving PDEs. If the feed flow is constant, the Engineering Data Book provides a practical and simplified method, by which the MTZ height is solely dependent on the superficial velocity and corrected with the sieve size.

From a product perspective, the essential difference between the dehydration adsorption and DR PSA is that in a DR PSA process, the feed gas is separated into two products of high purity rather than just purified. This means during a DR PSA cycle, the packed bed is alternatively purged with the heavy and light refluxes for production of heavy extract and light raffinate, which leads to time variance of mass transfer zone length in the bed and thus does not meet the GPSA condition where constant and unidirectional feed flow is essential. In this chapter, we firstly reviewed the GPSA method for dehydration bed sizing to provide a general guidance. And to determine the fixed bed geometry for the DR PSA system, we presented a second method to replace the saturation capacity with an effective adsorbent capacity, which includes the MTZ effect and temperature, feed composition corrections. This method is more general compared to the GPSA method and was found adequate for the upscale application of DR PSA nitrogen rejection from low quality fuel using Norit RB3 as the adsorbent.

4.2 Review of GPSA method for adsorption bed sizing

The first step is to determine the bed diameter, which depends on the superficial velocity. The bed diameter should be kept small to prevent channeling during the regeneration step. However, too small a bed diameter will increase the superficial velocity and thus the pressure drop, and high pressure drop can cause attrition to the adsorbent. The pressure drop is
calculated by a modified Ergun equation, which relates the pressure drop (i.e. $\Delta P$ in kPa) to superficial velocity (i.e. $V$ in m/h).

$$\frac{\Delta P}{L} = B\mu V + C\rho V^2$$  \hspace{1cm} \text{Eq. 4-1}$$

Where $L$ is the length of packed bed in m, $\mu$ the dynamic viscosity in mPa.s, and $\rho$ the density of gas phase in kg/m$^3$. Coefficient $B$ and $C$ for Eq. 4-1 are shown in Table 4-1:

**Table 4-1 Coefficient values for typical adsorbents (Adapted from Engineering Data Book 2004$^8$)**

<table>
<thead>
<tr>
<th>Particle Type</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2 mm bead (4×8 mesh)</td>
<td>0.0693</td>
<td>$3.75 \times 10^{-7}$</td>
</tr>
<tr>
<td>3.2 mm extrudate</td>
<td>0.0893</td>
<td>$5.23 \times 10^{-7}$</td>
</tr>
<tr>
<td>1.6 mm bead (8×12 mesh)</td>
<td>0.1881</td>
<td>$5.74 \times 10^{-7}$</td>
</tr>
<tr>
<td>1.6 mm extrudate</td>
<td>0.2945</td>
<td>$8.86 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

The Engineering Data Book recommends the design pressure drop should be between 35-55 kPa, higher pressure drop is not appropriate as the adsorbent is fragile and can be crushed by the total bed weight and pressure drop forces. After the bed height has been determined, the total pressure drop needs to be checked. By setting the maximum allowable $\Delta P/L$ equal to 7.5 kPa/m, the superficial velocity (i.e. $V_{\text{max}}$) can be estimated, which allows the calculation for the bed minimum diameter (i.e. $D_{\text{minimum}}$):

$$D_{\text{minimum}} = \left(\frac{4q}{60\pi V_{\text{max}}}\right)^{0.5}$$  \hspace{1cm} \text{Eq. 4-2}$$

$$q = \frac{m}{60\rho}$$  \hspace{1cm} \text{Eq. 4-3}$$

Where $q$ and $m$ is the volumetric and mass feed rate, respectively. Round off to the nearest diameter (i.e. $D_{\text{selected}}$), for which $V$ and $\Delta P/L$ are adjusted as follows:

$$V_{\text{adjusted}} = V_{\text{max}} \left(\frac{D_{\text{minimum}}}{D_{\text{selected}}}\right)^2$$  \hspace{1cm} \text{Eq. 4-4}$$

$$\left(\frac{\Delta P}{L}\right)_{\text{adjusted}} \cong (7.5\text{kPa/m}) \left(\frac{V_{\text{adjusted}}}{V_{\text{max}}}\right)^2$$  \hspace{1cm} \text{Eq. 4-5}$$

The next step is to estimate the amount of water to be removed from the feed per cycle with a prescription of adsorption period and calculate the mass of adsorbent required for each bed.
An adsorption time of 8 to 12 hours are common, longer time may be acceptable especially if the feed gas is not water saturated. Longer an adsorption period means less regeneration time, which may extend the bed life because cyclic heating and condensed water related caking formation are the major reasons for bed degeneration, but larger beds and additional capital investments.

In commercial practice, the adsorption is carried out in a vertical fixed bed of adsorbent, with feed gas flowing from top of the bed to prevent fluidization. As noted in Section 1.53, the adsorption process is not instantaneous, which leads to formation of a mass transfer zone (MTZ) in the bed. Thus the bed can be thought of as operating with three zones, as shown in Figure 4-1. The top or equilibrium zone is where the adsorbent is saturated with water in equilibrium with the wet inlet gas and no additional adsorption occurs. The middle or mass transfer zone is where the water concentration is reduced from $y_{in}$ in the inlet valve to the outlet valve $y_{out}$, in a smooth S-shaped curve. This zone usually holds 50% the water held by a comparable length of adsorbent in equilibrium. The MTZ would have a zero thickness if mass transfer rate was infinite. Once the MTZ has been formulated in the adsorbent bed, it travels in a constant length towards the bed outlet unless the feed rate and particle size or shape is changed. The feed gas dictates the $y_{in}$, and the regeneration gas dictates the $y_{out}$. The bottom of the bed is called active zone, where the adsorbent is yet to be used. As the adsorption taking place, the MTZ moves down to the bed outlet and cause a breakthrough. At breakthrough, water concentration in the product starts to increase with time and eventually reaches a value as that in the feed gas when the MTZ is completed displaced. This yields an S-shaped product concentration curve that mirrors what is shown in Figure 4-1. Usually, the adsorption service is terminated at the first sight of breakthrough and the bed then is switched into regeneration mode.
Both the water capacity and the rate at which the adsorbent capture water declines as the adsorbent ages. Thus sufficient bed loads of adsorbent is required such that after three to five years, the MTZ will be at the bottom of the bed at the end of adsorption step.

After three to five years, the saturated water loading of molecular sieve is thought to have declined to 13 kg of water per 100g adsorbent, which is about 65 % the capacity compared to the new adsorbent. Also, if the feed gas is not water saturated and the temperature is higher than 24 °C, the water capacity (i.e. \( W_r \) in kg) needs to be adjusted using factor \( C_{\text{SS}} \) (Figure 4-2) and \( C_T \) (Figure 4-3), respectively. Assuming the bulk density of molecular sieve is 675-735 kg/m³ for beads and 640-705 kg for pellets, the amount of adsorbent required can be calculated using Eq. 4-6 and the length of saturated zone using Eq. 4-7.

\[
S_S = \frac{W_r}{(0.13)(C_{\text{SS}})(C_T)} \quad \text{Eq. 4-6}
\]

\[
L_S = \frac{(S_r)(4)}{\pi(D)^2(\rho_{\text{bulk}})} \quad \text{Eq. 4-7}
\]

Where \( L_S \) is the length of packed bed saturation zone and \( S_S \) the adsorbent amount required in saturated zone. Note this is a conservative estimation that assumes the saturated zone holds all the water to be removed in the feed gas even though the MTZ usually holds about 50 % of the equilibrium water capacity.
The Engineering Data Book suggests that the length of MTZ can be estimated using the following equation:

\begin{equation}
\text{Length of MTZ} = \frac{1}{\text{Correction factor, } C_T}
\end{equation}
\[ L_{MTZ} = (Z)(V_{adjusted} / 640)^{0.3} \quad \text{Eq. 4-8} \]

Where the correction factor \( Z = 0.52 \) m for 3 mm sieve and 0.26 m for 1.5 mm sieve. The total bed height is the summation of the saturated zone and the MTZ height. It should be greater than the bed inner wall diameter, or 1.8 m, whichever is greater.

Finally, the overall pressure drop needs to be checked using \( (\Delta P/L)_{\text{adjusted}} \) for the selected bed diameter, \( D_{\text{selected}} \). The design pressure drop is the result multiplied times the total bed height, which, the Engineering Data Book suggests, should be within 35-55 kPa. The limitation of 55 kPa is important because the pressure drop would increase to two times higher after three years use and too high a pressure drop plus the bed weight will break down the adsorbent. If the design pressure drop exceeds this limitation, the bed diameter should be increased and the adsorbent amount required and the bed geometry recalculated.

4.3 Model upscaling

4.3.1 Upscaling of bed geometry and cycle flow

The dynamic DR PSA simulation in industrial scale was built directly upon previous lab scale simulation for the test of Norit RB3 described in Chapter 3. Each simulated bed of about 3 m length contains 40 spatial nodes. This is sufficient for use in upscale simulation considering that the default node number for a same length of bed is 20. The optimal cycle condition obtained in the previous simulation was used to provide the flow correlations among feed, heavy product and light reflux. Bed layer specifications of upscale cycle used that of a relevant lab scale simulation except that the bed dimensions were amplified to industrial size and the adsorbent particle diameter was set equal to 3.2 mm instead of the 1.6 mm used for lab scale rig. According to Eq. 4-1 shown above, larger a particle size can reduce the bed pressure drop and thus prevent from breaking down the adsorbent when industrial flow level was used\(^8\).

The bed geometry of experimental DR PSA apparatus was available in a few publications\(^{36,38,47-48}\). It was found that most often the lab scale twin-bed was constructed in 1 m length and 0.02 to 0.04 m diameter, at a length to diameter ratio about 50. Of course, such a design that is in analogy to thin tube could fasten the radius heat transfer from the bed internal to wall and the thus isothermal conditions could generally be achieved. However, this design is not viable
for most industrial application because too small a diameter significantly increases the superficial velocity, which will build up excessive pressure drop across the bed and leads to attrition of adsorbent. Therefore, to size a bed operating at industrial flow rates, the bed length to diameter ratio should be kept small in the first instance, so that it could be adequately general for use in most separation applications. In this sense, the bed diameter was firstly specified at 4.1 m, which was a maximum value common in use for adsorption bed in industry, followed by a conservative specification of bed length at 6.6 m to form a relatively low length to diameter ratio of 1.5. This length was meant to restrict the pressure drop in the first instance. As a larger bed volume is usually favorable for higher feed throughput, the determination of bed length in this regards will be discussed in the following part.

Once the bed geometry has been determined, the operating flow rate for the upscale DR PSA cycle can be calculated accordingly. Too high a flow rate would result in significant breakthrough, the opposite would lead to insufficient usage of bed volume and a situation where, because of inadequate heavy purge, little to no light product could come out through the pressure controlled outlet valve. This kind of energy inefficiency would diminish the capital incentive of using this DR PSA technique. Therefore, the upscale DR PSA cycle should operate at adequate flow rate while ensuring that the breakthrough is minimized, i.e. the optimal cycle condition should be used. Also notice that the $L_S$-flow and $L_{MTZ}$-flow correlations (Eq. 4-6 to 4-8) provided by the GPSA book is not applicable here because during a DR PSA cycle, the simultaneous production of extract and raffinate was accomplished by purging the bed alternatively with heavy and light reflux rather than a constant and unidirectional feed. Combining these considerations, in this work the operating flow was upscaled in proportion to the increase of bed volume from a laboratory scale simulation, while maintaining the optimal flow correlations among feed, heavy product and light reflux. This method replaced the ‘saturated zone’ depicted by the GPSA book with an ‘optimal bed usage’, which includes the MTZ effect and the temperature corrections. Specifically, for an upscale bed in 4.1 m diameter and 6.6 m length, the bed volume amplification factor was calculated to be $9.3 \times 10^4$. Applying this number for flow upscaled yielded a feed, heavy product, and light reflux at flow rate of 0.087 kmol/s, 0.065 kmol/s and 0.087 kmol/s, respectively as shown in Table 4-2a. The operation pressure were set same as that of the lab-rig simulation. Table 4-2b
shows the comparison of product purities between the simulated upscale and respective lab scale DR PSA cycle for the separation of 25 % nitrogen from methane using Norit RB3. The methane purities in both the heavy and light product streams from the simulated upscale cycle are very close to that from the lab-scale simulation, within 4 % absolute difference. This result suggests that separation performance close to the optimum obtained in lab-scale simulation can be achieved using our cycle upscaling method, because of the similar fractional usage of bed volume.

Table 4-2a Bed geometry and cycle flow correlation up-scaled from an optimal four step PLA cycle determined during the Norit RB3 test in Chapter 3.

<table>
<thead>
<tr>
<th>Bed geometry</th>
<th>Laboratory rig</th>
<th>Up-scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hb (m)</td>
<td>0.97</td>
<td>6.6</td>
</tr>
<tr>
<td>Db (m)</td>
<td>0.035</td>
<td>4.1</td>
</tr>
<tr>
<td>Flow scaling (amp factor 93369)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F_F (kmol/s)</td>
<td>9.29×10^{-07}</td>
<td>8.68×10^{-2}</td>
</tr>
<tr>
<td>F_LR (kmol/s)</td>
<td>9.29×10^{-07}</td>
<td>8.68×10^{-2}</td>
</tr>
<tr>
<td>F_H (kmol/s)</td>
<td>6.97×10^{-07}</td>
<td>6.51×10^{-2}</td>
</tr>
</tbody>
</table>

Table 4-2b Comparison of simulated separation performance of the upscale DR PSA cycle with the corresponding lab-scale result at the optimal cycle condition, with a feed containing 75 % methane in nitrogen.

<table>
<thead>
<tr>
<th>Performance</th>
<th>Lab rig</th>
<th>Up-scale</th>
<th>Difference(abs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy product CH₄ %</td>
<td>90.9 %</td>
<td>91.8 %</td>
<td>0.9 %</td>
</tr>
<tr>
<td>Light product CH₄ %</td>
<td>33.7 %</td>
<td>37.5 %</td>
<td>3.8 %</td>
</tr>
</tbody>
</table>

4.3.2 Bed height study and pressure drop check

Following from above result, the effect of various bed length in a range of (6.6 – 20) m was further investigated, while maintaining the bed diameter constant at 4.1m. Accordingly, the flow rate of feed, light reflux and heavy product were also increased proportionally with the respective increase of the bed volume so that the bed volume could be fully utilized, and the as-calculated flow rate to be used in simulation test were shown in Table 4-3. The operating
pressure and the cycle step time was kept unchanged. The result was plotted as the product purities and pressure drop across the low pressure bed as a function of the bed length, as shown in Figure 4-4. Since higher bed pressures reduce the superficial velocity, only the pressure drop across the low pressure bed is tracked here. As the bed length was increased, there was little to no changes of the methane purities in the heavy and light product, suggesting that steady separation performance could be achieved at various bed volume under this cycle upscaling rule. However, the pressure drop across the low pressure bed was increased significantly, reaching 44 kPa at bed length of 20 m. Since the separation performance was around the optimum already, the maximum allowable bed length can be estimated straightforward with respect to the pressure drop limitation. From the trend shown in this figure, the maximum allowable bed length for this specific cycle was about 22 m for a 55 kPa pressure drop limitation, at which the highest feed throughput was around 0.3 kmol/s. Notice that this number could be slightly higher if using high pressure feed injection, as the volumetric flow through the bed would be reduced at higher pressure.

Table 4-3 Flow rate of feed, light reflux and heavy product up-scaled in proportion to the increase of bed volume for the investigation of bed height effect on the DR PSA separation performance

<table>
<thead>
<tr>
<th>Bed height (m)</th>
<th>Feed (kmol/s)</th>
<th>Light reflux (kmol/s)</th>
<th>Heavy product (kmol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.6</td>
<td>8.68×10^{-02}</td>
<td>8.68×10^{-02}</td>
<td>6.51×10^{-02}</td>
</tr>
<tr>
<td>8</td>
<td>1.05×10^{-01}</td>
<td>1.05×10^{-01}</td>
<td>7.89×10^{-02}</td>
</tr>
<tr>
<td>10</td>
<td>1.31×10^{-01}</td>
<td>1.31×10^{-01}</td>
<td>9.86×10^{-02}</td>
</tr>
<tr>
<td>15</td>
<td>1.97×10^{-01}</td>
<td>1.97×10^{-01}</td>
<td>1.48×10^{-01}</td>
</tr>
<tr>
<td>20</td>
<td>2.63×10^{-01}</td>
<td>2.63×10^{-01}</td>
<td>1.97×10^{-01}</td>
</tr>
</tbody>
</table>
Figure 4-4 Effect of increasing bed height on the separation performance and bed pressure drop of the DR PSA cycle, for which the flow rate of feed, light reflux and heavy product was up-scaled in proportion with the increase of bed volume.

4.4 Flow study for upscale DR PSA processing of low grade fuel using Norit RB3

Following from above section, this case study is attempted to demonstrate the number of bed unit required with feed flow rate characterizing what being commonly used in a gas plant. This study is restricted to the application in upgrading low quality fuel (i.e. 25 % N₂ + 75% CH₄) using Norit RB3 as shown above, and as temperature cycling is not usually used in a PSA process, the adsorbent aging effect is not considered.

Most solid adsorbent based PSA systems for physical nitrogen removal from methane operate at relatively small feed flow rate as compared with cryogenic distillation. Up to date, a processing capacity of 2-30 MMscfd is common, a feed flow rate higher than 30 MMscfd is not usual to use.⁶ The first two columns of Table 4-4 show three selected feed flow rate in MMscfd and the equivalent values in kmol/s. As higher superficial velocities increases the MTZ thickness, a large bed diameter of 4.1 m is used. Following our flow scaling rule that the feed rate should be increased in proportion with the bed capacity, the bed height can be directly estimated from this correlation (Figure 4-5a). Usually the bed height to diameter ratio
should be within 2-6, for which the design bed height is adjusted and thus the number of bed unit required can be determined. Using the pressure drop-bed height correlation obtained in the Figure 4-4, the design pressure drop can be checked (separately plotted in Figure 4-5b). If this design pressure drop exceeds the 55 kPa limitation, the bed diameter or bed number should be increased and the bed height re-estimated.

**Table 4-4 Bed geometry determined by our scaling method for the upscale DR PSA application in fuel upgrading at selected industrial flow characteristics.**

<table>
<thead>
<tr>
<th>Feed (MMscfd)</th>
<th>Feed (kmol/s)</th>
<th>Bed height (m)</th>
<th>Bed height adjusted (m)</th>
<th>Bed NO.</th>
<th>Pressure drop (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.027671</td>
<td>3</td>
<td>8.2</td>
<td>1</td>
<td>4.8</td>
</tr>
<tr>
<td>15</td>
<td>0.207533</td>
<td>15.4</td>
<td>15.4</td>
<td>1</td>
<td>22.5</td>
</tr>
<tr>
<td>30</td>
<td>0.415067</td>
<td>30.7</td>
<td>15.4</td>
<td>2</td>
<td>22.5</td>
</tr>
</tbody>
</table>
Figure 4-5 Correlation of a) feed flow rate and bed height and b) pressure drop and bed height obtained in the upscale simulation of DR PSA separation of 75% CH₄+ 25 %N₂ mixture by use of our upscaling method, which is, increasing the optimal cycle flows in proportion with the increase of bed capacity.
4.5 Choice of feed inlet position

The dual reflux nature of DR PSA cycle allows intermediate feed injection at various bed axial positions. The addition of feed inlet port means however increased capital investment. Thus it is desirable to operate the DR PSA cycle with a selected inlet port by which the performance reaches an optimum. By simulation means, we here investigated the effect of feed inlet position on the separation performance of an upscale DR PSA cycle constructed for upgrading of low grade fuel using Norit RB3. This study is to confirm the existence of optimal feed inlet position and to make an optimal choice for this specific DR PSA separation.

Figure 4-6 shows the simulated product purities of the upscale DR PSA cycle at various feed inlet positions for the separation of 75 % methane in nitrogen. Methane extract at purity in excess of 0.9 was only available using feed inlet located between 0.4 and 0.6 fractional length of the bed, within which, the best performance occurred and corresponded to a feed inlet located at the exact middle of the bed. In contrast, the separation performance was decreased rapidly using feed inlet positions close to the top and bottom of the bed. This existence of an optimal feed port position can be interpreted by means of methane concentration distributions along the length of the bed, as shown in Figure 4-7. In the case of zf = 0.2, methane concentration trajectories from the enriching section underwent a sharp decrease at the feed position and the stripping section had to start with a much lower concentration. This sharp decrease was considered as a perturbation to the methane concentration distribution in the bed and is due to the mixing between the feed flow and the downstream available in the neighborhood of the feed position. This phenomenon always results in lower separation performance and this effect was more significant at feed position of zf = 0.1. Diagne et al experimentally investigated the performance of DR PSA cycle separating CO2 and air mixture at various feed positions from a 20 % CO2 feed, and similar result was observed.37-38 In the case of zf = 0.8, this mixing problem was remarkable again and resulted in a lower methane concentration in the enriching section than that in the stripping section. Thus, the optimal feed inlet position should correspond to a position at which there is no such concentration perturbation. In the case of zf = 0.5, the concentration jump at the feed inlet position was diminished by the end adsorption step, characterized by a smooth transition of concentration trajectories and the methane wave penetrated most deeply into the stripping section. This
explains why the best separation performance was obtained using this optimal feed inlet position.

Figure 4-6 Effect of various feed inlet position on the separation performance of the up-scale DR PSA cycle for the separation of 75 % CH₄ + 25 % N₂ mixture.
Figure 4-7 Changes of methane composition distribution along the bed at the end of a) low pressure purge/feed step and b) high pressure purge step, as a function of feed inlet position.

4.6 Conclusions

The DR PSA simulation in industrial scale was investigated for the separation of 75 % CH₄ + 25 % N₂ mixture using activated carbon Norit RB3, which was identified in previous work to
be a promising adsorbent for upgrading of low quality fuel gas. The flow rate of feed, light reflux and heavy product for the upscale cycle used the optimal correlations identified from previous simulation of a relevant laboratory scale cycle and it was found by upscaling the operating flow rates in proportion to the increase of bed volume, separation performance close to the optimum obtained in previous lab scale simulation could be reproduced. Under this flow upscaling rule, a maximum allowable bed length was determined with respect to the pressure drop limitation and a highest feed throughput was thereby estimated. This investigation depicts a simple but effective path of using the laboratory outcome towards future industrial commission of DR PSA technique.

Study on effect of feed inlet position on the performance of the process revealed that a concentration jump occurring at the feed inlet position always resulted in lower separation performance. An optimal feed inlet position was identified at the exact middle of the bed, at which the concentration jump could be diminished, characterized by a smooth transition of methane concentration at the feed position. This simulation study further elucidates the process behavior and provides useful insights for future industrial practitioners.
Chapter 5 Preliminary Simulation Investigation of DR PSA Cycles for Helium Recovery

Abstract

This work presents a preliminary DR PSA simulation using Norit RB3 as the adsorbent to recover dilute helium from methane or/nitrogen dominant stream at a composition representative of the industrial overhead product from nitrogen rejection unit. A four step PLA cycle, along with the optimal cycle condition obtained in previous chapter was used. The impact of N2 presence in feed was found akin to that of CH4 through the simulation separations of binary feedstocks containing 4 % helium in CH4 or N2, which yielded a helium raffinate up to 40 % purity with 68 % He recovery, and better performance could be expected at a combination of reduced feed time and light reflux flow rate, a comparable result to that obtained by cryogenic distillation. For the separation of ternary feed comprising of He, CH4 and N2, the potential of by-production of highly purified N2 through an axil bed port was demonstrated by means of composition distributions, which to the author’s knowledge, represents the first time this has been attempt for the DR PSA separations. This simulation study of DR PSA technology suggests a low cost separation process for commercial applications in helium recovery and upgrading from subquality natural gas sources.

5.1 Introduction

Helium is a unique gas with a wide range of medical, scientific and industrial applications because of its chemically inert nature and extremely low boiling point and small molecule size. The only viable source of helium is from some selected natural gas field, where the helium concentration can justify the cost of infrastructure required to bring it to market. Few gas plants are dedicated only to the production of helium. In fact, the helium recovery facility is typically an addition to a gas plant, where helium is produced as a by-product when cryogenic nitrogen removal is used to meet the pipeline gas specifications. Adsorption processes is in common use for final stage purification to produce 99.995 % purity helium product, but so far there is no alternative commercial processes that is competitive with cryogenic distillation at
flow rate characteristic of large LNG facility operations. Das et al. reports a pilot scale PSA unit that is capable of producing 99.0 vol% helium product from a natural gas feed containing 0.06 vol% helium. However, this pilot PSA plant is of great complex; the helium purification process involved four stages, with each stage associated with a preset three-bed seven-step cycle to remove selected impurities from a He mixture containing CH₄, N₂, CO₂ and C₂⁺; the adsorbent used requires prior laboratory work of material synthesis and pellet formation, which somehow degrades the economic advances of PSA processes. Although with astonishing helium purity achievements, this complexity required stems from the fact that the conventional PSA processes are confined by the thermodynamic limitations and thus, in general need iterative adsorption stages to ensure high product quality. With our rigorous DR PSA model, we here presented a four step DR PSA cycle, which used commercially available adsorbent Norit RB3, along with the optimal cycle condition obtained in previous work, to preliminarily investigate the recovery of helium from a pilot scale feed at composition representative of the industrial overheads from nitrogen rejection unit. Our objective is to produce helium raffinate at purity purities comparable to that obtained from expensive cryogenic distillation, which to the author’s knowledge represent the first time this has been attempted on the DR PSA system.

5.2 Model preparation

5.2.1 Specifications for the bed layer module

Parameter terms with respect to helium physical properties and adsorption characteristics were specified via the bed layer module. As helium is known to have little adsorption at ambient temperature on carbonaceous adsorbents, the isotherm parameters IP1 and IP2(IP4) for helium(Table 2-1, Eq. 2-6), which respectively, represents the saturated solid loading and adsorption enthalpy, were set equal to zero. Since extended Langmuir isotherm was used to include adsorption competition effect, the parameter IP3 accounting for this effect of helium was required to be zero, otherwise the inclusion of this term will unrealistically reduce the adsorption capacity of methane or nitrogen on the adsorbent. The helium molecular diffusivity at 1.63×10⁻⁴ m²/s was calculated with Chapman-Enskog theory and the adsorbed phase heat capacity was estimated at 0.021 MJ/kmol/K. Furthermore, due to the no helium adsorption assumption, the impact of helium adsorption kinetics was diminished, thus any value of mass
transfer coefficient used will result in the same separation performance. Here we used the system default value at 0.05 s⁻¹. All the other parameters for the specification of bed layer module are shown in Table 5-1.

Table 5-1 Bed layer specifications in the framework of Aspen Adsorption for the simulation of DR PSA recovery of 4% lean helium in methane or/and nitrogen using Norit RB3 as the adsorbent.⁷

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed half-length, $L$</td>
<td>0.485</td>
<td>m</td>
</tr>
<tr>
<td>wall thickness, $w_1$</td>
<td>0.0016</td>
<td>m</td>
</tr>
<tr>
<td>bed layer diameter, $D_b$</td>
<td>0.035</td>
<td>m</td>
</tr>
<tr>
<td>inter-particle void fraction, $\epsilon_i$</td>
<td>0.433</td>
<td>m³ void/m³ bed</td>
</tr>
<tr>
<td>intra-particle void fraction, $\epsilon_p$</td>
<td>0.397</td>
<td>m³ void/m³ bead</td>
</tr>
<tr>
<td>bulk density of bed layer, $\rho_s$</td>
<td>439.325</td>
<td>kg/m³</td>
</tr>
<tr>
<td>particle diameter, $d_p$</td>
<td>0.0015</td>
<td>m</td>
</tr>
<tr>
<td>particle shape factor, $sfac$</td>
<td>0.85</td>
<td>n/a</td>
</tr>
<tr>
<td>mass transfer coefficient, $MTC_{,i}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$MTC_{,methane}$</td>
<td>0.42</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>$MTC_{,nitrogen}$</td>
<td>0.765</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>$MTC_{,helium}$</td>
<td>0.05</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>molecular diffusivity, $D_{m,i}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_{m,methane}$</td>
<td>$2.17 \times 10^{-05}$</td>
<td>m²/s</td>
</tr>
<tr>
<td>$D_{m,nitrogen}$</td>
<td>$2.00 \times 10^{-05}$</td>
<td>m²/s</td>
</tr>
<tr>
<td>$D_{m,helium}$</td>
<td>$1.63 \times 10^{-04}$</td>
<td>m²/s</td>
</tr>
<tr>
<td>isotherm parameters $IP_{,i}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$IP_{1}, methane$</td>
<td>$6.58 \times 10^{-07}$</td>
<td>kg/kmol/bar</td>
</tr>
<tr>
<td>$IP_{1}, nitrogen$</td>
<td>$7.30 \times 10^{-07}$</td>
<td>kg/kmol/bar</td>
</tr>
<tr>
<td>$IP_{1}, helium$</td>
<td>0</td>
<td>kg/kmol/bar</td>
</tr>
<tr>
<td>$IP_{2}, methane$</td>
<td>2077.09</td>
<td>K</td>
</tr>
<tr>
<td>$IP_{2}, nitrogen$</td>
<td>1722.53</td>
<td>K</td>
</tr>
<tr>
<td>$IP_{2}, helium$</td>
<td>0</td>
<td>K</td>
</tr>
<tr>
<td>$IP_{3}, methane$</td>
<td>$1.19 \times 10^{-04}$</td>
<td>1/bar</td>
</tr>
<tr>
<td>$IP_{3}, nitrogen$</td>
<td>$1.75 \times 10^{-04}$</td>
<td>1/bar</td>
</tr>
<tr>
<td>$IP_{3}, helium$</td>
<td>0</td>
<td>1/bar</td>
</tr>
<tr>
<td>$IP_{4}, methane = IP_{2}, methane$</td>
<td>2077.09</td>
<td>K</td>
</tr>
<tr>
<td>$IP_{4}, nitrogen = IP_{4}, nitrogen$</td>
<td>1722.53</td>
<td>K</td>
</tr>
<tr>
<td>$IP_{4}, helium = IP_{4}, helium$</td>
<td>0</td>
<td>K</td>
</tr>
<tr>
<td>specific heat capacity of adsorbent, $C_{p_s}$</td>
<td>$1.00 \times 10^{-03}$</td>
<td>MJ/kg/K</td>
</tr>
<tr>
<td>specific heat capacity of wall, $C_{p_w}$</td>
<td>$5.00 \times 10^{-04}$</td>
<td>MJ/kg/K</td>
</tr>
<tr>
<td>specific heat capacity of adsorbed phase, $C_{p_{a,i}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{p_{a,methane}}$</td>
<td>0.036</td>
<td>MJ/kmol/K</td>
</tr>
<tr>
<td>$C_{p_{a,nitrogen}}$</td>
<td>0.029</td>
<td>MJ/kmol/K</td>
</tr>
<tr>
<td>$C_{p_{a,helium}}$</td>
<td>0.021</td>
<td>MJ/kmol/K</td>
</tr>
<tr>
<td>heat of adsorption, $\Delta H_i$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta H_{methane}$</td>
<td>-17.27</td>
<td>MJ/kmol</td>
</tr>
<tr>
<td>$\Delta H_{nitrogen}$</td>
<td>-14.32</td>
<td>MJ/kmol</td>
</tr>
<tr>
<td>$\Delta H_{helium}$</td>
<td>0</td>
<td>MJ/kmol</td>
</tr>
<tr>
<td>adsorbent thermal conductivity, $k_a$</td>
<td>$5.00 \times 10^{-07}$</td>
<td>MW/m/K</td>
</tr>
<tr>
<td>wall thermal conductivity, $k_w$</td>
<td>$1.60 \times 10^{-05}$</td>
<td>MW/m/K</td>
</tr>
<tr>
<td>wall density, $\rho_w$</td>
<td>7800</td>
<td>kg/m$^3$</td>
</tr>
</tbody>
</table>

5.2.2 Choice of cycle configuration

In the study, a four step cycle was used, with low pressure feed injection and pressure reversal by heavy reflux, i.e. the PLA configuration. Concurrent blowdown was used to ensure that the desorbate stay in the enriching section and thus does not contaminate the helium raffinate. And since the feed method has been found to cause little difference in the separation performance (Section 3.3), this study is restricted to the low pressure feed configuration. The cycle sequence is shown in detail in Figure 3-1. As with the adsorbent Norit RB3, cycle condition was set to be the optimum obtained in section 3.5 in the first instance, except with blowdown time reduced to 60 s for faster cycling (Table 5-2). Note that a feed helium composition at 4 %, which representative of the overhead waste of the industrial nitrogen rejection unit, was used for all the simulation tests.$^7$

Table 5-2 Cycle parameters for the simulation of DR PSA recovery of 4% lean helium in methane and/or nitrogen using Norit RB3 as the adsorbent. (The cycle condition shown is referred to the optimum obtained in Chapter 3, further adjustments of selected parameters are presented in the following section to study the parameters)

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>feed concentration(helium), $y_{Feed}$</td>
<td>0.04</td>
</tr>
<tr>
<td>feed flow rate, $F_f$ (SLPM)</td>
<td>1.25</td>
</tr>
<tr>
<td>Feed temperature, $T_F$ (°C)</td>
<td>29</td>
</tr>
<tr>
<td>heavy product flow rate, $F_{H}$ (SLPM)</td>
<td>1.2</td>
</tr>
<tr>
<td>light reflux flow rate, $F_{LR}$ (SLPM)</td>
<td>1.25</td>
</tr>
<tr>
<td>dimensionless feed position, $z/L$ (-/-)</td>
<td>0.5</td>
</tr>
<tr>
<td>high pressure, $P_H$ (kPa)</td>
<td>510</td>
</tr>
<tr>
<td>low pressure, $P_L$ (kPa)</td>
<td>155</td>
</tr>
<tr>
<td>pressure ratio, $P_{ratio}$ (-/-)</td>
<td>3.3</td>
</tr>
<tr>
<td>feed/Purge step time, $t_F/t_{PU}$ (s)</td>
<td>90</td>
</tr>
<tr>
<td>BD/PR step time, $t_{BD/EO/PR}$ (s)</td>
<td>60</td>
</tr>
</tbody>
</table>

5.3 Preliminary cycle optimization for binary feed mixture

Feed gas composition is probably the most important of the factors that dictate the design of industrial helium recovery processes with cryogenic distillation. Depending on the gas reservoir regions, raw natural gas fed into a gas plant can vary significantly in the nitrogen
concentration, which determines whether a single column, or dual column design of cryogenic fractionation unit should be used. For helium recovery by use of DR PSA process, which is analogy to the distillation method, we essentially assessed the separations of N₂ + He in comparison with that of CH₄ + He mixture before moving to use a ternary feed at the same helium concentration (4 % He + 26 % CH₄ +70 % N₂). We have demonstrated that feed time and light reflux flow rate can be adjusted to reduce the cycle breakthroughs, whereas heavy product can be used to tune the separation towards more stripping or enriching oriented nature. Hence these parameters were used here to adjust the cycle towards yielding a best of helium raffinate performance with the 4 % helium feed. In addition, this binary feed was extended at a higher helium composition of 13.3 %, which is equivalent to the same helium to methane ratio in the ternary feed, to preliminarily investigate the impact of various feed helium concentrations on the cycle performance.

Prior to running simulation test of binary mixture, the twin-bed module was fully swept with the feed gas to flush away the unwanted third component in the system. This operation was terminated when the concentration of the third component was reduced below 1×10⁻¹⁰, at which the Adsim would ignore the component presence as this concentration is 1000 times smaller than the equation residuals. We found this approach better than manually stipulating a zero concentration value for the bed or tank module, because the latter often caused a solver failure.

5.3.1 Effect of feed time and light reflux flow rate

A 1.25 SLPM binary feed containing 4 % helium in methane or nitrogen was tested at various light reflux flow rate and feed step time, and the results are plotted as product purities and helium recovery shown in Figure 5-1. The performance trend shows that helium raffinate purity and helium recovery could be improved by decreasing the light reflux flow rate and feed step time. At 0.3125 SLPM light reflux flow rate, helium composition was increased from 4 % in feed to 40 % in the light product at 68 % recovery, whereas much lower performance was observed at higher light reflux flow rate. Similarly, at 60 s feed step time, the cycle produced higher helium purity than a longer feed step time, although this improvement was less remarkable as compared with that by decreasing the light reflux flow rate. This result suggests that a further improvement of raffinate performance for helium could be achieved.
with a combination of lower light reflux flow rate and shorter feed step time. Also, the helium raffinate performance from methane feed was found higher than that from nitrogen feed. This should be attributed to the higher methane equilibrium capacity on Norit RB3, which resulted in a higher selectivity. The methane or nitrogen extract purities exhibited little to no change from the feed composition over the investigated range of these two parameters, due to fact that these two components were already of high purity in feed and were less likely to be further concentrated.

Figure 5-1 Separation performance and helium recovery by the DR PSA process at various a-b) light reflux flow rate and c-d) feed time, from a 1.25 SLPM binary feed containing 4 % helium in methane or nitrogen.

Figure 5-2 shows the changes of methane concentration distribution along the bed over a cycle, obtained at 0.625 SLPM light reflux and 90 s feed step time for the CH₄ + He separation. At the end of blow down step, methane was desorbed from the adsorbent and fully filled the bed gas phase. In the light purge step, the methane concentration across the bed was decreased but still remained in excess of 80 %. By the end of pressurization step, a concentration wave front was formed at around z/L = 0.1 by filling in pure methane heavy reflux from z/L = 1, which created a 0.1 fractional bed volume of helium at 60 % purity at the top of the bed. This portion of helium was pushed out completely in the following heavy purge step, but at severe methane breakthrough, the helium raffinate was contaminated and yielding a lower helium purity of 20 %
and helium recovery of 30%. Since the bed predominantly contained methane, the breakthrough was imminent. This also reasons why the helium raffinate performance could be increased at lower light reflux flow rate and shorter feed step time.

Figure 5-2 Changes of methane concentration distribution along the bed over a cycle for the DR PSA separation of CH$_4$ + He mixture, obtained at 0.625 SLPM light reflux and 90 s feed step time.

5.3.2 Effect of heavy product flow rate

Figure 5-3 shows the effect of increasing heavy product flow rate in a range of (0.6 - 1.2) SLPM, which is equivalent to a heavy product to feed ratio of 0.48 - 0.96, on the product purities and helium recovery by the DR PSA process for the 96% CH$_4$/N$_2$ + 4% He separation. As discussed in Chapter 3, the effect of increasing the heavy product flow rate is to shift the overall mass balance towards producing a lower heavy component purity in the extract, making it less likely to breakthrough to the light product. In the other direction, this adjustment could be used to improve the light component recovery, although this would come with degraded purification performance. At low heavy product flow rate of 0.6 SLPM relative to 1.2 SLPM, the helium recovery at 68% could be achieved, which was about 7 times higher than that at 1.2 SLPM. However this came with a lower helium raffinate purity at 5%. It is noteworthy that the heavy extract purities appeared to be insensitive to this adjustment and
remained at around 96 %, which was largely due to the high CH₄ or N₂ concentration in feed. As shown previously, the bed contained predominantly the heavy component with this He-lean feed, the breakthrough was imminent and the separation performance was low in general. Therefore, solely adjusting the heavy product flow rate could not make a viable tuning of helium raffinate purity or helium recovery as required.

Figure 5-3 Effect of increasing heavy product flow rate on the a) separation performance and b) helium recovery of the DR PSA cycle separating a 1.25 SLPM binary feed containing 4 % helium in methane or nitrogen.

5.3.3 Effect of feed helium composition

The very lean helium fed to a DR PSA cycle is shown above to be the primary reason for the significant breakthrough of heavy component into the helium raffinate, because the bed contains predominantly the heavy component. In this section, the impact of feed helium composition on the DR PSA cycle was investigated to provide an insight into this specific breakthrough contributed by a feed.

An extension of feed helium composition at 13.3 %, which is equivalent to the same helium to methane feed ratio as that of the industrial waste stream, was tested and compared with the 4 % helium feed at three light reflux flow rates ranging from 0.625 SLPM to 2.5 SLPM. As the feed methane concentration was reduced, the flow rate of heavy product was also reduced to 1.08 SLPM accordingly, maintaining the heavy product to feed ratio consistent with the feed composition. Other cycle parameters were maintained unchanged. The simulation results are shown in Figure 5-4 as helium raffinate purity and recovery as a function of light reflux flow rate. Helium was concentrated from 13.3 % in feed to 20 % in light product at 2.5 SLPM light reflux and was further improved to 45 % at lower light reflux of 0.625 SLPM. In contrast, less than half the raffinate performance was obtained at 4 % helium feed composition. Also, with
the 13.3 % helium feed, the helium recovery achieved was on average 10 % better than that from the 4 % feed.

Figure 5-4 Comparison of helium purity and recovery between 4 % and 13.3% feed helium composition at various light reflux flow rate.

Figure 5-5 shows a comparison of methane wave front position at the high pressure step of the DR PSA cycle between 4 % and 13.3 % feed helium composition. The effect of increasing the helium feed composition is to cause the methane wave front to recede, making it less likely to breakthrough into the light product. At 13.3 % feed helium composition, the helium concentrated at the top of bed by the end of pressurization step has about twice the volume than that at 4 % feed helium composition. When heavy purge occurs, this yielded a higher helium purity in the light product. In contrast, at 4 % helium feed composition, the methane wave front propagated through the stripping end of the bed, significantly degrading the helium raffinate performance. Thus it is clear now that at a higher helium feed concentration, the improvement of helium raffinate purity was made by the reduced breakthrough rather than the increased amount of helium in feed.
5.4 Preliminary investigation of ternary feed separation

A ternary feed comprising 4 \% helium, 26 \% methane and 70 \% nitrogen was investigated at the flow and pressure conditions specified in Table 5-1. The composition distribution change over the cycle was examined to identify a potential position along the bed where a third product stream could be drawn (Figure 5-6). During the counter-current blowdown step (Figure 5-6a), methane and nitrogen are desorbed and removed from the bottom of the bed (z/L=1). As the bed is free of helium, the top of the bed (z/L = 0) is saturated with pure nitrogen, and methane is primarily concentrated at the bottom of the bed with composition up to 40 \%. In the low pressure purge step (Figure 5-6b), methane and nitrogen are pushed out from the bed bottom, leaving a lower composition distribution across the bed and in the same time helium enters the bed in the light purge gas. In the following step (Figure 5-6c), the bed is re-pressurized with heavy gas entering from the bottom, and helium is pushed into the bed top in 0.2 fractional volume at a composition up to 40 \%, with the remainder made up by nitrogen. As methane is retained primarily at the bed bottom, the bed middle part is vastly concentrated with nitrogen at a composition in excess of 90 \%. This component distribution established
from the top to bottom of the bed shows a good consistency with the respective order of equilibrium capacities. In the final high pressure purge step (Figure 5-6d), helium is completely purge out with some extent of nitrogen breakthrough, producing a light product consisting of 8 % helium and 92 % nitrogen, and the bed is then returned to the initial state of the blowdown step. The separation performance is close to that obtained in a binary mixture test with same helium feed composition. Again, as the bed contains predominantly nitrogen, the purity of helium raffinate is degraded due to the nitrogen breakthrough. Figure 5-6c shows that there is a fairly good separation at position z/L = 0.2 in the bed, at which nitrogen composition is over 95 %. Thus, a third product may be drawn from this position to obtain a highly purified nitrogen, which could also mitigate the nitrogen breakthrough into the helium product. As the concentration wave propagates along the bed over the cycle, trial and error may be required to locate an optimal product port around this position.

Figure 5-6 Changes of gas phase concentration over the bed during a DR PSA cycle that was used to separate a 1.25 SLPM ternary feed comprising of 4 % helium, 26 % methane and 70 % nitrogen.

5.5 Conclusions

The model of DR PSA cycle using Norit RB3 as the adsorbent was further applied in the simulation of helium recovery from a 1.25 SLPM feed at helium compositions representative of the industrial overhead product from the nitrogen rejection unit. The tests of binary feed
containing 4 % helium in methane or nitrogen showed that the cycle was capable of producing helium raffinate up to 40 % purity at 68 % helium recovery or better, which was comparable with that obtained by cryogenic distillation. Analysis of composition distribution along the bed revealed that better performance can be expected at a combination of shorter feed time and lower light reflux flow rate, suggesting great potential for industrial applications in recovery of trace helium in ventilation from cryogenic plant and upgrading of crude helium product.

Study on heavy product showed that decreasing the heavy product flow rate significantly increased the helium recovery but at the cost of degrading the helium purity in the light product. Due to the low separation performance in general, adjusting the heavy product flow rate is not viable to tune for more helium raffinate purity or helium recovery as required. Extending the feed helium composition at 13.3 % resulted in an average improvement of helium raffinate purity by 20 % as well as helium recovery by 10 %, due to the receding of methane wave front.

A ternary feed comprising of 4 % helium, 26 % methane and 70 % nitrogen was tested and it was found that the purity of helium raffinate was close to that in the binary mixture test at the same helium feed composition. The changes of composition distribution along the bed was tracked over the cycle and it was revealed that the composition distribution established from the top to bottom of the bed was associated with the order of equilibrium capacity, with helium concentrated at the top and nitrogen and methane at the middle and bottom respectively. As the bed contained predominantly nitrogen, the helium raffinate purity was limited. However, by the end of pressurization step a fairly good separation occurred at z/L = 0.2 of the bed, at which a large portion of nitrogen was concentrated at a composition over 95 %, with helium and methane primarily distributed at the top and bottom of the bed, respectively. It can be thereby hypothesized that a third product of highly purified nitrogen may be extracted from this position, which at the same time, could also serves as an supplementary mean of mitigating the nitrogen breakthrough to the helium product.
Chapter 6 Conclusions and Recommended Future Work

6.1 Conclusions

This research presents the construction, verification and optimization of a dynamic simulation of dual reflux pressure swing adsorption cycles towards the goal of developing high performance PSA processes for nitrogen removal and helium recovery from natural gas to improve the LNG plant efficiency. The research described in this thesis has made a number of contributions towards the attainment of this goal and can be summarized as follows:

- A literature review of current state of modelling study on the DR PSA technique with respect to the process benchmark and optimization identified the strength and limitation of each modelling technique. This contribution is important not only for the development of the DR PSA model in this research, but could provide useful insights into various numerical methods, such as the method of characteristics for analytical solutions and the method of lines for dynamic integration of governing equations.

- The non-isothermal capability of a dynamic simulation of dual reflux pressure swing adsorption process constructed in this work was demonstrated to be critical for accurate prediction of cycle characteristics and separation performance, especially when influential adsorption heat was involved in the process. Fixed bed dynamics involved rigorous energy balances across over the gas phase, solid phase and wall phase, in contrast to previously reported dynamic simulation where isothermal and/or isobaric condition was assumed to simplify the governing equations.

- Full automation of cycle sequence of the DR PSA model and data acquisition by a self-coded algorithm using Aspen Custom Modeler (ACM) language not only reduced iterative labor, but improved the quality, accuracy and precise of process control in a dynamic simulation. This algorithm allowed for self-estimation of required compressor speed, which was shown to be crucial for reproducing a qualitative cyclic pressure profile.

- The reliability and robustness of the DR PSA model was verified by benchmarking
against a most detailed set of experimental DR PSA data available in the literature (up to 2015), which involved the separation of C_2H_6 + N_2 mixture. By reasonably estimating the key parameters, the as-reproduced cycle characteristics in terms of product purity, pressure and temperature profile could quantitatively match the corresponding published data, giving a comprehensive reassessment of the real DR PSA process.

- This rigorous DR PSA model was updated with bed pressure regulating modules and benchmarked to adapt our pilot DR PSA experiments of CH_4 + N_2 separation, which respectively, involved the test of CH_4 equilibrium selective (Norit RB3) and N_2 kinetically selective (CMS 3K-172) adsorbents. At cyclic steady state, similarity of model predictions with experimental records in terms of cycle characteristics of pressure, temperature and flow profiles was qualitatively established and good agreement of product purities were found over a wide range of flow regime and feed composition conditions.

- The parameter study on feed step time and light reflux flow rate revealed that the best separation performance should correspond to an optimal bed volume usage, where breakthrough is reduced to a minimum. The adjustment of heavy product flow rate could be used to shift the separation towards more extract or raffinate oriented nature as required. By parametrically varying the sorption rate, it was also found that the kinetic separation of methane and nitrogen mixture using CMS 3K-172 was strongly limited by the slow sorption rate of nitrogen rather than the competitive adsorption of methane.

- Adsorbent performance comparison between Norit RB3 and CMS 3K-172 provides evidence that it is the magnitude of selectivity rather than the preference for a component that matters for the DR PSA separation. This result suggests, surprisingly, that for the N_2 rejection application, an equilibrium CH_4 selective adsorbent in a DR PSA process works as well or better than a kinetically N_2 selective adsorbent.

- The simulation test of Norit RB3 showed that the DR PSA cycle was capable of producing highly enriched methane extract at methane recovery in excess of 99 %,
from a feed containing 75 mol % methane in nitrogen, suggesting great potential of future application in upgrading low quality fuel gas. In contrast, the test of CMS 3K-172 exhibited much lower separation performance and thus this adsorbent was less likely to be applied for industrial natural gas processing. The high methane recovery achieved suggests the process with Norit RB3 is more energy efficient than with CMS 3K-172.

- The DR PSA simulation in industrial scale was investigated for the separation of 75 % CH$_4$ + 25 % N$_2$ mixture using activated carbon Norit RB3. The industrial GPSA method for adsorption bed sizing was reviewed, and the calculation of bed height was identified to be the key step. The cycle upscaling method presented in this thesis provided a simple but effective strategy for future industrial commission and optimization of the DR PSA technique using the outcomes from laboratory simulations. The simulation study also identified the existence of an optimal feed inlet position, through detailed analysis of bed composition distribution change over the cycle.

- The DR PSA model was further applied in the separation and recovery of diluted helium from industrial N$_2$-rich waste using Norit RB3. Under several operating conditions, the cycle could produce a helium raffinate up to 40 % purity at 68 % helium recovery or better from a binary feed containing 4 % helium in methane or nitrogen, which is comparable with that obtained by cryogenic distillation. The preliminary analysis of simulation results for the test of binary feed suggested that improvements of helium recovery can be made with a combination of short feed time and low light reflux flow rate. The test of ternary feed comprising of helium, methane and nitrogen identified a third product port position along the bed for future study, from which a highly enriched nitrogen product could be draw, serving as a supplementary mean of improving the helium raffinate purity.

6.2 Recommended future work

Although adjusting the feed step time and light reflux flow rate could obtain an optimum of separation performance by reducing the breakthrough to a minimum, the broadened mass
transfer curve, as a consequence of the adsorption nature, limits the effectiveness of this optimization and thus perfect separation is practically not achievable. It is suggested that providing improvements to adsorbent selectivity for the methane and nitrogen mixture could mostly sharpen the mass transfer curve and thus push the product purities higher. This modification may include CH₄ equilibrium selective adsorbent such as Norit RB series with respect to the methane equilibrium capacity, and N₂ kinetically selective adsorbent like CMS series with respect to the sorption rate of nitrogen. Simulation tests could serve as a supportive foundation predicting the separation performance as well as lower capital costs associated with physically commissioning the adsorbent modification process.¹³, ⁶¹-⁶³

A four step cycle was used for all the benchmark and process optimization tasks described in this thesis. As discussed in Chapter 2, the purity of heavy extract would degrade over the feed/purge step as contaminated by the breakthrough of light purge gas. In several cases, the highest enrichment in fact occurs earlier during the blow down step, where the highly enriched heavy effluent goes to pressurize the low pressure bed. It is recommended to use an intermediate blowdown step to drop the bed pressure to what provides the highest transient enrichment and draw the effluent as the heavy extract, which in turn, could improve the purity of light product as dictated by the overall mass balance. This requires addition of a new step in between the current feed and blowdown step, which could be implemented by modifying the cycle script. Once the modification is completed, the test of the new step duration and product flow rate could be commissioned and an optimal value would be obtained through tracking the time evolution of product concentration.

Chapter 4 has illustrated the effect of feed inlet position on the separation performance and identified the existence of an optimal feed inlet located at the middle of the column. In future work this investigation could be expanded at N₂-rich feed compositions representative of the dilute methane in fugitive emissions from oil and gas product facilities, in ventilation air from coal mining operation, and low grade source of natural gas. With the analysis of simulation results, a possible range of optimal feed port location may be identified. This will provide not only useful insights of performance trend but also enhanced understanding of process design for future industrial practitioners.
The test of ternary feed consisting of helium, nitrogen and methane reveals that a good separation of highly enriched nitrogen occurs at about 0.2 fractional bed length from the top when the bed was pressurized with heavy gas, suggesting that a third product of nitrogen extract may be drawn from this position. Model modification will be required with respect to the addition of a third product port, stream connections and control valves. The stripping section of the bed (in the model) will need to be split into two bed layers in series, connected with a gas tank module which serves as the product port. From this tank, a portion of product streams can be drawn via a control valve, which is meant to regulate the flow rate so that the bed composition distribution is not likely to be perturbed. To collect the nitrogen extract at each half of the cycle, an additional product tank should be used and of course, at steady pressure. These modifications are relatively easy to implement but the main challenge is the increase of computation cost, along with numerical stability issue as the model complexity will be increased. Furthermore, as the concentration wave propagates along the bed, the location of the best separation may vary during the high pressure purge step, and thus trial and error may be required to locate an optimal product port position.

From a thermodynamics perspective, the essential difference between PSA and TSA process is that in the PSA system, the energy required to achieve the separation is put into the system as mechanical work rather than heat. Since mechanical energy is in general more expensive than heat, the efficient utilization of energy for an economic separation process is essentially important. Such consideration suggests the PSA separation of nitrogen from methane in larger scale units could be potentially accomplished by a temperature swing process. The numerical model developed in this work could be adapted to study the TSA nitrogen rejection with little to no modification. Trap door zeolites that offer significant selectivity by temperature change in a range of 50 °C could be the adsorbent of choice, as suggested by Li et al. and Shang et al.64-65
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Appendix A

Table A-1 Isotherm and kinetics properties of CH₄ and N₂ sorption on Norit RB3 and CMS 3K-172, with respective bed packing condition calculated for DR PSA simulation.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Units</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norit RB3</td>
<td>CMS 3K</td>
<td>Aspen default</td>
<td></td>
</tr>
<tr>
<td>Eᵢ</td>
<td>0.433</td>
<td>0.379</td>
<td>m⁻³ void/m⁻³ bed</td>
</tr>
<tr>
<td>RHOs</td>
<td>439.325</td>
<td>657.916</td>
<td>kg/m⁻³</td>
</tr>
<tr>
<td>Rp</td>
<td>1.50×10⁻⁰³</td>
<td>1.00×10⁻⁰³</td>
<td>m</td>
</tr>
<tr>
<td>SFac</td>
<td>0.850</td>
<td>0.779</td>
<td>n/a</td>
</tr>
<tr>
<td>MTC(*)</td>
<td></td>
<td></td>
<td>Lumped resistance for LDF</td>
</tr>
<tr>
<td>MTC(&quot;CH₄&quot;)</td>
<td>0.420</td>
<td>1.264×10⁻⁰⁴</td>
<td>1/s</td>
</tr>
<tr>
<td>MTC(&quot;N₂&quot;)</td>
<td>0.765</td>
<td>1.069×10⁻⁰²</td>
<td>1/s</td>
</tr>
<tr>
<td>IP(*)</td>
<td></td>
<td></td>
<td>T-dependent Langmuir isotherm</td>
</tr>
<tr>
<td>IP(1,&quot;CH₄&quot;)</td>
<td>6.58×10⁻⁰⁷</td>
<td>2.05×10⁻⁰⁹</td>
<td>kg/kmol/bar</td>
</tr>
<tr>
<td>IP(1,&quot;N₂&quot;)</td>
<td>7.30×10⁻⁰⁷</td>
<td>5.91×10⁻⁰⁷</td>
<td>kg/kmol/bar</td>
</tr>
<tr>
<td>IP(2,&quot;CH₄&quot;)</td>
<td>2077.094</td>
<td>2549.041</td>
<td>K</td>
</tr>
<tr>
<td>IP(2,&quot;N₂&quot;)</td>
<td>1722.533</td>
<td>1895.965</td>
<td>K</td>
</tr>
<tr>
<td>IP(3,&quot;CH₄&quot;)</td>
<td>1.19×10⁻⁰⁴</td>
<td>6.30×10⁻⁰⁵</td>
<td>1/bar</td>
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<tr>
<td>IP(3,&quot;N₂&quot;)</td>
<td>1.75×10⁻⁰⁴</td>
<td>2.80×10⁻⁰⁴</td>
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</tr>
<tr>
<td>IP(4,&quot;CH₄&quot;)</td>
<td>2077.094</td>
<td>2549.041</td>
<td>K</td>
</tr>
<tr>
<td>IP(4,&quot;N₂&quot;)</td>
<td>1722.533</td>
<td>1895.965</td>
<td>K</td>
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